

New Avenues for Organic Redox Materials as Sustainable Lithium-ion Battery Cathodes

Deepak Gupta* ^a
 Shilpa Jain Gupta* ^b
 Alexandru Vlad* ^a

^a Institute de la Matière Condense et des Nanosciences (IMCN),
 Université catholique de Louvain, Place L. Pasteur 1,
 1348 Louvain-la-Neuve, Belgium

^b Department of Chemistry, Shivaji College, University of Delhi,
 Mahatma Gandhi Marg, Shivaji Enclave, Raja Garden, New Delhi,
 Delhi 110027, India

*deepakg2003@gmail.com, shilpajain@shivaji.du.ac.in,
 alexandru.vlad@uclouvain.be



Received: 24.08.2022

Accepted after revision: 01.12.2022

DOI: 10.1055/s-0042-1757981; Art ID: OM-2022-08-0034-REV

License terms:

© 2023. The Author(s). This is an open access article published by Thieme under the terms of the Creative Commons Attribution License, permitting unrestricted use, distribution, and reproduction so long as the original work is properly cited. (<https://creativecommons.org/licenses/by/4.0/>).

Abstract As the demand for electrification of means of transportation and storage of electrical energy for later use is skyrocketing, rechargeable Li-ion batteries (LIBs) are at the heart of this revolution. Acknowledging the carbon footprints, environmental concerns and cost of the commercial cathode materials, this is the high time to advocate sustainable alternatives. This review aims at establishing the potential of organic redox-active molecules as a burgeoning class of sustainable solid cathode materials for LIBs. The materials are classified according to their structural features (molecules, metallo-organic complexes, and organic/metal-organic frameworks) and electrochemical performance to lay emphasis on practical applications and bottlenecks in commercialization. However, these materials are still in early stages of development, and new frontiers have been explored in the last five years.

Key words: batteries, Li-ion batteries, organic materials, energy storage

Introduction

While scientists, researchers, technocrats, and entrepreneurs are pondering over climate change, pollution, resource depletion and energy security, green energy storage technologies (ESTs) are providing a window of opportunity to take the bull by the horns.¹ Having a squint at the present ESTs, Li-ion batteries (LIBs) are leading from the forefront due to their wide range of applications, ranging from pocket devices to grid-scale installations.² Beginning with powering electronic gadgetry such as phones and computers a decade ago, at present LIBs are running our cars and homes with

plans to fuel air and space travel in future.³ Consequently, aggressive research activities on electrode materials and the surge in the LIB production have led to 85% reduction in prices over the last decade. As the demand for energy and its storage is increasing exponentially, the world energy storage market is estimated to grow as much as \$426 billion in the next decade where the LIB market has already touched the \$50 billion mark worldwide.⁴ Right from the beginning of the LIB age, it relies mostly on uninterrupted supply of expensive metals such as Co, Ni, Mn, Al, Fe, Cu and Li. On the flipside, the cathode materials based on these metals are now posing serious concerns related to availability of raw material, mining and synthesis cost, supply chain bottlenecks, geopolitical situations, and issues surrounding end of life such as toxicity and recycling.⁵ Therefore, the immediate challenge is not only to address these concerns but also to upgrade the storage capacity, the cell voltage and durability of the present LIBs to meet the future demands. This brings the concept of greener and sustainable batteries containing environmentally benign, economic, abundant, and safer organic electroactive materials. This review focuses on presenting an overview of state-of-the-art of organic cathode materials applied in various forms such as small molecules, metal complexes, and organic/metal-organic frameworks (MOFs) in LIBs over the period of last five years.

Organic materials are composed of earth-abundant elements such as H, C, N, O, S and P. Apart from lower environmental footprints, energy-economic synthesis, cost and recycling, one of the most attractive features of organic redox materials is high structure and property tunability (Figure 1).⁶ Recent efforts in developing organic materials were mainly aimed at structural modification of organic molecules containing the most common redox unit, i.e. carbonyls.⁷ This is because the charge/discharge potential, specific capacity, cycling stability and cycling rate of the Li-ion cells are dictated by the molecular structure of the material. For

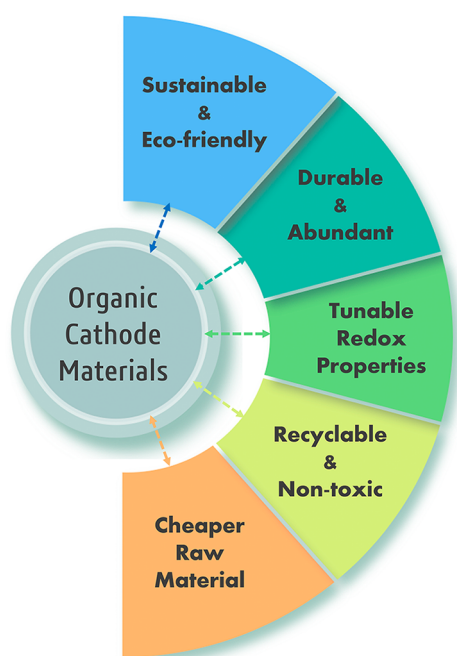


Figure 1 Characteristics of organic electrode materials.

example, the specific capacity is directly calculated from the molecular weight and number of electrons per redox unit per molecule. Interestingly, the same redox unit can be implemented in a variety of structural configurations such as polymers and frameworks to upgrade the cycling stability and rate capability by adopting facile synthesis pathways.⁸ In addition to these favorable features, the redox activity of organic materials is not limited to Li-ions but can be straightforwardly implemented to more sustainable chemistries such as Na, K, Mg, Ca, Al, etc.⁹ Adding to their versatility, the organic redox materials can be utilized both in the solid state (conventional battery cell configuration), or as hybrid organic-inorganic materials, and in solution (e.g. redox flow batteries) with aqueous and non-aqueous electrolytes. Along with their implementation in half-cell configurations with Li (or other metal ions) negative electrodes, studies on all-organic batteries are increasing lately. All of these advantages over commercial inorganic materials offer plentiful opportunities towards sustainable, affordable, durable and renewable electrochemical energy storage.

The Road Ahead ...

The organic materials have attracted great attention on the sustainability benchmark; however, the journey towards commercialization of an all-organic battery has just begun. Despite featuring a number of favorable properties, there

are still landmarks to be reached in terms of material properties, gravimetric and volumetric energy metrics and long-term cycling (> 10,000 charge cycles). At the material level, the major impediments towards these goals are active material degradation during cycling, undesirable dissolution in electrolytes, poor intrinsic conductivity (electrical and ionic), and additional cost of additives. Significant efforts have been made to overcome these shortcomings.

For example, in order to tackle the solubility of active materials in battery electrolytes and to increase the cell potential, molecular engineering methods have been utilized to install ionic functional groups which may or may not take part in the redox mechanisms but cause charge-density alterations within the molecule.^{6b} Thanks to the facile synthesis pathways, the redox-active molecules can be installed either on a polymeric backbone or can act as a part of the building units in the long-range frameworks to curb the solubility issues; however, this significantly affects the specific capacity (Figure 2). Novel solid-state electrolytes are still in early stages of infancy with only countable reports on all solid-state organic batteries. The ability to tune the structural features is highly advantageous; however, there are still goals of achieving the right material with high energy density and cycling stability that can provide lighter, fast charging and long-lasting batteries.



Figure 2 Various modes of application of organic electrode materials as LIB cathodes.

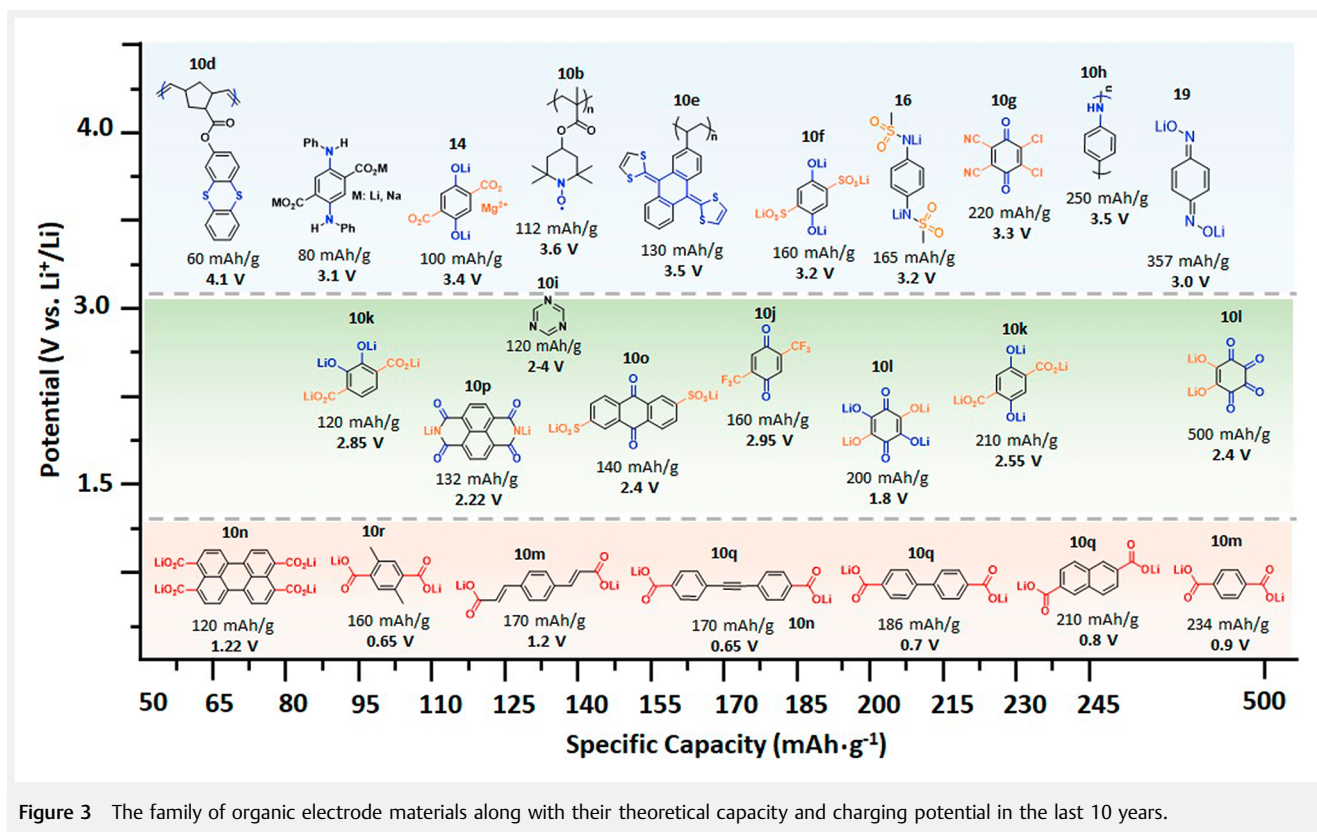


Figure 3 The family of organic electrode materials along with their theoretical capacity and charging potential in the last 10 years.

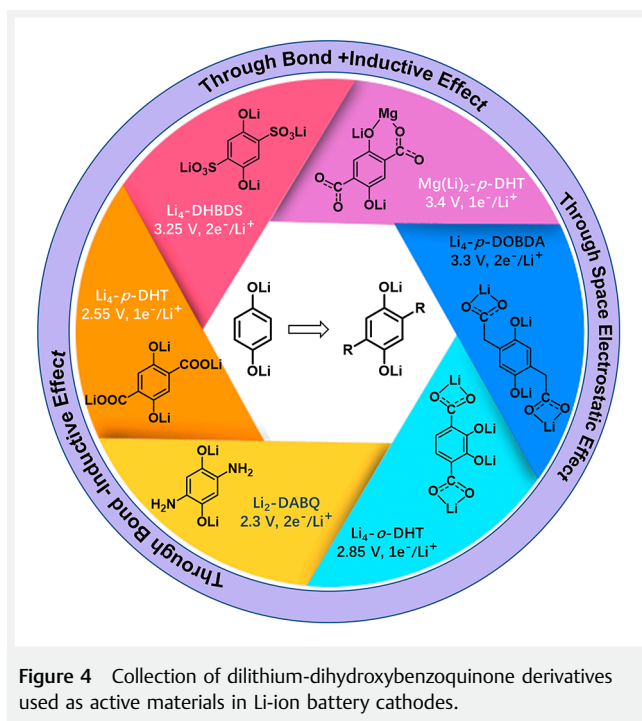
This is because little effort has been paid to discover new redox chemistries which are beyond the conventional carbonyl- and carboxylate-based redox mechanisms (Figure 3).¹⁰ Therefore, future research endeavors in the field of organic batteries would be directed towards designing newer redox mechanisms to achieve higher redox potential and number of electrons taking part in the redox reaction. However, the recent efforts have provided meaningful conclusions, and there are still various directions that remain unexplored.

Organic Molecules for Li-ion Cathodes

Classically, molecular organic compounds laid the foundation of organic cathodes for rechargeable batteries where the carbonyl-enolate is the most studied redox couple in cathodes. The widely studied *p*-benzoquinone (BQ) and its derivatives display an average discharge potential of ~ 2.7 V vs. Li⁺/Li and provides sufficient opportunities to upgrade the battery properties such as redox potential, specific capacity and number of cycles. It can be used in the lithiated (reduced) form as an active cathode material. Upon charging/oxidation, the enolate redox units lose one electron and one Li⁺ ion to generate carbonyl groups. Poizot et al. and Vlad et al. demonstrated that functionalization of the dilithium salt of *p*-dihydroxybenzene with electron-donating groups

such as carboxylates¹¹ (Li₄-*p*-DHT) and amines¹² (Li₂-*p*-DABQ) has profound effect on redox potential and cycling stability of the Li-ion cell (Figure 4). The +I effect of these groups causes an increase in charge density on the aromatic ring and leads to a decrease in oxidation potential of the compounds; however, there is a positive effect on cycling stability facilitated by inter-molecular non-covalent weaker interactions reducing the solubility of the active material in battery electrolytes.

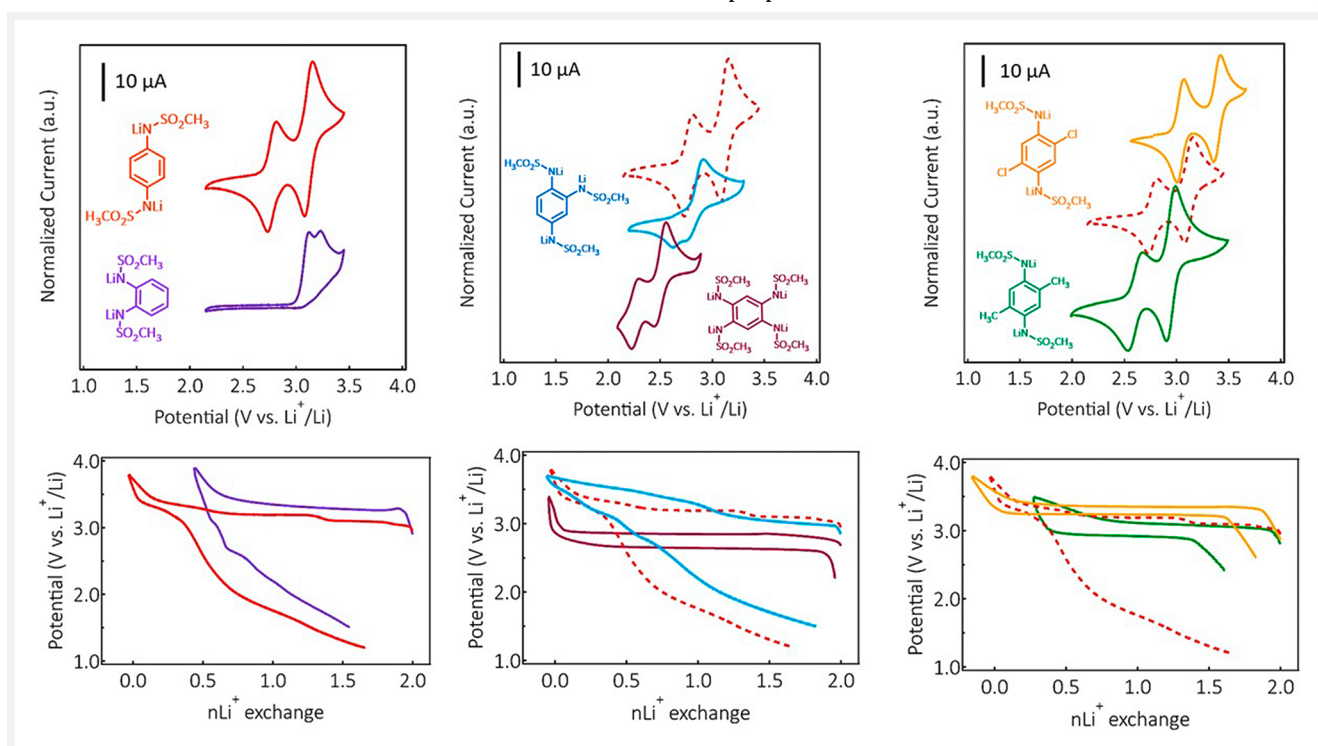
Logically, decorating the *p*-dihydroxybenzene core with electron-withdrawing groups must have the opposite effect on oxidation potential. This is indeed the case where Lakraychi et al. were the first one to demonstrate that functionalizing the aromatic core of *p*-dihydroxybenzene with lithiated electron-withdrawing sulfonate groups led to an increase in the oxidation potential by 300 mV.¹³ The development of lithiated organic cathode materials possessing high discharge potential (> 3 V vs. Li⁺/Li) is desirable as well as challenging. Interestingly, in Li₄-*p*-DHT, when two of the lithium ions are replaced by divalent metal ions such as Mg²⁺, Ca²⁺ and Ba²⁺, there is a significant voltage gain of nearly +800 mV in the half-cell configuration with Li metal as the negative electrode.¹⁴ This gain in voltage strongly depends on the ionic potential (electronegativity) of the spectator metal ion which causes stabilization of the aromatic π -electron distribution. Thus, facile structural modification in



the form of either functional group installation or by inserting secondary metal-ions has a profound effect on cell performance parameters.

Very recently, Sieuw et al. presented another example of how minute structural modifications could have a dramatic effect on battery performance.¹⁵ By a smart structural move, carboxylates in *p*-DHT were replaced by acetate groups. The additional methylene ($-\text{CH}_2-$) bridges allow the carboxylate groups to attain two different stereochemical configurations. In the solid state, the most preferred configuration is the one where carboxylates are closer to the enolate groups, which is highly suitable for through-space intramolecular electronic charge modulation. As a result of this, Li_4 -*p*-DOBDA displayed unexpected amplification of the redox potential, which is 650 mV (vs. Li^+/Li) higher than Li_4 -*p*-DHT. Once again, implementation of effortless organic synthesis methodologies leads to highly efficient organic redox materials with superior energy yardsticks to the typical inorganic ones; however, there is enough room to improve cycling stability and energy efficiency.

Quinones have laid the groundwork for practical organic positive electrodes; however, there is serious dearth of Li-ion-containing air-stable materials which strictly hamper their technological proliferation. Since the organic cathode chemistries proposed so far rely solely on the low redox potential quinone–enolate couple, the possibilities of tuning the properties remain limited. This set the tone for discovery



Biosketches



Deepak Gupta is a senior researcher in the group of Professor Alexandru Vlad. Working on an ERC-funded project, his research is focused on developing sustainable materials for energy storage and light-rechargeable batteries. He has published around 20 research articles in these areas. He did his PhD from University of Delhi with generous grant from CSIR (India). He was awarded the prestigious DAAD Fellowship to work as a visiting research scholar at the Freie Universität Berlin.



Shilpa Jain Gupta is working as Assistant Professor at Department of Chemistry, Shivaji College, University of Delhi (India). She did her PhD at the Department of Chemistry, University of Delhi. She is an eminent scholar with various accolades on her name in under-graduate teaching and scientific presentations. Her research interests are in the direction of developing sustainable porous materials for energy storage applications.



Alexandru Vlad is working as Professor at the Institute of Condensed Matter and Nanosciences, Université Catholique de Louvain, Belgium. He has established himself as one of the leading researchers in the field of energy storage systems, particularly rechargeable batteries. He has published around 100 research articles in high-rated journals such as Nature Energy and Nature Materials. His research is funded by prestigious agencies such as ERC, Marie-Curie, HYDRA, FNRS, etc.

of novel redox chemistries to address the existing bottlenecks. In the quest for next-generation redox centers for high-energy organic batteries, Wang et al. presented a series of conjugated sulfonamides as the first example of n-type, Li-containing, air-stable redox centers outside the galaxy of enolates.¹⁶ The unique structural design of sulfonamides consists of sulfonyl groups connected to an aromatic amine core (Figure 5).

While the electrochemical reaction takes place at the anilino centers, the sulfonyl groups offer charge delocalization over the redox centers, which is extremely important in tuning the redox potential of the material. The rich structure–property–charge storage performance of this novel class of high-performance air-stable organic cathode materials is established by a reversible 2-electron redox, high redox potential between 2.85 and 3.45 V and exceptional ambient stability. Banking on design versatility by appending a variety of functional groups, an improved electrochemical performance could be obtained in terms of high specific capacity

and improved cycling stability where the best performing derivatives could deliver specific energies of $> 500 \text{ Wh} \cdot \text{kg}^{-1}$. Moreover, the sulfonamide redox is invariably compatible with cheaper organic anodes, thereby making all organic high-performance batteries possible. This vividly insightful report not only pushed the limits of the present organic electrodes in terms of energy metrics but also paved the way for newer redox chemistries beyond conventional enolate-based materials. Interestingly, the sulfonamide redox could be conveniently extended to sodium- and potassium-ion batteries and unequivocally established the versatility of organic electrode materials for alkali cation storage.¹⁷ In the quest for novel redox materials towards high-performance organic electrodes, dinitrobenzene and its derivatives were implemented as redox-reversible cathodes which can accept two electrons.¹⁸ Along with a discharge voltage plateau at $\sim 2.5 \text{ V}$, this material class displays high theoretical specific capacity of $> 600 \text{ mAh} \cdot \text{g}^{-1}$. However, the poor cycling performance due to very high solubility of the oxidized phases

remained a challenge; the best performing isomer could retain nearly 50% of the theoretical capacity after 50 cycles. Thus, dinitrobenzenes represent an exciting class of highly sustainable and economic electrode materials, and their performance is still far from competing with other state-of-the-art systems.

The implementation of enolate-based materials as organic electrodes has successfully oiled the wheels for the discovery of novel redox chemistries where recent research endeavors have established that organic materials are taking giant strides towards a sustainable energy future. In an upcoming report, Vlad et al. have revealed another novel redox chemistry which has never been studied in the organic electrode materials so far.¹⁹ These materials are based on the oximate-nitroso redox couple with exceptional structural modifications during the electrochemical processes (Figure 6). The skeleton of the oximate redox functionality proposed here exemplifies a fusion of two important families of organic electrochemical storage mechanisms, namely the conjugated carbonyls and nitroxides. As the conjugated non-aromatic redox systems have scarcely been studied in organic electrode materials, the acyclic oximate derivatives have attracted immediate attention due to their rich chemistry as well as low molecular weight, translating to high design diversity and theoretical capacity. The conjugated oximate family is not limited to two-electron redox chemistry,

higher capacity ($> 300 \text{ mAh} \cdot \text{g}^{-1}$) can be achieved with proper molecular engineering via incorporating multiple number of oximate units, which can lead to energy density of $> 1 \text{ kWh} \cdot \text{g}^{-1}$, which is the highest among all the commercial as well as organic electrodes reported so far (LiFePO_4 : $550 \text{ Wh} \cdot \text{kg}^{-1}$, LiCoO_2 : $550 \text{ Wh} \cdot \text{kg}^{-1}$, LiMn_2O_4 : $490 \text{ Wh} \cdot \text{kg}^{-1}$, NMC622: $690 \text{ Wh} \cdot \text{kg}^{-1}$, LNMO: $570 \text{ Wh} \cdot \text{kg}^{-1}$). Although cycling stability is a concern for majority of organic materials, the higher oxidation potential ($\sim 3 \text{ V vs. Li/Li}^+$) and outstanding capacity ($\sim 350 \text{ mAh} \cdot \text{g}^{-1}$) achieved with oximate-based cathodes are promising considering the pristine, non-functionalized structure of the redox unit.

Metal–Organic Complexes for Li-ion Cathodes

After successful implementation of molecular organic materials as electrodes for secondary batteries, researchers shifted focus towards metallo-organic materials. The idea behind introducing the metal component to the organic redox materials was conceived to address the inherent bottlenecks of solubility, electrical conductivity and property tuning. Classically, metal complexes are long known for a high degree of structure tunability and reversible and multi-electron electrochemical properties in natural as well as synthetic systems.²⁰ Moreover, metal complexes possess inter-

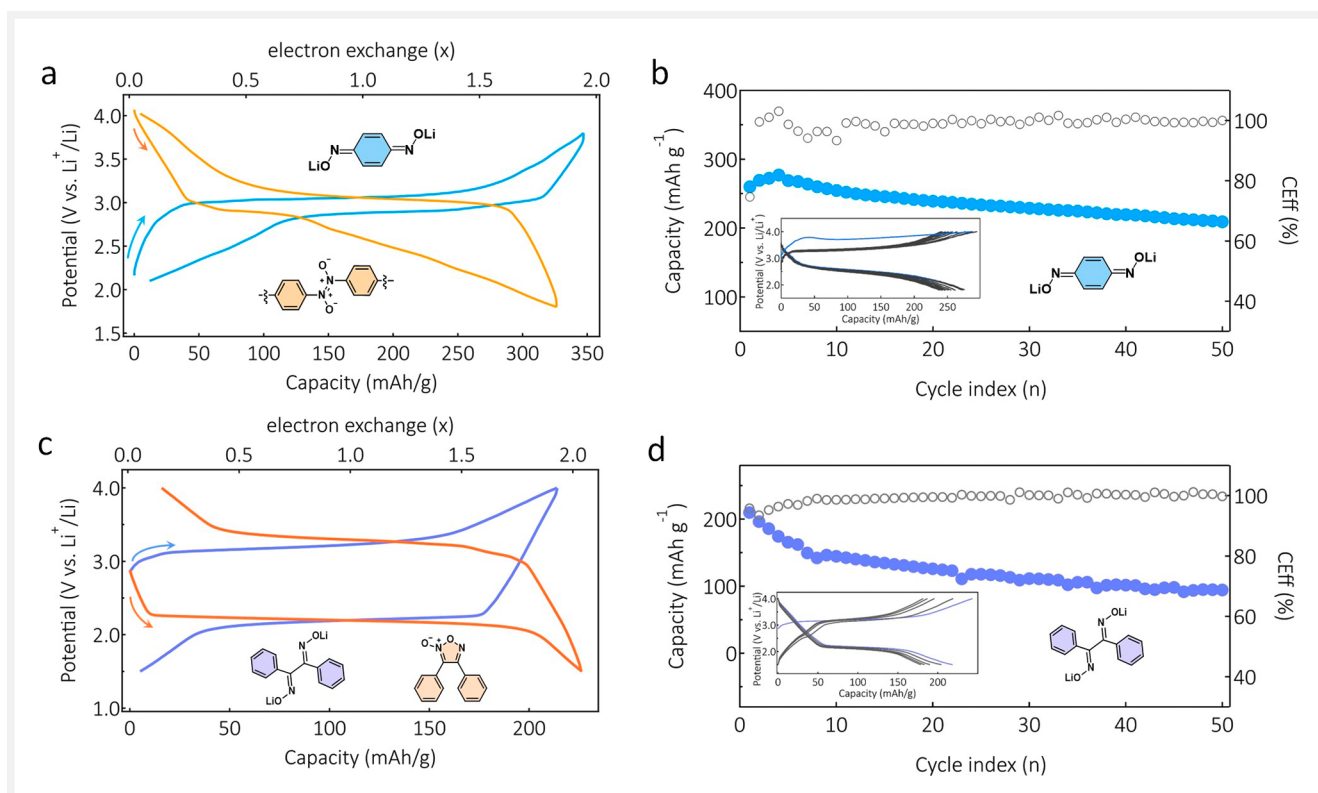


Figure 6 Electrochemical (liquid state) and Li-cell performance of various oximate derivatives.

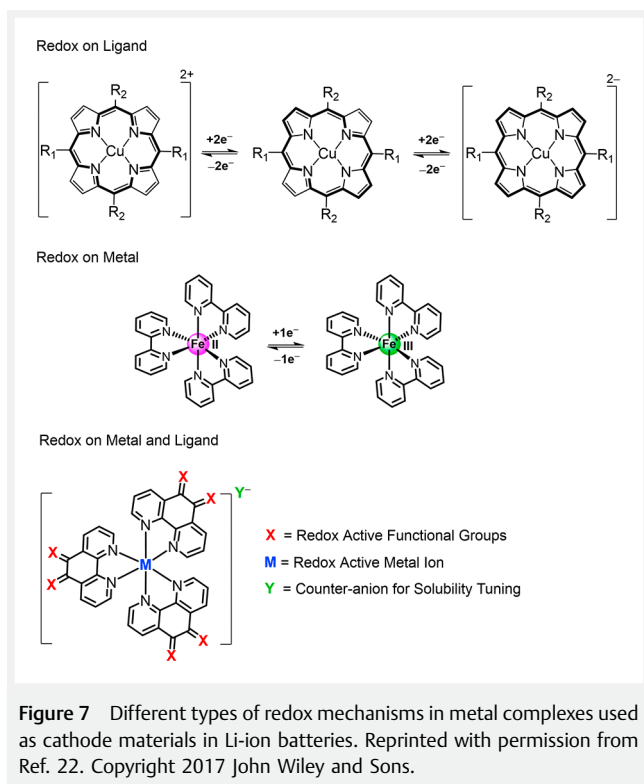
component (metal to ligand, ligand to metal) charge transfer ability which might promote higher electronic conductivity when employed as an active electrode material. Metal complexes possess donor–acceptor orbitals and display metal-to-ligand charge transfer via these orbitals. Because of the phenomenon of orbital mixing in metal complexes, new molecular orbitals and electronic states are generated which allow asymmetric electron density distribution. This has indirect influence on electronic delocalization within the metal complex structure. The 4d and 5d transition metals have low-lying atomic orbitals that mix with ligand orbitals efficiently and show significantly higher metal-to-ligand charge transfer. These phenomena provide additional pathways for electronic transitions. In addition, not only the structural tunability, but also the redox properties of metal complexes are highly dependent on the type of metal ion, type of coordinated organic ligand and redox media.²¹

Metal complexes possess bifunctional properties of metal-ions and organic linkers where both can take part in the redox process. Therefore, metal complexes have the advantages of high capacity, structural modification, tunable solubility in battery electrolytes and redox potential tuning. Intrigued by favorable properties of metal complexes, few attempts were made to utilize these as an active material in Li-ion electrodes lately. Porphyrins are naturally occurring metal complexes with attractive electronic, photophysical and photochemical properties (Figure 7).²² These are known

to accept multiple electrons via a π -conjugated aromatic system where the metal-ion is redox silent. In a Li-ion cell configuration as the active cathode material, Cu-porphyrin displayed promising properties, such as up to four electron redox, rapid redox conversion, and stable cycling at high currents due to higher electronic conductivity and redox stability of the porphyrin rings.

In the metal–porphyrin complex discussed above, the redox reaction takes place at the porphyrin core, whereas the metal plays only the structural role. As mentioned above, that metal-ion in the complex can also take part in the redox reaction, this can be a way to increase the specific capacity of the metallo-organic electrode materials. This concept was established by using a simpler Fe(bipyridyl)₃·2BF₄ coordination complex as the active cathode material in both Li-half-cell and full cell configurations.²³ The redox reaction takes place at the metal-ion with a well-known redox couple, Fe(II)/Fe(III). When coupled with Li anodes, the iron-based material displayed high discharge voltage approaching 4 V, whereas with LTO (Li₄Ti₅O₁₂) anode, the full cells exhibit a voltage of nearly 2.2 V. Thus, a stable voltage plateau and a coulombic efficiency (CE) of 99%, where the power density was comparable to the current state-of-the-art aqueous systems, established that commonly known, cheaper organic/metallo-organic redox materials are a suitable bet for sustainable high performance ESTs; however, there is still room for improvement. The above-mentioned examples confirmed that how different components of the transition metal complexes (organic ligand and metal ions) can be independently employed to perform the redox functions in an electrode.

Recently, Lakraychi and coworkers unveiled the concept of bipolar redox activity in metal complexes where both the ligand and transition metal ions take part in redox reactions independently (Figure 8).²⁴ The 1,10-phenanthroline-5,6-dione was employed as a unique ligand which possess a redox-active group (dione-diol) as well as a chelating group to coordinate with a variety of transition metal-ions. The three dione groups on the ligands undergo reversible 6-electron reduction, whereas the metal-ion can undergo additional redox events. Moreover, all the complexes allow exchange of counter-anions which provides a convenient handle to control the solubility of the complexes in organic solvents. Thus, the unique structural design and redox properties prompted the investigation of these complexes as cathode materials for electrochemical charge storage. The preservation of the bipolar redox activity in the solid phase is evidenced by the additional capacity attained at high potential, for example, an additional plateau at approximately 3.6 V (vs. Li⁺/Li) corresponds to the Co²⁺/Co³⁺ redox couple. A similar plateau at 4.1 V corresponds to the Fe²⁺/Fe³⁺ redox couple in the solid-state redox profile of the iron-based complex.



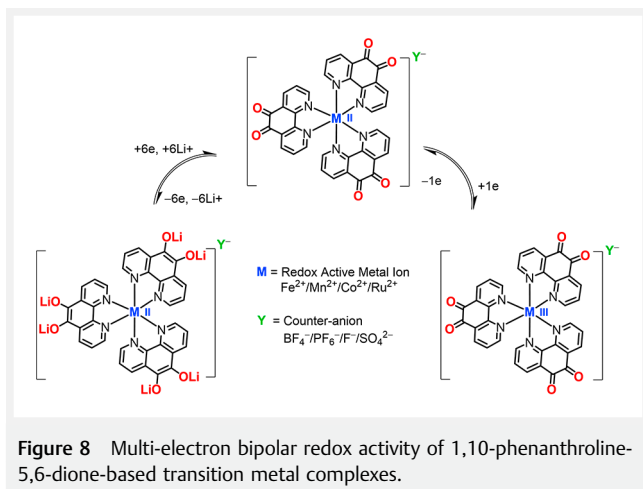


Figure 8 Multi-electron bipolar redox activity of 1,10-phenanthroline-5,6-dione-based transition metal complexes.

As mentioned above, the anion exchange not only has profound effect on the solubility of metal complexes but also influences the overall molecular weight of the complex, leading also to higher theoretical capacities. Therefore, the type of anion can directly influence the cyclability and finally the cell performance. It is not excessive to claim that transition metal complexes possess all the characteristics of sustainable energy storage materials where a combined redox activity of the metal-ion as well as organic ligands could be accessed to achieve superior battery performance (Figure 9). Interestingly it has recently been deciphered that the redox activity of the Ru(II)(1,10-phenanthroline-5,6-dione)₃ derivative of the above-mentioned transition metal

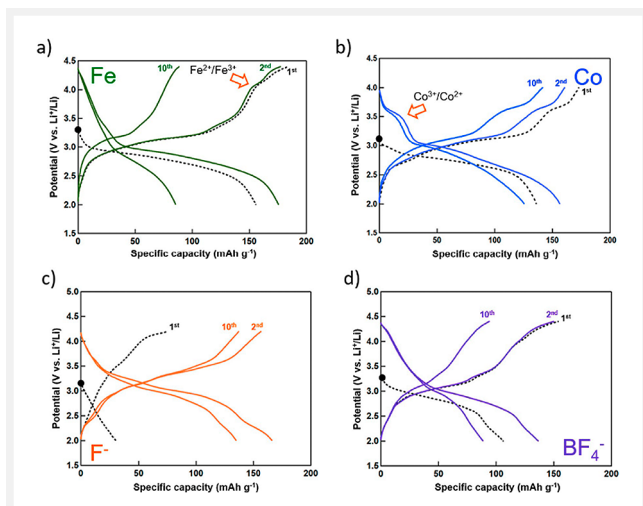


Figure 9 a, b) The galvanostatic charge–discharge curves for iron(II)–1,10-phenanthroline-5,6-dione and cobalt(II)–1,10-phenanthroline-5,6-dione complexes. c, d) The galvanostatic charge–discharge curves for iron(II)–1,10-phenanthroline-5,6-dione containing different counter-anions (F⁻ and BF₄⁻). Reprinted with permission from Ref. 24. Copyright 2020 John Wiley and Sons.

complexes can be modulated by visible light. Upon reduction of the dione groups (6 electrons) electrochemically, the reduced product can undergo spontaneous oxidation under visible light with the release of the 6 electrons. This ability of the material to undergo photo-redox activity can be translated into a visible light charging effect (Figure 10).²⁵ When implemented as a cathode in the Li-cell configuration, the galvanostatic charge–discharge storage capacity was found to be increased by 100% in the presence of visible light (470 nm).

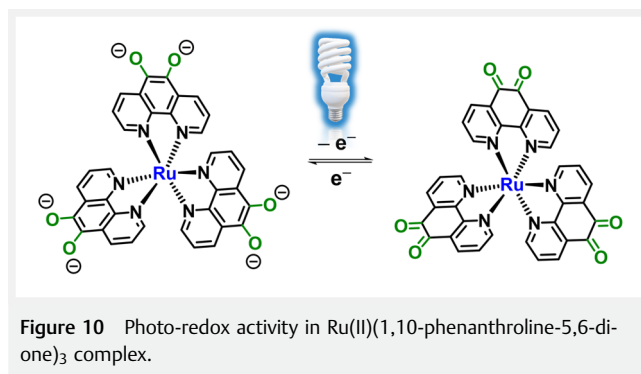
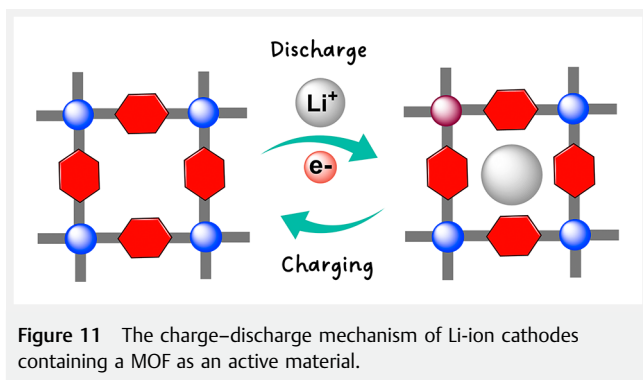


Figure 10 Photo-redox activity in Ru(II)(1,10-phenanthroline-5,6-dione)₃ complex.

Metal–Organic Frameworks for Li-ion Cathodes

MOFs are highly efficient porous materials consisting of a large array of metal-ions and organic donors (linkers) joined together by weaker coordination bonds in 3 dimensions.²⁶ As a result of intriguing structural features, MOFs have found significant applications in gas storage, molecular sieving, catalysis, membranes for ion transport and water harvesting.²⁷ Recently, MOF materials have made a sharp turn in the direction of energy storage and conversion, which have been addressed in few recent review articles. However, the chemical stability of the MOFs comes with a fair share of apprehensions owing to the labile nature of the coordination bonds; the exceptional stability of a variety of MOFs under electrochemical conditions such as electrolytes, electroactive species and redox potential is especially appealing for successful and efficient battery operations. This development is not unreasonable but rather built upon favorable structural features of the MOFs, such as long-range electronic communication between the components, presence of open channels for mass transport, possibility of cavity functionalization and redox properties of the components. Most interestingly, the physico-chemical properties of the MOFs can also be efficiently tuned by varying the coordinating metal ions and organic donor atoms based on their coordination ability, which serves as a guiding principle to establish a structure–property–performance relationship.

In terms of energy storage applications, MOFs have been found to be highly suitable possessing the inherent properties of classical inorganic porous electrode materials.²⁸ For example, the open sites on the metal ions and on the functionalized linkers can interact with redox-active and mobile guests such as oxygen and Li-ions. Therefore, MOFs can inherit the properties of both metal ion/clusters and organic linkers to extract the redox properties in such hybrid scaffolds to achieve energy storage materials (Figure 11). Additionally, the tunable microporous channels ensure facile and exclusive movement of the species across the MOF layers to prevent undesirable migration towards the anode (Li metal in the case of LIBs). Lastly, researchers have found that certain MOFs possess good ionic as well as electronic conductivity, which are essential for faster mobilization of ions and electrons during the electrochemical process. Moreover, most of the MOFs exhibit high surface areas, which is highly advantageous for superior sorption of guest species.



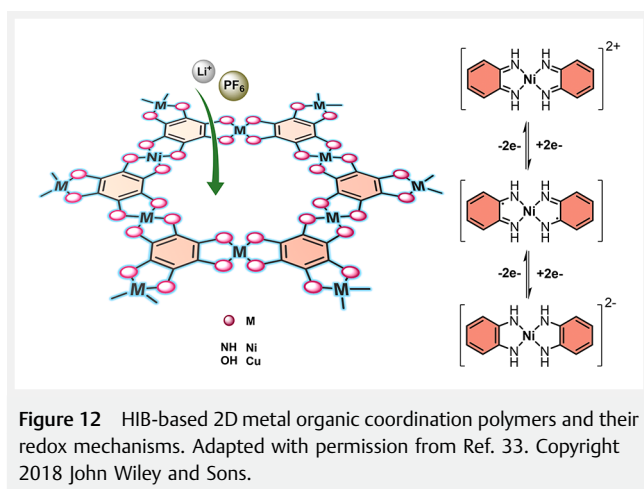
Fundamentally, MOFs are interesting materials possessing most of the essential prerequisites to serve as a desirable platform for future sustainable alternatives for energy storage applications; however, there are plenty of practical bottlenecks towards their commercialization.²⁹ The major issue is related to the capacity of the MOF-based cathode composites where only limited capacity of the materials can be accessed due to poor compatibility of the various components in terms of the electronic conductivity. Moreover, the capacity of the cathodes is significantly lower as compared to those of anode materials and depends on the cycling rates (lower capacities are obtained at higher cycling rates). This capacity mismatch is a major limitation towards superior practical performance. The poor stability window of the MOFs in various organic as well as aqueous solvent formulations leads to difficulties in achieving the cathode composites. In most of the cases, the chemical states of the redox centers (metal-ion/organic linkers) in the pristine and charge/discharge states remain unresolved making it difficult to predict the presence of radicals, redox states of the metal and type of bonding in the organic linkers. Despite fa-

vorable properties, materialistic competence of MOFs and the rapid development experienced in the past few years, replacement of the modern-day materials by MOFs in ESTs still requires rigorous efforts.

Owing to the inherent drawbacks of MOFs, a large number of reports describe the utilization of MOFs in the form of nanocomposites containing an electrically conducting component such as graphene prepared by physical or in-situ methods. Since this spotlight review specifically aims at highlighting the potential of organic materials for energy storage in various forms, the MOF-based nanocomposite materials will not be discussed. Thanks to the molecular engineering approach, the conductivity, redox activity and stability of the MOFs have been significantly improved keeping the energy storage application at the center stage. The pioneering work of Tarascon et al. was the first report on the application of a pristine MOF (MIL-53(Fe)) as an active cathode material.³⁰ Taking advantage of the mixed-valence states of the metal-ion ($\text{Fe}^{2+}/\text{Fe}^{3+}$) and redox stability during charge–discharge processes, MIL-53 displayed a reversible redox chemistry (upon Li insertion–deinsertion) with a stable voltage–current profile where the MOF undergoes a biphasic phase transition. However, MIL-53 exhibited a limited number of inserted Li ions per formula unit resulting in a moderate gravimetric electrochemical capacity of $75 \text{ mAh} \cdot \text{g}^{-1}$; this report marked the beginning of MOFs for rechargeable intercalation materials in positive electrodes of Li-based batteries.

As mentioned above that MOFs exhibit inherently lower conductivities (electronic/ionic) and poor redox performances, significant efforts have been paid to upgrade these properties in order to achieve practical MOF-based positive electrodes. Recently, new design approaches for MOFs have opened the doors for superior electrochemical performances as positive electrodes in LIBs. For example, by designing planar conjugated ligands, a library of two-dimensional (2D) MOFs with a layered structure have been synthesized.³¹ As a result of the sheet-like structure, high degree of anisotropy and larger surface area have been achieved, which leads to significant upgradation in the electronic conduction as well as density of the material. The 2D structure offers a large in-plane electronic delocalization allowing accessibility to all the redox sites with faster electronic mobility within the layer and ionic mobility in the open channels. Moreover, the layers have the ability to stack in an ordered manner to further enhance the existing properties as well as to generate the new ones. On the device performance side, the low capacity of the MOF materials can be significantly improved by introducing redox activity in the organic ligand core, thereby combining the electrochemical properties of both the components of the conjugated skeleton. Intrigued by this, the researchers have shifted the focus to develop novel 2D MOFs for practical energy storage applications.³²

Nishihara and coworkers presented the first utilization of a hexaiminobenzene-based (HIB) 2D MOF as an active cathode material in LIB half-cell configuration (Figure 12).³³ Apart from the facile synthesis methodology and attractive structural features (2D sheet structure with regular pores), this MOF exhibits very high electronic conductivity comparable to those displayed by metals (800 S/m). This MOF material displayed a ligand-centered multi-electron redox which is accompanied by both cation and anion insertions, thanks to the porous nature of the MOF. As a result of such distinguished properties, this MOF displayed a high specific capacity of $155 \text{ mAh} \cdot \text{g}^{-1}$ with stable cycling performance in battery configurations. This value was claimed to be the highest among the MOF-based cathode materials and comparable to the commercial inorganic cathodes.



This work paved the way for 2D MOFs as promising electrochemical energy storage materials for LIB cathodes. On similar lines, Chen and coworkers used the tetrahydroxybenzoquinone as the tridentate ligand to form the isostructural 2D MOFs which displayed comparable electrochemical performance by undergoing similar redox mechanism during the charge–discharge processes.³⁴ While 2D layered MOFs showed great promise as electroactive materials in LIB cathodes, there are meaningful limitations related to low capacity, which is due to inaccessibility of the metal-ion redox. Therefore, the specific capacity of MOF materials can be significantly improved provided the metal-based redox processes can also be performed during the charge–discharge along with the organic linker.

Long and coworkers demonstrated that combined metal and ligand-centered redox chemistries can be achieved in MOFs to obtain a high specific capacity unlike commercial cathode materials which solely rely of metal-based redox (Figure 13).³⁵ The key to this is to have close-lying reduction potentials of the metal-ion and the coordinated ligand. As a result of conductivity and metal–ligand covalency, this Fe-

chloranilate MOF could deliver a high energy density up to 533 Wh/kg . However, the energy density (especially the specific capacity) and long-term cycling stability are not as good as those of commercial inorganic materials; these outcomes ascertained the impact of combined redox chemistries of both the components of MOF on superior battery performance, thereby pushing the limits of organic-based materials closer to practical applications. Thus, synergistic effects of metal–ligand coordination chemistry allow exploration of newer electrochemical mechanisms in MOFs which holds the key for their implementation as next-generation ESTs. This requires continued development of the synthesis and structure aspect to promote electronic conduction, ionic diffusion, and electrochemical pathways.

Very recently, Vlad and coworkers came up with a breakthrough in MOF-based materials for LIB cathodes by designing an anionic MOF with lithium cation reservoir property and reversible redox (Figure 14).³⁶ These structural aspects are very similar to those of commercial inorganic cathodes. Interestingly, the accurate chemical and structural changes not only enable reversible redox, but also induce a million-fold electrical conductivity increase by virtue of efficient electronic self-exchange facilitated by mix-in redox. Therefore, these is one of the first alkali-earth ion doped MOFs possessing electrical conductivity along with reversible redox activity. These MOF cathodes has the generic formula $\text{Li}_2\text{-M-DOBDC}$ (wherein $\text{M} = \text{Mg}^{2+}$ or Mn^{2+} ; $\text{DOBDC}^{4-} = 2,5\text{-dihydroxybenzene-1,4-dicarboxylate}$) by rational control of the ligand to transition metal stoichiometry and SBU topology in the archetypal CPO-27.

When applied as active cathode materials in half-cell LIB configurations, these MOF materials displayed satisfactory performance in terms of specific capacity, redox potential and cycling stability. One of the structural highlights of these MOFs is the uncoordinated nature of the phenolic-OH group of the DOBDC ligand, which are coordinated to metal-ions (Mg/Mn) via carboxylate bridges only. This allows the exchange of the acidic hydroxyl protons with alkali-earth metal ions using a base reversibly. As a result of an efficient charge transport mechanism within the framework, these MOFs displayed semi-conducting behaviour where the Mn derivative possesses the lowest activation energy ($E_a = 0.37 \text{ eV}$) in the lithiated state suggesting a smaller band gap and hence a higher charge carrier density. In the solid-state electrochemistry investigations as in LIBs, these MOFs displayed superior performances as compared to the classical Mn-CPO-27 MOF with reversible exchange of 0.3 and $1.1 \text{ e}^-/\text{Li}^+$ equivalents. Moreover, due to the presence of Mn^{2+} in $\text{Li}_2\text{-Mn-DOBDC}$, a significant increase in redox potential by nearly 800 mV with respect to $\text{Li}_4\text{-DOBDC}$ was observed which can be attributed to the high ionic potential and polarizing power of Mn^{2+} as compared to Li^+ ions. Overall, a capacity retention of 91% and an average CE of 99.7% after 100 cycles at a high average discharge potential of 3.2 V vs. $\text{Li}^+/\text{Li}^\circ$

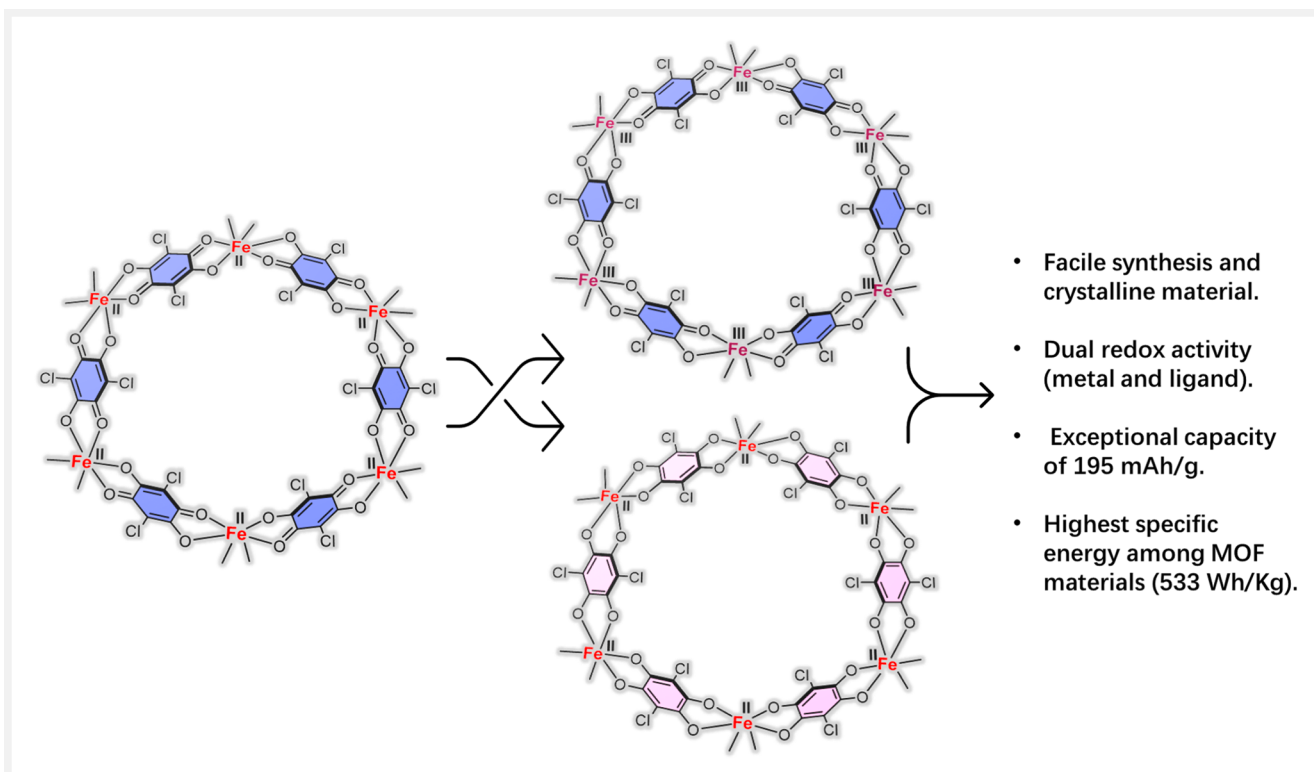


Figure 13 Chloranilic acid-based metal organic coordination polymers possessing both metal- and ligand-centered redox processes. Adapted with permission from Ref. 35. Copyright 2020 American Chemical Society.

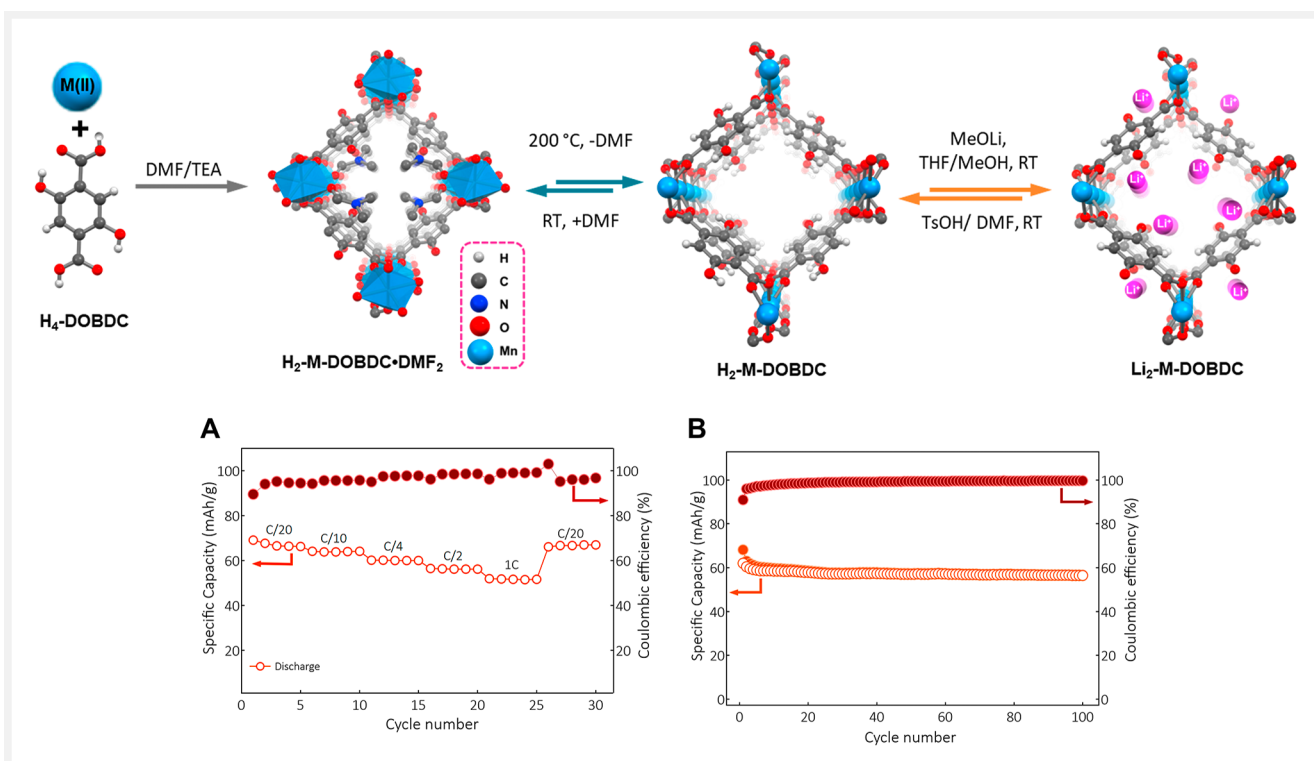


Figure 14 DOBDC-based metal organic coordination polymers as LIB cathode materials. Reprinted with permission from Ref. 36. Copyright 2021 American Chemical Society.

could be achieved with $\text{Li}_2\text{-Mn-DOBDC}$, thanks to the rigid interconnected framework. Whereas the specific capacities obtained with these MOF cathodes remain lower than expected, it is supposedly penalized by the intrinsic limitations of the DOBDC linker and therefore, opens the door to investigate other combinations of redox-active linkers and transition metal chemistries. Additionally, the concept of lithium-doped MOFs can be straightforwardly extended to other alkali-/alkaline-earth metals such as Mg^{2+} and Ca^{2+} to design more sustainable energy storage possibilities.

Conclusions and Outlook

It is not outrageous to say that organic materials possess all the necessary features and might hold the key for future sustainable ESTs. However, organic materials showed great promise in the direction of cost, availability, handling, and sustainability, and one should also accept the fact that organic cathodes are at an infancy stage and there is plenty of room for improvement in terms of gravimetric capacity, redox potential, and cycling stability. In terms of electrochemical energy storage properties in LIB configurations, organic materials possess high energy density, high power density and air stability. For example, benzoquinone being the simplest and cheapest organic redox molecule displays a redox potential of 2.8 V with a theoretical capacity of $496 \text{ mAh} \cdot \text{g}^{-1}$, which amounts to a theoretical energy density of $1400 \text{ Wh} \cdot \text{kg}^{-1}$ (as compared to $550 \text{ Wh} \cdot \text{kg}^{-1}$ obtained from commercial LiCoO_2). This validates the fact that organic materials are a perfect replacement for the commercial inorganics in terms of energy metrics, abundance, cost of the battery and environmental footprint; however, the low mass density and material dissolution remain inherent bottlenecks. In order to realize the long-cherished dream of commercial organic batteries, there are challenges at the material level related to electronic/ionic conductivity, achieving full capacity of the material, stability of the material at high potential ($> 3 \text{ V vs. Li}^+/\text{Li}^\circ$), stability in redox media (solubility or degradation) and achieving practically high specific energy density in full cell configurations. Small organic molecules are long known as redox-active compounds that can undergo electron transfer reactions in the liquid state. The successful implementation of the redox chemistry of these compounds in the solid state led to the advent of organic batteries (Table 1). The major drawback leading to the inferior performance of these materials is the solubility in redox media causing material loss and shuttling of cathode material to the anode. Nevertheless, the possibilities to modify the molecular structure to upgrade the redox potential, specific capacity and intermolecular interactions are some of the exceptional features that provide a solid ground for further development. Conversely, the high solubility of the active material in the redox media is a boon to redox flow batteries

Table 1 The known organic redox mechanisms that have been implemented as cathodes in lithium-ion batteries

Name of the Redox Active Group	Reversible Redox Mechanism
Conjugated Carbonyl	
Disulfide	
Conjugated Azo group	
Conjugated Nitrile	
Conjugated Amine	
Ether	
Thioether	
Nitroxide Radical	
Conjugated Sulfonamide	
Conjugated/Non-conjugated Oximate	
Many more to be discovered.....	

which are emerging as future grid-scale energy storage platforms. Therefore, organic redox materials are slowly heading forward and finding applications in redox flow batteries either in the form of small molecules or as metal-organic complexes.

Targeting property tuning and solubility, the small organic molecules are being tested in a variety of structural domains such as polymers, covalent organic frameworks, and MOFs. These chemical modifications have upgraded the material properties and therefore the battery performance significantly. With the introduction of redox activity and charge transport mechanisms, the MOF territory has been extended beyond the conventional area of gas storage to energy storage. While containing all the properties of small organic molecules, MOFs possess the advantages of low (or no) solubility, high stability in redox media, higher density, better conductivity, and porosity. With the advent of alkali-earth metal-doped structures, MOFs are not far enough to the commercial inorganic cathodes in terms of structural features, chemical formulation, and electrochemical properties. Thanks to rigorous efforts, researchers are now able to prepare full organic cells; however, the performance is not comparable to the commercial inorganic material-based devices. Thus, the landscape of organic materials is rapidly expanding by addressing the inherent bottlenecks

closing towards “green energy storage” solutions. Most importantly, the direct implementation of the same organic materials for a variety of ESTs such as Li, Na, K, Mg, Zn, and Al is the most attractive feature of organic electrodes.

Funding Information

A.V. and D.G. acknowledges the European Research Council under the European Union’s Horizon 2020 Research and Innovation Program (grant agreement no. 770870, MOOIRE, ERC-CoG).

Conflict of Interest

The authors declare no conflict of interest.

References

- (1) MIT Energy Initiative. *The Future of Energy Storage*, Massachusetts Institute of Technology: Cambridge, 2022.
- (2) (a) Goodenough, J. B.; Park, K.-S. *J. Am. Chem. Soc.* **2013**, *135*, 1167. (b) Grey, C. P.; Hall, D. S. *Nat. Commun.* **2020**, *6279*, 1. (c) Duffner, F.; Kronemeyer, N.; Tübke, J.; Leker, J.; Winter, M.; Schmich R. *Nat. Energy* **2021**, *6*, 123.
- (3) (a) Vishwanathan, V.; Epstein, A. H.; Chiang, Y.-M.; Tekeuchi, E.; Bradley, M.; Langford, J.; Winter, M. *Nature* **2022**, *601*, 519. (b) Fichtner, M. *Batteries Supercaps* **2021**, *4*, 1. (c) Reddy, M. V.; Mauger, A.; Julien, C. M.; Paolella, A.; Zaghbi, K. *Materials* **2020**, *13*, 1884.
- (4) (a) Armand, M.; Tarascon, J. M. *Nature* **2008**, *451*, 652. (b) Kwade, A.; Haselreider, W.; Leithoff, R.; Modlinger, A.; Dietrich, F.; Droeder, K. *Nat. Energy* **2018**, *3*, 290. (c) Masias, A.; Marcicki, J.; Paxton, W. A. *ACS Energy Lett.* **2021**, *6*, 621. (d) U.S. Environmental Protection Agency. The Official U.S. Government Source for Fuel Economy Information. www.fueleconomy.gov (accessed December 12, 2022).
- (5) (a) Baars, J.; Domenech, T.; Bleischwitz, R.; Melin, H. E.; Heidrich, O. *Nat. Sustainability* **2021**, *4*, 71. (b) Poizot, P.; Dolhem, F. *Energy Environ. Sci.* **2011**, *4*, 2003. (c) Zhao, L.; Lakraychi, A. E.; Chen, Z.; Liang, Y.; Yao, Y. *ACS Energy Lett.* **2021**, *6*, 3287. (d) Friebe, C.; Lex-Balducci, A.; Schubert, U. S. *ChemSusChem* **2019**, *12*, 4093. (e) Poizot, P.; Dolhem, F. *Energy Environ. Sci.* **2011**, *4*, 2003.
- (6) (a) Poizot, P.; Gaubicher, J.; Renault, S.; Dubois, L.; Liang, Y.; Yao, Y. *Chem. Rev.* **2020**, *120*, 6490. (b) Esser, B.; Dolhem, F.; Becuwe, M.; Poizot, P.; Vlad, A.; Brandell, D. *J. Power Sources* **2021**, *482*, 228814. (c) Lakraychi, A. E.; Dolhem, F.; Vlad, A.; Becuwe, M. *Adv. Energy Mater.* **2021**, *11*, 210156. (d) Lakraychi, A. E.; Vlad, A. *Chim. Nouv.* **2018**, *127*, 1.
- (7) (a) Oubaha, H.; Gohy, J.-F.; Melinte, S. *ChemPlusChem* **2019**, *84*, 1. (b) Häupler, B.; Wild, A.; Schubert, U. S. *Adv. Energy Mater.* **2015**, *5*, 1402034.
- (8) (a) Dolphijn, G.; Gauthy, F.; Vlad, A.; Gohy, J.-F. *Polymers* **2021**, *13*, 986. (b) Sieuw, L.; Ernould, B.; Gohy, J.-F.; Vlad, A. *Sci. Rep.* **2017**, *7*, 4847. (c) Dolphijn, G.; Isikli, S.; Gauthy, F.; Vlad, A.; Gohy, J.-F. *Electrochim. Acta* **2017**, *255*, 442. (d) Cheng, L.; Du, X.; Jiang, Y.; Vlad, A. *Nano Energy* **2017**, *41*, 193. (e) Sandu, G.; Ernould, B.; Rolland, J.; Cheminet, N.; Brassinne, J.; Das, P. R.; Filinchuk, Y.; Cheng, L.; Komsiyiska, L.; Dubois, P.; Melinte, S.; Gohy, J.-F.; Lazzaroni, R.; Vlad, A. *ACS Appl. Mater. Interfaces* **2017**, *9*, 34856. (f) Vlad, A.; Balducci, A. *Nat. Mater.* **2017**, *16*, 161. (g) Vlad, A.; Singh, N.; Melinte, S.; Gohy, J.-F.; Ajayan, P. M. *Sci. Rep.* **2016**, *6*, 22194. (h) Vlad, A.; Arnould, K.; Ernould, B.; Sieuw, L.; Rolland, J.; Gohy, J.-F. *J. Mater. Chem.* **2015**, *3*, 11189. (i) Ernould, B.; Devos, M.; Bourgeois, J.-P.; Rolland, J.; Vlad, A.; Gohy, J.-F. *J. Mater. Chem.* **2015**, *3*, 8832. (j) Vlad, A.; Singh, N.; Rolland, J.; Melinte, S.; Ajayan, P. M.; Gohy, J.-F. *Sci. Rep.* **2014**, *4*, 4315.
- (9) (a) Liang, Y.; Yao, Y. *Joule* **2018**, *2*, 1690. (b) Lee, S.; Kwon, G.; Ku, K.; Yoon, K.; Jung, S.-K.; Lim, H.-D.; Kang, K. *Adv. Mater.* **2018**, *30*, 1704682. (c) Kim, D. J.; Yoo, D.-J.; Otley, M. T.; Prokofjevs, A.; Pezzato, C.; Owczarek, M.; Lee, S. J.; Choi, J. W.; Stoddart, J. F. *Nat. Energy* **2019**, *4*, 51. (d) Lee, M.; Hong, J.; Lopez, J.; Sun, Y.; Feng, D.; Lim, K.; Chueh, W. C.; Toney, M. F.; Cui, Y.; Bao, Z. *Nat. Energy* **2017**, *2*, 861. (e) Wang, J.; Liu, X.; Jia, H.; Apostol, P.; Guo, X.; Lucaccioni, F.; Zhang, X.; Zhu, Q.; Morari, C.; Gohy, J.-F.; Vlad, A. *ACS Energy Lett.* **2022**, *7*, 668. (f) Wang, J.; Vlad, A. *Nat. Energy* **2020**, *5*, 945.
- (10) (a) Dühnen, S.; Betz, J.; Kolek, M.; Schmich, R.; Winter, M.; Placke, T. *Small Methods* **2020**, *4*, 2000039. (b) Janoschka, T.; Hager, M. D.; Schubert, U. S. *Adv. Mater.* **2012**, *24*, 6397. (c) Lakraychi, A. E.; Dolhem, F.; Vlad, A.; Becuwe, M. *Adv. Energy Mater.* **2021**, *11*, 2101562. (d) Shadik, Z.; Tan, S.; Wang, Q.-C.; Lin, R.; Hu, E.; Qu, D.; Yang, X.-Q. *Mater. Horiz.* **2021**, *8*, 471. (e) Häupler, B.; Burges, R.; Friebe, C.; Janoschka, T.; Schmidt, D.; Wild, A.; Schubert, U. S. *Macromol. Rapid Commun.* **2014**, *35*, 1367. (f) Lakraychi, A. E.; Deunf, E.; Fahsi, K.; Jimenez, P.; Bonnet, J.-P.; Djedaini-Pillard, F.; Becuwe, M.; Poizot, P.; Dolhem, F. *J. Mater. Chem. A* **2018**, *6*, 19182. (g) Chen, L.; Liu, S.; Zhao, L.; Zhao, Y. *Electrochim. Acta* **2017**, *258*, 677. (h) Macdiarmid, A. G.; Yang, L. S.; Huang, W. S.; Humphrey, B. D. *Synth. Met.* **1987**, *18*, 393. (i) Sukaushi, K.; Nickerl, G.; Wissner, F.M.; Nishio-Hamane, D.; Hosono, E.; Zhou, H.; Kaskel, S.; Eckert, J. *Angew. Chem. Int. Ed.* **2012**, *51*, 7850. (j) Yokoji, T.; Matsubara, H.; Satoh, M. *J. Mater. Chem. A* **2014**, *2*, 19347. (k) Gottis, S.; Barres, A.-L.; Dolhem, F.; Poizot, P. *ACS Appl. Mater. Interfaces* **2014**, *6*, 10870. (l) Chen, H.; Armand, M.; Courty, M.; Jiang, M.; Dolhem, F.; Tarascon, J.-M.; Poizot, P. *J. Am. Chem. Soc.* **2009**, *131*, 8984. (m) Armand, M.; Grugeon, S.; Vezin, H.; Laruelle, S.; Ribiere, P.; Poizot, P.; Tarascon, J.-M. *Nat. Mater.* **2009**, *8*, 120. (n) Renault, S.; Oltean, V. A.; Araujo, C. M.; Grigoriev, A.; Edstrom, K.; Brandell, D. *Chem. Mater.* **2016**, *28*, 1920. (o) Wan, W.; Lee, H.; Yu, X.; Wang, C.; Nam, K.-W.; Yang, X.-Q.; Zhou, H. *RSC Adv.* **2014**, *4*, 19878. (p) Shi, Y.; Tang, H.; Jiang, S.; Kayser, L. V.; Li, M.; Liu, F.; Ji, F.; Lipomi, D. J.; Ong, S. P.; Chen, Z. *Chem. Mater.* **2018**, *30*, 3508. (q) Lakraychi, A. E.; Dolhem, F.; Vlad, A.; Becuwe, M. *Adv. Energy Mater.* **2021**, *11*, 2101562. (r) Lakraychi, A. E.; Dolhem, F.; Djedaini-Pillard, F.; Thiam, A.; Becuwe, M. *J. Power Sources* **2017**, *359*, 198.
- (11) Renault, S.; Gottis, S.; Barres, A.-L.; Courty, M.; Chauvet, O.; Dolhem, F.; Poizot, P. *Energy Environ. Sci.* **2013**, *6*, 2124.
- (12) Sieuw, L.; Jouhara, A.; Quarez, E.; Auger, C.; Gohy, J.-F.; Poizot, P.; Vlad, A. *Chem. Sci.* **2019**, *10*, 418.
- (13) Lakraychi, A. E.; Fahsi, K.; Aymard, L.; Poizot, P.; Dolhem, F.; Bonnet, J.-P. *Electrochim. Commun.* **2017**, *76*, 47.
- (14) Jouhara, A.; Dupre, N.; Gaillot, A.-C.; Guyomard, D.; Dolhem, F.; Poizot, P. *Nat. Commun.* **2018**, *9*, 4401.
- (15) Sieuw, L.; Lakraychi, A. E.; Rambabu, D.; Robeyns, K.; Jouhara, A.; Borodi, G.; Morari, C.; Poizot, P.; Vlad, A. *Chem. Mater.* **2020**, *32*, 9996.

- (16) Wang, J.; Lakraychi, A. E.; Liu, X.; Sieuw, L.; Morari, C.; Poizot, P.; Vlad, A. *Nat. Mater.* **2021**, *20*, 665.
- (17) (a) Wang, J.; Liu, X.; Jia, H.; Apostol, P.; Guo, X.; Lucaccioni, F.; Zhang, X.; Zhu, Q.; Morai, C.; Gohy, J.-F.; Vlad, A. *ACS Energy Lett.* **2022**, *7*, 668. (b) Wang, J.; Guo, X.; Apostol, P.; Liu, X.; Robeyns, K.; Gence, L.; Morari, C.; Gohy, J.-F.; Vlad, A. *Energy Environ. Sci.* **2022**, *15*, 3923.
- (18) Liu, X.; Ye, Z. *Adv. Energy Mater.* **2020**, *11*, 2003281.
- (19) Wang, J.; Apostol, P.; Rambabu, D.; Liu, X.; Guo, X.; Robeyns, K.; Lakraychi, A. E.; Morari, C.; Gohy, J.-F.; Gupta, D.; Vlad, A.; *Research Square*; **2022**, preprint; doi: 10.21203/rs.3.rs-1346580/v1 (*Nat. Commun.*, manuscript under consideration).
- (20) Pierpont, C. G. *Coord. Chem. Rev.* **2001**, *216*, 99.
- (21) Kaim, W. *Eur. J. Inorg. Chem.* **2012**, *2012*, 343.
- (22) Gao, P.; Chen, Z.; Zhao-Karger, Z.; Mueller, J. E.; Jung, C.; Klyatskaya, S.; Diemant, T.; Fuhr, O.; Jacob, T.; Behm, R. J.; Ruben, M.; Fichtner, M. *Angew. Chem. Int. Ed.* **2017**, *56*, 10341.
- (23) Zheng, Q.; Niu, Z.; Ye, J.; Zhang, S.; Zhang, L.; Li, L.; Zhao, Y.; Zhang, X. *Adv. Funct. Mater.* **2017**, *27*, 1604299.
- (24) Lakraychi, A. E.; Kreijger, S. D.; Gupta, D.; Elias, B.; Vlad, A. *ChemSusChem* **2020**, *13*, 2225.
- (25) Gupta, D.; Lakraychi, A. E.; Boruah, B. D.; Kreijger, S. D.; Troian-Gautier, L.; Elias, B.; Volder, M. D.; Vlad, A. *Chem. Eur. J.* **2022**, *28*, e202201220.
- (26) Yaghi, O. M.; O'Keefe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705.
- (27) Furukawa, H.; Cordova, K. E.; O'Keefe, M.; Yaghi, O. M. *Science* **2013**, *341*, 1230444.
- (28) (a) Zhang, X.; Dong, P.; Song, M.-K. *Batteries Supercaps* **2019**, *2*, 591. (b) Li, S.-L.; Xu, Q. *Energy Environ. Sci.* **2013**, *6*, 1656. (c) Wang, Z.; Tao, H.; Yue, Y. *ChemElectroChem* **2019**, *6*, 5358.
- (29) (a) Reddy, R. C. K.; Lin, X.; Zeb, A.; Su, C.-Y. *Electrochem. Energy Rev.* **2022**, *5*, 312. (b) Zhang, L.; Liu, H.; Shi, W.; Cheng, P. *Coord. Chem. Rev.* **2019**, *1*, 293.
- (30) Ferey, G.; Millange, F.; Morcrette, M.; Serre, C.; Doublet, M.-L.; Greneche, J.-M.; Tarascon, J.-M. *Angew. Chem. Int. Ed.* **2007**, *46*, 3259.
- (31) Xie, L. S.; Skoruppskii, G.; Dincă, M. *Chem. Rev.* **2020**, *120*, 8536.
- (32) (a) Liu, J.; Song, X.; Zhang, T.; Liu, S.; Wen, H.; Chen, L. *Angew. Chem. Int. Ed.* **2021**, *60*, 5612. (b) Zhang, C.; Fan, K.; Chen, Y.; Wu, Y.; Wang, C. *ACS Appl. Electron. Mater.* **2021**, *3*, 1947. (c) Sakaushi, K.; Nishihara, H. *Acc. Chem. Res.* **2021**, *54*, 3003.
- (33) Wada, K.; Sakaushi, K.; Sasaki, S.; Nishihara, H. *Angew. Chem. Int. Ed.* **2018**, *57*, 8886.
- (34) Jiang, Q.; Xiong, P.; Liu, J.; Xie, Z.; Wang, Q.; Yang, X.-Q.; Hu, E.; Cao, Y.; Sun, J.; Xu, Y.; Chen, L. *Angew. Chem. Int. Ed.* **2020**, *59*, 5273.
- (35) Ziebel, M. E.; Gaggioli, C. A.; Turkiewicz, A. B.; Ryu, W.; Gagliardi, L.; Long, J. R. *J. Am. Chem. Soc.* **2020**, *142*, 2653.
- (36) Rambabu, D.; Lakraychi, A. E.; Wang, J.; Sieuw L.; Gupta D.; Apostol P.; Chanteux, G.; Goossens, T.; Robeyns, K.; Vlad, A. *J. Am. Chem. Soc.* **2021**, *143*, 11641.