

Organic Electrode Materials and Engineering for Electrochemical Energy Storage

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Organic batteries are considered as an appealing alternative to mitigate the environmental footprint of the electrochemical energy storage technology, which relies on materials and processes requiring lower energy consumption, generation of less harmful waste and disposed material, as well as lower CO₂ emissions. In the past decade, much effort has been made from fundamental understanding to practical applications in this

direction. This Special Collection aims to highlight the current dynamic research environment devoted to the field of organic chemistry and materials as applied to electrochemical energy storage systems and devices. In particular, it reveals how diverse the organic materials are in the context of Li-ion, but also next-generation, post-Li battery technologies.

50 years ago, pretty much at the same time when the first man walked on the Moon, battery scientists were also developing the first organic battery.^[1] Whereas space science has “rocketed” since, the battery field, including organic batteries, has seen fewer disruptive advancements. However, in recent years, there has been a renaissance in the field of organic batteries, with exponential growth driven by concerns about sustainability and the criticality of raw materials for the upcoming demand in battery technology.

It should be noted that organic chemistry and materials have been pervasive in modern battery construction from the very beginning, despite their role being less acknowledged. Aprotic electrolytes are based on carbonate organic solvents and the organic chemistry has shown in recent years how it can be used to design and synthesize new organic solvents and salts

to meet the ever-increasing demand for higher energy, safer, and longer-lasting batteries. The separators and binders used in batteries are the results of years of development and research, which have led to the creation of special polymer materials that can withstand the harsh working environment of a Li-ion cell. Furthermore, thin-film coatings, pouch-cell casings, and special additives designed through organic chemistry can be used to fulfill specific tasks. The list of applications for organic chemistry in battery technology is extensive and continues to grow as the field evolves.

In recent years, there has been a renewed interest in using organic materials as the active charge and ion storage components in batteries. This is due to the rapidly growing global demand for batteries, which has called for improved cell technologies capable of satisfying a variety of requirements according to the final application. As a result, researchers are exploring the potential of organic materials to meet these demands and develop more efficient, sustainable, and cost-effective battery technologies. Through fundamental research and practical applications, the field of organic battery materials is expanding and could play a crucial role in shaping the future of battery technology.^[2]

The search for next-generation electrochemical energy storage systems is being accelerated by market diversification and different application requirements, with sustainability and the dependency on raw critical materials becoming increasingly important parameters to consider. In this context, organic materials are at the top of the list. Although some argue that the current organic chemistry industry is still heavily reliant on the oil and gas industry and petrochemistry, the rising importance of biomass valorization provides a great opportunity to use natural compounds or their derivatives. Organic battery materials have thus become an exciting realm for exploration, with many chemistries available for positive and negative electrode materials. These extend from Li-ion storage

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to Na-ion and K-ion,^[3] with recent developments showcasing great potential and superior performances for divalent (Mg^{2+} , Ca^{2+} , Zn^{2+}) and even trivalent (Al^{3+}) cation storage.^[4]

Another major advantage of organic redox materials is their versatility in terms of solubility, which can be easily tuned through simple chemical functionalization. While conventional solid electrode cells require completely insoluble materials, highly soluble compounds are ideal for redox flow batteries (RFBs). In addition to this, organic battery materials are being considered as a more cost-effective and energy-efficient option for recycling, although further research is needed to confirm this aspect.

Despite the promise of organic battery materials, there are still several fundamental challenges that need to be addressed before they can be integrated into practical energy storage devices at a large scale. One of the main challenges is the relatively low energy content (both gravimetric and volumetric) of organic materials. To address this, researchers need to develop organic materials with both high operating voltage and high capacity. Although several milestones have been individually attained in these directions,^[5,6] combining them into a single material remains an open challenge. Gravimetric

density and electronic conductivity of organic electrode materials are also important aspects, and herein again significant progress has been attained.^[7] Additionally, solubility is a double-edged sword that can be either beneficial or detrimental depending on the application. High solubility is desirable for redox flow batteries but not for solid electrode cells, where solubility must be completely suppressed. At the electrode and device level, both, chemical and mechanical factors during operation are interrelated and can lead to complex degradation phenomena.

As the field of electrochemical energy storage continues to become more interdisciplinary, success will depend on extensive exploration across various fields around the world. This will require research and development in a variety of disciplines, including organic chemistry, material science, engineering, and physics. Exploring these technologies will require interdisciplinary approaches, such as organic synthesis and materials chemistry, interface design, electrolyte innovation, electrode engineering, and more. By combining expertise from various fields, we can overcome challenges and push the boundaries of what is possible in organic battery technology.



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Yan Yao is a Hugh Roy and Lillie Cranz Cullen distinguished professor at the University of Houston. In 2008, he received his Ph.D. in materials science and engineering from UCLA and went on to Stanford University for postdoctoral studies after spending two years in industry. He began his career at the University of Houston as an Assistant Professor in 2012 and became Full Professor in 2020. Dr. Yao's research is focused on bridging the scientific and technical gaps in the battery landscape that today's Li-ion batteries do not address. Dr. Yao made seminal contributions to a wide range of innovative materials and chemistries created from low-cost, abundant resources. He's also recognized for his work on developing an *in situ* diagnostic platform that combines structural, chemical, and mechanical techniques to better understand the mechanisms of solid-state batteries. For his work, he received the Office of Naval Research Young Investigator Award, Clarivate Analytics' Highly Cited Researcher Award, Scialog Fellow, and Cullen College of Engineering Professorship. Yao is a senior member of the National Academy of Inventors and IEEE, as well as a Fellow of the Royal Society of Chemistry.

This Special Collection provides an in-depth look at the rapidly evolving research landscape surrounding electrochemical energy storage technologies based on redox-active organic materials. With two review articles and more than 20 original contributions, this collection offers valuable insights into cutting-edge research efforts from around the world, covering a wide range of systems, including p-type and n-type redox systems, storage of monovalent alkali (Li^+ , Na^+ , K^+) ions, as well as divalent (Mg^{2+} , Ca^{2+} , Zn^{2+}) ions. The collection also includes investigations into both aqueous and non-aqueous systems, bio-sourced organic battery materials, covalent organic frameworks, as well as electrolyte and electrode composite engineering, with additional fundamental studies on organic molecular design and advanced characterization techniques, among others. This highlights the vast diversity of organic materials used for batteries and underscores the interdisciplinary nature of research in this field.

Both review articles focus on materials-level developments, with advanced materials as well as electrode engineering aspects being highlighted. Wang et al. review the chemical reactions, topology structure design, and regulation methods of crystalline covalent organic frameworks (COFs) and their application as electrode materials in metal-ion batteries (Li^+ , Na^+ , K^+ , Zn^{2+} , Mg^{2+} , and Al^{3+}). Tang et al. focus on the preparation of organics electrode materials/MXene composites and their applications as electrode materials for energy storage and highlight the composite materials synergy as helpful for enhancing the electrochemical performance of energy storage devices and facilitating the practical application of organic electrodes in energy storage.

The original contributions span over a wide range of applications and materials, with many of these converging also many concepts. For example, Yu et al. make use of thionin, a biological dye, for high-performance bipolar-type redox material for aqueous rechargeable zinc batteries. Chen et al. have developed a simple and scalable synthesis of a new class of anthranthrone-based organics from the cheap and commercially available dye vat orange 3. The obtained electrode materials display excellent performance and stability in secondary batteries, and highlight anthranthrone as a promising building block in conjugated polymers for energy-storage applications.

Li-ion and monovalent cation storage dominates still this field, most certainly given the similarity and easier adaptation of knowledge and technology accumulated over the past decades on Li-ion and recently, lithium, sodium, and potassium batteries (including ion shuttle systems, as well as metal anode type cells). Accordingly, many developments are being undertaken in order to bring organic lithium storage systems as close as possible to conventional inorganic-based systems. Wang et al. have explored a coordination strategy to fabricate the Co-ion intercalated two-dimensional COF, based on β -ketoenamine linkers, found to deliver improved lithium-storage performances and mechanism as the anode for lithium organic batteries. Through mechanistic studies, authors have also found

that the coordination of Co ion in adjacent two layered structure of COF can activate the Li^+ storage of aromatic ring in the original COF, with higher utilization of redox-active sites. Wang et al. present a study on conjugated azo compounds for Na-ion storage. They found that the conjugation in a linear polymer (terephthalaldehyde-4,4'-diazoniline) overcomes the disadvantage of poor solubility and stability of conventional small azo-based molecules, and results in excellent rate performance when applied as the electrode in sodium-metal batteries. Additionally, Mohammadirooubari et al. report on a series of functionalized polymers for Na- and K-ion batteries. The authors studied the electrochemical performance of three carbonyl- and azo-based polymers, demonstrating that the polymer with naphthalene backbone structure is the best, as compared with the ones with benzene and biphenyl structures, due to faster kinetics and lower solubility in the electrolyte.

Higher solubility on the opposite is advantageous for redox flow batteries (RFB), and many efforts are being concentrated in this direction as well. This Special Collection also contains a series of original developments on RFB, focusing on many of the complex aspects of this technology. For example, Peng et al. designed a polyethylene glycol (PEG) functionalized viologen redox active material (termed by the authors as PEGylated viologen anolyte) with low membrane permeability as well as high solubility in neutral pH water solution, with excellent performances attained when applied in a crossover-free and high-capacity aqueous organic redox flow cell. A different approach was implemented by Caianiello et al. wherein a new hydroxylated tetracationic viologen was effectively prepared by selecting a dimethylaminoethanol derivative as a permanently charged moiety. The compound showed enhanced solubility and after pairing with TEMPOL in an aqueous RFB cell, a performance of 300 galvanostatic cycles at a current density of 40 mA cm^{-2} , using a low-cost membrane was attained. A cationic ammonium functionalization strategy was also applied by Singh et al., yet using a two-electron redox naphthalene diimide redox center. This was designed to improve the solubility in neutral aqueous solutions, and when used as negolyte in aqueous RFB were found stable at a concentration of 0.3 M for 300 cycles without significant chemical degradation or crossover. Finally, Wu et al. disclose a study on low redox potential quinone derivatives. Amongst the three studied anthraquinones with C, N, O-linked water-soluble chains, the nitrogen-linked one showed the lowest redox potential of -0.62 V vs. SHE. Pairing this composition with a ferrocyanide catholyte resulted in a cell with an output voltage of 1.14 V, and very low capacity-fade rate of 0.025%/day at pH=14.

Rechargeable aqueous Zn-ion batteries have attracted vivid attention over recent years given their advantage of high safety and low cost, as well as the high specific capacity of Zn metal anode, such as (820 mAh g^{-1} or 5855 mAh cm^{-3}), low reduction potential (-0.76 V vs. SHE), and relatively higher abundance than Li in earth's crust. Whereas inorganic oxide host materials have been initially targeted, the sluggish Zn^{2+} intercalation

kinetics into solid crystalline frameworks results in poor power capability, and organic materials have been found again promising alternatives within this respect. New advances in this direction are provided in this Special Collection as well. For instance, **Yang et al.** unravel the factors affecting the performances of quinone-based polymer cathodes in aqueous Zn-ion batteries. Three different dihydroxynaphthalene monomers have been electrodeposited onto mesoporous activated carbon to prepare the polymer cathodes, and have been found to vary in terms of capacity and cycling stability, with the key factors behind this divergence being investigated and presented by combining experiment with theory. **Li et al.** detail high-performance aqueous zinc organic batteries by designing chalcogen atom (S or O) substituted indacene dione derivatives. One interesting finding is the increased redox potential of the O-atom substituted derivatives given the higher electro-negativity.

The great versatility of organic chemistry also reflects on the ability to fine tune the properties through molecular design. **An et al.** study the influence of the position and the number of the cyano groups on the solubility, redox potential, rate performances, and cyclic stability of hexaazatrifluorophthalene derivatives through combining electrochemical and DFT analyses. **Lužanin et al.** unveil the true limits of the electrochemical performance of organic cathodes in multivalent batteries through cyclable symmetric cells. These are applied for detailed electrochemical characterization of organic poly-(anthraquinonyl sulfide) cathodes in Li, Mg, and Ca electrolytes. **Desmaizieres et al.** report a systematic comparative study of cycling stability and rate performance between anisyl-substituted polyvinyl- and poly(styrylphenothiazines) as positive battery electrode materials and found that in the cross-linked styrene derivative, the π -interactions are facilitated due to the longer spacing to the phenothiazine side groups, leading to a high cycling stability yet at a reduced specific capacity. **Park et al.** designed and prepared the ortho isomer of triptycene tribenzoquinone to increase the redox potential while not penalizing its high specific capacity. The materials were tested for alkali metal batteries and were found to show a high energy density of 950, 770, and 600 Wh kg⁻¹ in Li, Na, and K cells, respectively.

Whereas a lot of focus is oriented on n-type metal cation storage materials, p-type redox materials, with anion charge compensation, thus potentially enabling metal-free batteries is another important mainstream in the field of organic batteries. This collection highlights in particular the work of **Hatakeyama-Sato et al.** on quadruply fused aromatic heterocycles toward attaining 4 V-class organic cathode-active materials. The newly synthesized dimethylfluoroflavin-substituted polymer displays reversible charge/discharge at high potentials of 3.5 and 4.1 V (vs. Li/Li⁺) as a cathode-active material for organic secondary batteries. A hybrid supercapacitor device is presented by **Gallastegui et al.** wherein the redox potential of a catechol-polymer redox system is increased after ambient storage, proving how the aging effect can have benefits such as an increase in the voltage output, specific capacitance,

cyclability, and Coulombic efficiencies of the device. The aging effect is explained by the autoxidation of the catechol groups and subsequent crosslinking of NPs due to catechol dimer formation.

Finally, electrode and device engineering are also essential aspects to be further optimized for organic batteries, given the many associated issues such as solubility, insulating nature, and low gravimetric density of organic materials. And a series of original contributions dealing with engineering aspects are also available in this Special Collection. **Wakamatsu et al.** report on nanohybrid materials consisting of oxidized polyoxometalates and carbon nanohorns, yielding high capacity even at high current densities owing to synergistic effects of the super-reduction of polyoxometalates and the increased electrical double layer capacitance. **Yu et al.** integrate carbonyl-rich imine-based conjugated microporous polymers with carbon nanotubes, and attain superior lithium storage performances as a result of large π -conjugated structure, abundant redox-active centers, and high material utilization. **Liu et al.** detail the beneficial effect of a highly concentrated electrolyte of 5 M LiTFSI in DME that is found to improve the cycling stability of 5,7,12,14-pentacenetrone cathode material, and the polarity adjustment rule further address the dissolution issue of small organic molecules. Additionally, through the investigation of the relationship between solvent/electrolyte property and dissolution, as well as the interactions between electrode and electrolyte, a guiding rule of the dependence of dissolution on polarity is proposed. **Cheng et al.** discuss how a high-areal-capacity and low-temperature rechargeable lithium-ion battery can be achieved based on perylene-3,4,9,10-tetracarboxylic dianhydride cathode and find that the π -conjugation results in a highly conductive material, which are favorable for the low-temperature performance at high mass loading.

In summary, predicting the ideal battery configuration and composition for the future is a difficult task at this stage. Moreover, it is clear that each application, such as portable electronics, automotive, and residential markets, will rely on different battery chemistries and configurations, making it even harder to predict. Although recycling batteries is a major effort, the aspects of sustainability still require practical and industrial importance, which remains a widely debated topic. Organic battery materials will undoubtedly have their place in the electrochemical energy storage landscape of the future. It is difficult to predict the exact location, role, and scale of organic batteries. Nonetheless, we need to be prepared for this possibility. The widespread adoption of lithium-ion batteries, which are crucial in mitigating climate change, will depend on incentives and investment in infrastructure. Contingencies cannot be anticipated in research, hence investing in creative researchers and keeping all options open for battery technologies is crucial.

We would like to extend our gratitude to all the contributing authors for their outstanding work, as well as to the reviewers for their careful assessment and constructive feedback on the

manuscripts. We are confident that this collection will serve as a source of inspiration for future researchers in the field of organic battery materials and applications. Lastly, we would like to express our appreciation to the *Batteries & Supercaps* editorial team for their exceptional efforts in organizing, managing submissions, and bringing together such a remarkable Special Collection.

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