Bottom-Up Design of Configurable Oligomer-Derived Conducting Metallopolymers for High-Power Electrochemical Energy Storage

Evgeniya Vorobyeva, Franziska Lissel, Mathieu Salanne, Maria R Lukatskaya

HAL Id: hal-03372932
https://hal.sorbonne-universite.fr/hal-03372932v1

Submitted on 11 Oct 2021

Bottom-Up Design of Configurable Oligomer-Derived Conducting Metallopolymers for High Power Electrochemical Energy Storage

*Evgeniya Vorobyeva[1], Franziska Lissel[2,*], Mathieu Salanne[3,*], Maria R. Lukatskaya[1,*]*

[1] Electrochemical Energy Systems Laboratory, Department of Mechanical and Process Engineering, ETH Zurich, 8092 Zurich, Switzerland, Email: mlukatskaya@ethz.ch

[2] Institute of Macromolecular Chemistry, Leibniz-Institut für Polymerforschung Dresden e.V., Dresden, Saxony 01069, Germany; Faculty of Chemistry and Food Chemistry, Technische Universität Dresden, Dresden, Saxony 01062, Germany; Institute of Organic Chemistry and Macromolecular Chemistry, Friedrich Schiller University Jena, Jena, Thuringia 07743, Germany; Email: lissel@ipfdd.de

[3] Réseau sur le Stockage Electrochimique de l'Energie (RS2E), CNRS FR3459, 33 rue Saint Leu, 80039 Cedex Amiens, France; Sorbonne Université, CNRS, Physicochimie des Électrolytes et Nanosystèmes Interfaciaux, PHENIX, F-75005 Paris, France; Institut Universitaire de France (IUF), 75231 Paris, France. Email: mathieu.salanne@sorbonne-universite.fr

ABSTRACT. In this Perspective, we sketch out a vision of fast charging and self-healable energy systems that are primarily organic, feature only abundant elements, and operate with ions other than lithium. Using conductive oligomers as highly configurable building blocks, it is possible to create intrinsically adaptable conductive polymeric networks that can be rejuvenated and recycled using simple and safe chemical treatments. Using the versatile organic chemistry toolbox, these oligomers can be further functionalized, for example, with redox-active sidechains for high charge storage capacity, and ligands capable of complexing metal centers. Crosslinking with metal ions converts the soluble oligomers into insoluble supramolecular networks to yield high-performing electrode materials. The oligomer-based approach can, thus, provide an exceptional level of control to the design of organic-based battery materials.
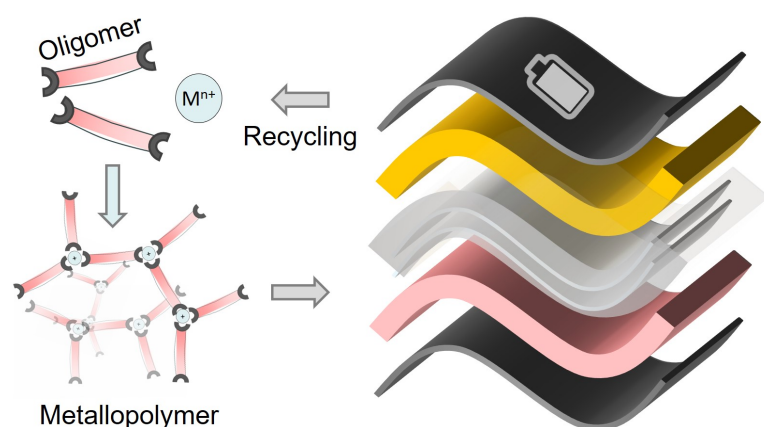
Lithium-ion batteries (LiBs) are one of the most mature battery technologies in the current market. Owing to their high energy density,[1] the demand for LiBs has grown substantially since their first commercialization in 1991 by Sony.[2] To date, LiBs not only dominate the market for portable electronic devices, but also are increasingly used in electric vehicles and grid-level energy storage systems.[3] It is predicted that the demand of batteries will increase tenfold by

2030, ultimately projecting a shortage of stable supply of the elements such as Li and Co, and causing further increase in their prices, while also affecting Ni supply and pricing.[4]

These concerns[5] particularly hinder the continual development of LiBs for large-scale energy storage applications[6,7] and have prompted the development of post-lithium energy storage systems (PLiES) using cations such as Na^+, K^+, Ca^{2+}, Mg^{2+}, Zn^{2+}, and Al^{3+} to store charge, which are much more abundant than Li.[8,9] However, replacing Li-ions with cations of larger size and/or charge poses several challenges associated with differences in ion radii and strength of cation–solvent interactions[10] and calls for the deep revision and re-exploration of the cathode and electrolyte chemistries.[11] Inorganic transition metal oxides are widely developed and studied as cathode candidates for PLiES but, upon charging, tend to display irreversible phase transformations resulting in a decrease in both voltage and capacity during charge/discharge as well as generally poor power density.[12] In addition, the relatively low amount of crystallographic interstitial vacancies for storing larger charge-carrier ions results in strongly limited energy densities for intercalation-based materials.[13] It is clear that desirable increases in the energy and power densities are not possible with current technologies and new redox chemistries between charge-carrier ions and host materials beyond the traditional 'intercalation' mechanisms are required.[14] Here, one might look to the field of supercapacitors for inspiration.

Supercapacitors are high power, high cycle life devices that typically have 2–5 times lower energy densities compared to batteries and are routinely used complementarily or in tandem with batteries when fast energy uptake and delivery is required.[15] Supercapacitors are based on the electrosorption of ions at the surface of highly porous materials such as carbon,[1] and/or fast reversible surface redox reactions such as in two-dimensional transition metal carbides (MXenes)[16] or hydrated RuO_2.[17] Because the charge storage mechanism differs from traditional intercalation, most materials for supercapacitors can operate with larger ions.

3

Organic-Based Energy Storage

Organic-based materials could provide an attractive solution for PLiES, potentially yielding sustainable and cost-effective energy storage systems based on the most abundant elements (*e.g.*, C, N, O, and Na).[7] Researchers have examined various types of organic materials, such as organic radical compounds,[18] organodisulfides, carbonyl compounds,[19] and hierarchical carbon/nitrogen architectures[20] for use as electrode materials.[21] Unfortunately, despite high theoretical capacity, their high solubility in electrolytes and insufficient electronic conductivity result in unacceptably low cycling stability and even poorer power density*,* critically limiting a widespread industrial application.[22] Lack of intrinsic electrical conductivity also translates into severe challenges related to the manufacture of electrodes with industrially relevant areal capacities because it requires the addition of large amounts (30–80%) of conductive carbon additives, which drastically affects the energy density of the resulting composite.[21] To address this issue, researchers have explored strategies such as immobilizing the organic molecules in polymeric frameworks to mitigate solubility and introducing intrinsic electrical conductivity through extended (backbone) conjugation.

Using conductive polymers is one of the strategies for introducing electrical conductivity into organic-based energy storage materials. Batteries based on conducting polymers, such as polyaniline,[23] polypyrrole,[22] and polythiophene and its derivatives,[24] were among the first organic-based systems explored for charge storage.[25] Their theoretical charge storage capacities are >200 mAh/g and their structural flexibility enables operation with charge-carrier cations beyond Li^+, making them attractive candidates for post-lithium organic energy storage.[26] However, the doping level of conductive polymers is typically below 50% (*i.e.* less than half of the redox-active groups undergo charging/discharging).[21] It is also worth noting that electrolyte chemistry (solvent, salt, concentration) plays a substantial role in the achievable degree of doping and cycling stability of conducting polymers.[24] To date, the most efficient

strategy for improving the doping level (other than electrolyte optimization) requires the use of sidechains with electron-donating or withdrawing groups, limiting their practical capacity.[25] In addition, during the redox process, intercalation of charged ions with their solvation shells can strongly affect the structure of the material and promote changes in the density of the electrode polymer:[27] Repetitive swelling and shrinking of the polymer during the intercalation/deintercalation process results in mechanical degradation of the electrode with cycling.[28–30] Some polymers are susceptible to an effect of overcharging that results in dissolution in the electrolyte. These factors drastically affect the cycling stability of the system,[24] necessitating revised approaches toward the design of conducting polymers for energy storage applications.

Synthetic Control *versus* Capacity Conundrum for Conductive Polymers

Currently, most conducting polymers used in charge-storage devices are structurally simple: Stripped-down heterocycles without sophisticated sidechains are condensed by either electropolymerization or by oxidative polymerization.[31] Neither method enables a substantial reaction control, and usually the reaction is conducted until an insoluble polymer material is obtained, which is then used as electrode. Due to the simple molecular structures of the monomer units, the resulting polymers have comparably high theoretical capacities. However, low reaction control and insufficient coupling selectivity inevitably leads to a polymer of low regularity with abundant structural defects, which in turn impairs crucial material properties such as conductivity and stability. When trying to mitigate their low performance by introducing functional sidechains (*e.g.*, redox-active groups to improve capacity), the problem is amplified: Poor coupling selectivity when polymerizing highly functionalized monomers often results in polymers with irregular structures and decreased stability.[32] The insolubility of the materials severely limits characterization possibilities, curtailing efforts to derive synthesis–property relationships. In addition, the insolubility of the polymer material does not

5

prevent its swelling and the associated long-term instability of the electrode.[28] Other polymerization mechanisms that enable a higher degree of reaction control and the possibility to condense highly functioned conjugated monomers require the utilization of metal catalysts.[33] The removal of the catalysts and characterization of the polymer requires a certain solubility of the material, which can be introduced *via* alkyl sidechains. In this manner, well-defined structures can be obtained, however, the resulting electrode materials again lack in capacity, power density, and cycling stability.[34]

Metal Centers for Stabilization of Organic Ligands.

Recently, an alternative based on metal–organic frameworks (MOFs) has been proposed. Metal–organic frameworks are porous materials constructed by the coordination of organic linkers to metal ions, creating extended networks and simultaneously immobilizing the ligand.[31] The high intrinsic porosity and surface area of MOFs enables ion access to redox-active sites.[35] However, their low electronic conductivity and insufficient chemical stability have limited energy applications of MOFs primarily to slow-charging batteries. Dincă and co-workers reported the synthesis of a few dozen electrically conducting MOFs[36] that demonstrated promise for supercapacitors due to their high power ability and good cycling stability.[37,38] However, their energy density is still insufficient to compete with batteries: Insights into the charge storage mechanism revealed that the organic linker plays the dominant role in the redox reaction, while the metal center is primarily a structural stabilizer.[11,39,40]

Synergistic strategies could potentially combine advantages of MOFs and conductive polymers to develop effective, organic-based electrode materials that possess excellent cycling stability and power density. An ideal organic-based material would combine a high density of redox-active sites in a conducting framework to enable a high capacity and a high-power electrode (**Figure 1a**). The material should be insoluble, to achieve a high cycling stability, and porous, to allow easy ionic accessibility of active sites, enabling the usage of larger charge-carrying

6

ions beyond Li-ion. Due to their structural versatility, metallopolymers could be one of the most promising platforms to create new energy storage materials to meet these requirements.
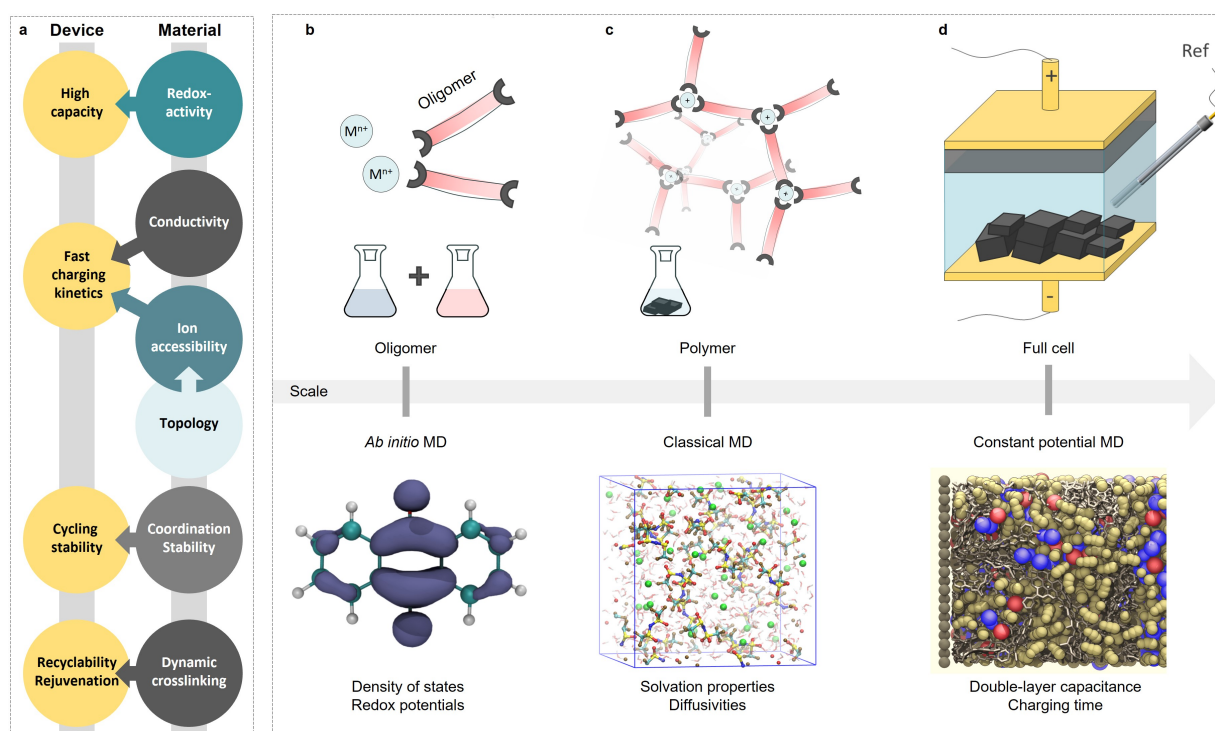

Figure 1. a) Influence of the material properties on the energy storage device characteristics. b–d) Various types of molecular dynamics (MD) simulations for gathering insights into fundamental aspects of the system from molecular to nanodevice level: b) *Ab initio* MD simulation of the redox-active and electrically conductive oligomers. Adapted with permission from ref 41. Copyright 2020 Royal Society of Chemistry. c) Classical MD for the characterization of the insoluble supramolecular structures. d) Constant potential MD for rationalization of the full cell. Adapted from ref 42. Copyright 2016 American Chemical Society.

Oligomer Approach

One way to achieve such highly configurable and highly performing organic-based electrode materials is to create metallopolymers based on coordinative networks of defined oligomers.

The use of highly functional oligomers crosslinked by metal complexes will result in insoluble and stable electrode materials that can potentially accommodate various metal cations, such as highly abundant Na^+. From a structural point of view, the oligomer approach entails two steps: First, conjugated oligomers with a defined number of repeating units (n = 4–10) are synthesized and, in a second step, they are crosslinked to yield insoluble supramolecular structures (**Figure 1b–d**).

Utilizing conjugated oligomers as conductive and redox-active building blocks has a number of advantages. One important benefit is the oligomers' intrinsic superior solubility.[43] This solubility not only enables easy handling and purification, but also complete structural characterization and—based on the characterization results—***targeted structural modification***. Altering molecular parameters such as backbone or sidechain layout enables the extensive manipulation of the material's properties. Also, the incorporation of redox-active sidechains and/or ligands to support redox-active metal centers is possible. Together with the intrinsic conductivity of the conjugated oligomer backbone, these functional groups can ensure high capacities and fast charging kinetics. Consequently, this approach offers exceptional configurability of the material's structure and properties, as well as better processability.

Upon crosslinking of the optimized oligomers, the metal–ligand interactions, which yield supramolecular structures, can serve multiple additional functions in the resulting material: Dynamic metal–ligand bonds can (**i**) enable the reconfiguration of the polymer during charge/discharge, positively affecting cycle life and perhaps ultimately yielding self-healing electrodes; and (**ii**) provide the option to recycle the material by removing and subsequently re-introducing the central ion, thereby opening the possibility to rejuvenate end-of-life electrodes. The establishment of metallopolymer-based materials with fast charging kinetics, high capacity, and high cycling stability can be achieved *via* two different structural layouts,

denoted here as *direct linkage* and *chain connection*. A schematic overview of these approaches is provided in **Figure 2**.
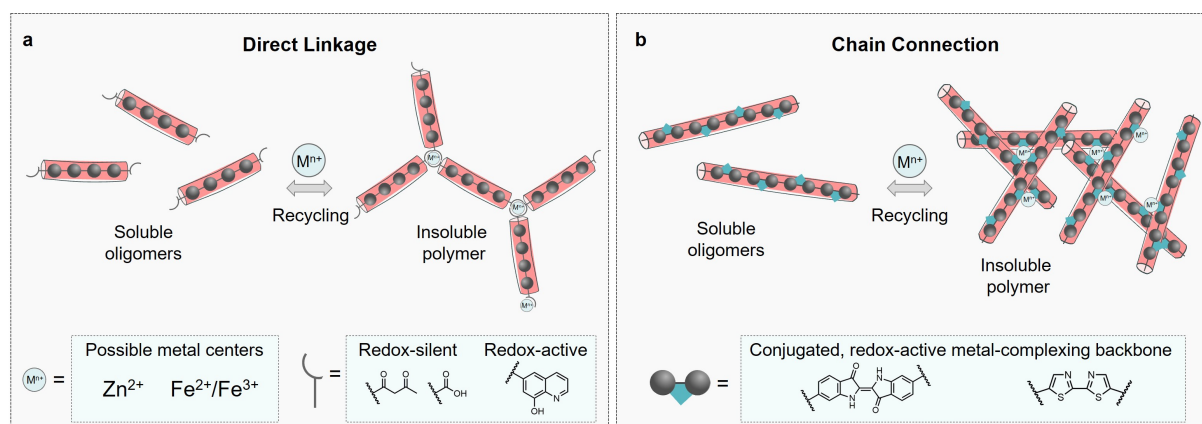

Figure 2. Schematic overview of the oligomer approaches for engineering metallopolymer-based materials: a) Direct linkage of the metal ion through redox-active or redox-silent heating groups; b) Chain connection approach that comprises crosslinking the oligomer redox-active backbones through the redox-active metal center. The dynamic nature of the crosslinking metal–ligand complexes enables recycling of the supramolecular network and, thus, the rejuvenation of the charge storage characteristics of the final electrode.

Direct linkage (**Figure 2a**) comprises the synthesis of conductive and redox-active oligomers (*e.g.*, oligothiophenes, oligopyrrole) with a defined number of repeating units and the modification of the terminal sites with chelating ligands (*e.g.* acetylacetonate) to enable crosslinking *via* metal ions (*e.g.*, Fe(acac)$_3$). The organic backbone of the oligomers can be further functionalized with redox-active sidechains (*e.g.*, tetrahydroxybenzene[32] or anthraquinone[44]) to improve their charge storage capacity. This design enables researchers to address and to mitigate potential problems regarding performance and synthesis; for example, the introduction of redox-active sidechains in oligomers can be understood as a strategy to enhance the capacity of a material. Yet, in all cases, the organic parts define the electrochemical

properties. The metal ions are primarily used for crosslinking, and their influence on electrochemical characteristics is mainly inductive.

Chain connection (**Figure 2b**) is a fundamentally different approach because the metal centers are complexed not by ligands located at the terminal sites of the oligomers, but by the monomeric units themselves. Because each repeating unit can complex a metal ion, the resulting supramolecular structure contains a high density of redox-active metal centers.[45,46] These metal centers play a tri-fold role: **(i)** crosslinking to define the topology of the resulting supramolecular material, **(ii)** tuning the redox potential of the organic building blocks, and **(iii)** actively contributing to the overall electrochemical response through their intrinsic redox activity. Promising chemistries for chain connection approach include bithiazole- and indigo-based conductive oligomers due to their high theoretical capacity.

In both approaches, the final step of crosslinking *via* metal ions enables the controlled formation of stable and insoluble materials. As a result, these methods offer features not readily found in conventional organic-based electrodes, such as the ability to self-heal, which, in turn, would positively affect the cycling stability.[47] Furthermore, the crosslinking metal complexes can be cleaved, for example *via* the addition of stronger ligands and subsequent reformation, potentially enabling recovery and recycling of the redox-active materials after prolonged electrochemical cycling.

Modeling: Moving Classical Molecular Dynamics Beyond Perfect Metal Electrodes for the Design and Development of Electrochemical Systems

The design of oligomer-derived conducting metallopolymers involves the use of several simulation techniques. As illustrated in **Figure 1**, the various components require calculations at either the electronic or the molecular scale. Electronic structure calculations facilitate characterization of the density of states using density functional theory (DFT) of the conductive backbone as well as the potentials of redox-active species using *ab initio* molecular dynamics

(MD; **Figure 1b**).[41] For each compound, several electrolytes should be tested in order to optimize the transport properties and the stability of the materials. Testing is done using classical MD performed on the pure liquids (**Figure 1c**). In particular, these simulations provide a full characterization of the structure of the solvation shells of the oligomers as well as the diffusivities of ionic species depending on the choice of electrolyte. The results of the simulations are directly comparable with experimental studies of rate-dependent electrochemical responses of the oligomers in different electrolytes. Both the theoretical and experimental results can be used to create a feedback loop and to guide the synthesis toward better-performing materials.

Finally, the experimental capacities and charging times can be systematically interpreted by simulating full electrochemical cells under operation conditions. These simulations will enable determinations of the double-layer structure and capacity of the device.[42] The state-of-art consists of performing constant potential MD (**Figure 1d**), in which the electrodes are set at fixed potentials. They are treated as perfect metallic conductors by allowing the atomic charges to fluctuate in response to the electrolyte species movement.[48] Although this model has recently been used for MOFs,[49] it is much better adapted to the case of bulk metallic electrodes and/or to nanoporous carbon materials, which have a simple chemical composition and structure and can generally be considered to be rigid. However, for systems that deviate from rigid behavior (*e.g.*, polymers or hybrid materials) this approach is not sophisticated enough because we expect different responses from the various moieties depending on their electronic structure and because flexibility is an important characteristic that governs device performance. A recent extension of the model to treat electrodes with different metallicities provides a good lead for developing the simulation tools that would be necessary to study conductive-polymer-based materials.[50] Coupled with DFT calculations of the redox potentials, these simulations will enable researchers to estimate the relative contributions of the faradaic and capacitive processes

11

to the overall performance and to guide experiments toward improved electrode design. The simulations will also provide a molecular scale view of ion accessibility within the porous structure and of the adsorption processes at the surface of the metallopolymer electrodes.

Outlook

The oligomer-based approach can potentially address drawbacks of the existing organic-based energy storage systems on all levels, from novel material design to full cell prototypes, as depicted in **Figure 1a**. Creating this new material class could simultaneously satisfy all of the following criteria.

(i) High capacity / high energy. High capacity and, hence, energy density of the metallopolymers could be realized *via* incorporation of small redox-active molecules capable of multielectron reactions as sidechains attached to conductive and redox-active oligomers. Numerous small molecule candidates should be screened both experimentally and theoretically to optimize overall energy density by taking into account both experimental capacity and operational voltage.

(ii) Fast charging kinetics. *a. Intrinsic electrical conductivity* realized through conductive oligomers and supramolecular networks is expected to ensure fast charging kinetics. The resulting fast charging kinetics has positive implications on the device level, ensuring that materials' performances (capacities and energy densities) can be translated for electrodes of industry-level thicknesses and attractive power density. *b. Ion accessibility* can be ensured by the incorporation of sidechains and through crosslinking geometries of metal complexes, which prevents aggregation of the otherwise densely packed oligomer chains and results in longer intermolecular distances. Thus, larger charge-carrier ions can be accommodated into the oligomer network during charge/discharge.

(iii) Cycling stability. Long-term cycling stability can be enabled through multiple strategies: *a. immobilization of redox moieties* on the polymer chain; *b. dynamic bonding* and, hence, the ability to self-heal is introduced *via* metal–ligand coordination; and *c.* introduction of *intrinsic porosity* through the topology of the coordination bonding to accommodate structural changes during charge/discharge.

(iv) Recyclability. *The controlled reversibility of the crosslinking step* enables the recycling of electrode materials by cleaving the coordination bond and subsequently reforming the supramolecular network.

REFERENCES

1. Zhang, M.; Song, X.; Ou, X.; Tang, Y. Rechargeable Batteries Based on Anion Intercalation Graphite Cathodes. *Energy Storage Mater.* **2019,** *16*, 65–84.
2. Kim, S.-W.; Seo, D.-H.; Ma, X.; Ceder, G.; Kang, K. Electrode Materials for Rechargeable Sodium-Ion Batteries: Potential Alternatives to Current Lithium-Ion Batteries. *Adv. Energy Mater.* **2012,** *2*, 710–721.
3. Chen, T.; Jin, Y.; Lv, H.; Yang, A.; Liu, M.; Chen, B.; Xie, Y.; Chen, Q. Applications of Lithium-Ion Batteries in Grid-Scale Energy Storage Systems. *Trans. Tianjin Univ.* **2020,** *26*, 208–217.
4. Curry, C. Lithiun-Ion Battery Costs and Market. *Bloomberg New Energy Finance* **2017**.
5. Sawicki, M.; Shaw, L. L., Advances and Challenges of Sodium Ion Batteries as Post Lithium Ion Batteries. *RSC Advances* **2015,** *5*, 53129–53154.
6. Quartarone, E.; Mustarelli, P. Review—Emerging Trends in the Design of Electrolytes for Lithium and Post-Lithium Batteries. *J. Electrochem. Soc.* **2020,** *167*, 050508.
7. Armand, M.; Tarascon, J. M. Building Better Batteries. *Nature* **2008,** *451*, 652–657.
8. Wang, H.; Chen, S.; Fu, C.; Ding, Y.; Liu, G.; Cao, Y.; Chen, Z. Recent Advances in Conversion-Type Electrode Materials for Post Lithium-Ion Batteries. *ACS Mater. Lett.* **2021,** *3*, 956–977.
9. Duffner, F.; Kronemeyer, N.; Tübke, J.; Leker, J.; Winter, M.; Schmuch, R. Post-Lithium-Ion Battery Cell Production and Its Compatibility with Lithium-Ion Cell Production Infrastructure. *Nat. Energy* **2021,** *6*, 123–134.

10. Walter, M.; Kovalenko, M. V.; Kravchyk, K. V. Challenges and Benefits of Post-Lithium-Ion Batteries. *New J. Chem.* **2020,** *44*, 1677–1683.

11. Feng, D.; Lei, T.; Lukatskaya, M. R.; Park, J.; Huang, Z.; Lee, M.; Shaw, L.; Chen, S.; Yakovenko, A. A.; Kulkarni, A.; Xiao, J.; Fredrickson, K.; Tok, J. B.; Zou, X.; Cui, Y.; Bao, Z. Robust and Conductive Two-Dimensional Metal−Organic Frameworks with Exceptionally High Volumetric and Areal Capacitance. *Nat. Energy* **2018,** *3*, 30–36.

12. Manthiram, A.; Knight, J. C.; Myung, S.-T.; Oh, S.-M.; Sun, Y.-K. Nickel-Rich and Lithium-Rich Layered Oxide Cathodes: Progress and Perspectives. *Adv. Energy Mater.* **2016,** *6*, 1501010.

13. Wang, F.; Wu, X.; Li, C.; Zhu, Y.; Fu, L.; Wu, Y.; Liu, X. Nanostructured Positive Electrode Materials for Post-Lithium Ion Batteries. *Energy Environ. Sci.* **2016,** *9*, 3570–3611.

14. Choi, J. W.; Aurbach, D. Promise and Reality of Post-Lithium-Ion Batteries with High Energy Densities. *Nat. Rev. Mater.* **2016,** *1*, 16013.

15. Dubal, D. P.; Ayyad, O.; Ruiz, V.; Gómez-Romero, P. Hybrid Energy Storage: The Merging of Battery and Supercapacitor Chemistries. *Chem. Soc. Rev.* **2015,** *44*, 1777–1790.

16. Anasori, B.; Lukatskaya, M. R.; Gogotsi, Y. 2D Metal Carbides and Nitrides (MXenes) for Energy Storage. *Nat. Rev. Mater.* **2017,** *2*, 16098.

17. Simon, P.; Gogotsi, Y. Perspectives for Electrochemical Capacitors and Related Devices. *Nat. Mater.* **2020,** *19*, 1151–1163.

18. Nishide, H.; Iwasa, S.; Pu, Y.-J.; Suga, T.; Nakahara, K.; Satoh, M. Organic Radical Battery: Nitroxide Polymers as a Cathode-Active Material. *Electrochim. Acta* **2004,** *50*, 827–831.

19. Wu, X.; Jin, S.; Zhang, Z.; Jiang, L.; Mu, L.; Hu, Y.-S.; Li, H.; Chen, X.; Armand, M.; Chen, L.; Huang, X. Unraveling the Storage Mechanism in Organic Carbonyl Electrodes for Sodium-Ion Batteries. *Sci. Adv.* **2015,** *1*, e1500330.

20. Zhang, Z.; Bao, J.; He, C.; Chen, Y.; Wei, J.; Zhou, Z. Hierarchical Carbon–Nitrogen Architectures with Both Mesopores and Macrochannels as Excellent Cathodes for Rechargeable Li–O$_2$ Batteries. *Adv. Funct. Mater.* **2014,** *24*, 6826–6833.

21. Lu, Y.; Chen, J. Prospects of Organic Electrode Materials for Practical Lithium Batteries. *Nat. Rev. Chem.* **2020,** *4*, 127–142.

22. Guo, F. M.; Xu, R. Q.; Cui, X.; Zhang, L.; Wang, K. L.; Yao, Y. W.; Wei, J. Q. High Performance of Stretchable Carbon Nanotube–Polypyrrole Fiber Supercapacitors under Dynamic Deformation and Temperature Variation. *J. Mater. Chem. A* **2016,** *4*, 9311–9318.

23. Jiménez, P.; Levillain, E.; Alévêque, O.; Guyomard, D.; Lestriez, B.; Gaubicher, J. Lithium N-Doped Polyaniline as a High-Performance Electroactive Material for Rechargeable Batteries. *Angew. Chem. Int. Ed.* **2017,** *56*, 1553–1556.

24. Novák, P.; Müller, K.; Santhanam, K. S. V.; Haas, O. Electrochemically Active Polymers for Rechargeable Batteries. *Chem. Rev.* **1997,** *97*, 207–282.

25. Schon, T. B.; McAllister, B. T.; Li, P.-F.; Seferos, D. S. The Rise of Organic Electrode Materials for Energy Storage. *Chem. Soc. Rev.* **2016,** *45*, 6345–6404.

26. Snook, G. A.; Kao, P.; Best, A. S. Conducting-Polymer-Based Supercapacitor Devices and Electrodes. *J. Power Sources* **2011,** *196*, 1–12.

27. Ibanez, J. G.; Rincón, M. E.; Gutierrez-Granados, S.; Chahma, M. h.; Jaramillo-Quintero, O. A.; Frontana-Uribe, B. A. Conducting Polymers in the Fields of Energy, Environmental Remediation, and Chemical–Chiral Sensors. *Chem. Rev.* **2018,** *118*, 4731–4816.

28. Wang, G.; Zhang, L.; Zhang, J. A Review of Electrode Materials for Electrochemical Supercapacitors. *Chem. Soc. Rev.* **2012,** *41*, 797–828.

29. Roberts, M. E.; Wheeler, D. R.; McKenzie, B. B.; Bunker, B. C. High Specific Capacitance Conducting Polymer Supercapacitor Electrodes Based on Poly(Tris(Thiophenylphenyl)Amine). *J. Mater. Chem.* **2009,** *19*, 6977–6979.

30. Wu, Q.; Xu, Y.; Yao, Z.; Liu, A.; Shi, G. Supercapacitors Based on Flexible Graphene/Polyaniline Nanofiber Composite Films. *ACS Nano* **2010,** *4*, 1963–1970.

31. Calbo, J.; Golomb, M. J.; Walsh, A. Redox-Active Metal–Organic Frameworks for Energy Conversion and Storage. *J. Mater. Chem. A* **2019,** *7*, 16571–16597.

32. Chang, C.-H.; Li, A.-C.; Popovs, I.; Kaveevivitchai, W.; Chen, J.-L.; Chou, K.-C.; Kuo, T.-S.; Chen, T.-H. Elucidating Metal and Ligand Redox Activities of a Copper-Benzoquinoid Coordination Polymer as the Cathode for Lithium-Ion Batteries. *J. Mater. Chem. A* **2019,** *7*, 23770–23774.

33. Baker, M. A.; Tsai, C.-H.; Noonan, K. J. T. Diversifying Cross-Coupling Strategies, Catalysts and Monomers for the Controlled Synthesis of Conjugated Polymers. *Chem. Eur. J.* **2018,** *24*, 13078–13088.

34. Mike, J. F.; Lutkenhaus, J. L. Recent Advances in Conjugated Polymer Energy Storage. *J. Polym. Sci., Part B: Polym. Phys.* **2013,** *51*, 468–480.

35. Wu, H. B.; Lou, X. W. Metal-Organic Frameworks and Their Derived Materials for Electrochemical Energy Storage and Conversion: Promises and Challenges. *Sci. Adv.* **2017,** *3*, eaap9252.

36. Xie, L. S.; Sun, L.; Wan, R.; Park, S. S.; DeGayner, J. A.; Hendon, C. H.; Dincă, M. Tunable Mixed-Valence Doping toward Record Electrical Conductivity in a Three-Dimensional Metal–Organic Framework. *J. Am. Chem. Soc.* **2018,** *140*, 7411–7414.

37. Skorupskii, G.; Trump, B. A.; Kasel, T. W.; Brown, C. M.; Hendon, C. H.; Dincă, M. Efficient and Tunable One-Dimensional Charge Transport in Layered Lanthanide Metal–Organic Frameworks. *Nat. Chem.* **2020,** *12*, 131–136.

38. Xie, L. S.; Skorupskii, G.; Dincă, M. Electrically Conductive Metal–Organic Frameworks. *Chem. Rev.* **2020,** *120*, 8536–8580.

39. Park, J.; Lee, M.; Feng, D.; Huang, Z.; Hinckley, A. C.; Yakovenko, A.; Zou, X.; Cui, Y.; Bao, Z. Stabilization of Hexaaminobenzene in a 2d Conductive Metal–Organic Framework for High Power Sodium Storage. *J. Am. Chem. Soc.* **2018,** *140*, 10315–10323.

40. Lukatskaya, M. R.; Feng, D.; Bak, S.-M.; To, J. W. F.; Yang, X.-Q.; Cui, Y.; Feldblyum, J. I.; Bao, Z. Understanding the Mechanism of High Capacitance in Nickel Hexaaminobenzene-Based Conductive Metal–Organic Frameworks in Aqueous Electrolytes. *ACS Nano* **2020,** *14*, 15919–15925.

41. Reeves, K. G.; Serva, A.; Jeanmairet, G.; Salanne, M. A First-Principles Investigation of the Structural and Electrochemical Properties of Biredox Ionic Species in Acetonitrile. *Phys. Chem. Chem. Phys.* **2020,** *22*, 10561–10568.

42. Burt, R.; Breitsprecher, K.; Daffos, B.; Taberna, P.-L.; Simon, P.; Birkett, G.; Zhao, X. S.; Holm, C.; Salanne, M. Capacitance of Nanoporous Carbon-Based Supercapacitors Is a Trade-Off between the Concentration and the Separability of the Ions. *J. Phys. Chem. Lett.* **2016,** *7*, 4015–4021.

43. Zhou, L.; Lv, F.; Liu, L.; Wang, S. Water-Soluble Conjugated Organic Molecules as Optical and Electrochemical Materials for Interdisciplinary Biological Applications. *Acc. Chem. Res.* **2019,** *52*, 3211–3222.

44. Choi, W.; Harada, D.; Oyaizu, K.; Nishide, H. Aqueous Electrochemistry of Poly(Vinylanthraquinone) for Anode-Active Materials in High-Density and Rechargeable Polymer/Air Batteries. *J. Am. Chem. Soc.* **2011,** *133*, 19839–19843.

45. Craig, D.; Goodwin, H.; Onggo, D.; Rae, A. Coordination of 2,2'-Bithiazole. Spectral, Magnetic and Structural Studies of the Iron(Ii) and Nickel(Ii) Complexes. *Aust. J. Chem.* **1988,** *41*, 1625–1644.

46. Beck, W.; Sünkel, K. Metal Complexes of Indigo and of Some Related Ligands. *Z. Anorg. Allg. Chem.* **2020,** *646*, 248–255.

47. Rao, Y.-L.; Chortos, A.; Pfattner, R.; Lissel, F.; Chiu, Y.-C.; Feig, V.; Xu, J.; Kurosawa, T.; Gu, X.; Wang, C.; He, M.; Chung, J. W.; Bao, Z. Stretchable Self-Healing Polymeric Dielectrics Cross-Linked through Metal–Ligand Coordination. *J. Am. Chem. Soc.* **2016,** *138*, 6020–6027.

48. Scalfi, L.; Limmer, D. T.; Coretti, A.; Bonella, S.; Madden, P. A.; Salanne, M.; Rotenberg, B. Charge Fluctuations from Molecular Simulations in the Constant-Potential Ensemble. *Phys. Chem. Chem. Phys.* **2020,** *22*, 10480–10489.

49. Bi, S.; Banda, H.; Chen, M.; Niu, L.; Chen, M.; Wu, T.; Wang, J.; Wang, R.; Feng, J.; Chen, T.; Dincă, M.; Kornyshev, A. A.; Feng, G. Molecular Understanding of Charge Storage and Charging Dynamics in Supercapacitors with MOF Electrodes and Ionic Liquid Electrolytes. *Nat. Mater.* **2020,** *19*, 552–558.

50. Serva, A.; Scalfi, L.; Rotenberg, B.; Salanne, M. Effect of the Metallicity on the Capacitance of Gold–Aqueous Sodium Chloride Interfaces. *J. Chem. Phys.* **2021,** *155*, 044703.

TABLE OF CONTENT
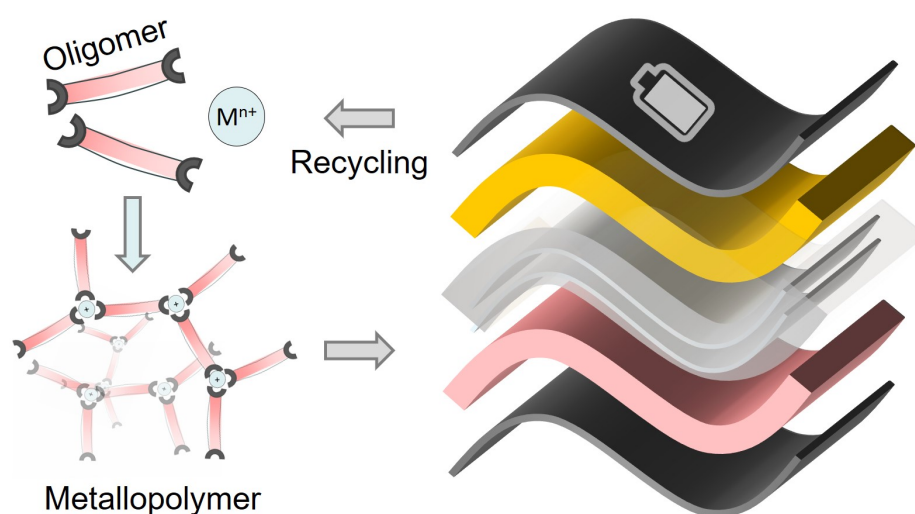
Suggested pull quotes

Organic-based materials could provide an attractive solution for post-lithium energy storage systems, potentially yielding sustainable and cost-effective energy storage systems based on the most abundant elements.

Due to their structural versatility, metallopolymers could be one of the most promising platforms to create new energy storage materials.