

Molecular design of functional polymers for organic radical batteries

J.C. Barbosa^a, A. Fidalgo-Marijuan^{b,c}, J.C. Dias^a, R. Gonçalves^d, M. Salado^{b,e}, C.M. Costa^{a,f,*}, S. Lanceros-Méndez^{a,b,g}

^a Physics Centre of Minho and Porto Universities (CF-UM-UP), and Laboratory of Physics for Materials and Emergent Technologies, LapMET University of Minho, 4710-057 Braga, Portugal

^b BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940 Leioa, Spain

^c Departament of Organic and Inorganic Chemistry, University of the Basque Country (UPV/EHU), 48940 Leioa, Spain

^d Centre of Chemistry, University of Minho, 4710-057, Braga, Portugal

^e Institute for Frontier Materials, Deakin University, Burwood, VIC, SA

^f Institute of Science and Innovation for Bio-Sustainability (IB-S), University of Minho, 4710-057 Braga, Portugal

^g IKERBASQUE, Basque Foundation for Science, 48009, Bilbao, Spain

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ABSTRACT

The growing demand for energy storage devices calls for the development of more efficient and sustainable systems. As the current lithium-ion batteries present several safety issues, as well as environmental hazards, some alternatives need to be taken into consideration. The area of organic materials based batteries is gaining interest as they allow for the replacing of the currently used metals, with significant environmental impact at the levels of extractions and processing, by organic redox-active materials, that are recyclable and environmentally friendly. In this review, an overview on the most recent advances in the field of organic radical batteries is provided, focusing on the different battery components and describing the main used materials and processes. The relevance of this topic for the development of a next generation of sustainable energy storage systems and the main challenges currently limiting the use of these kind of batteries are also addressed.

1. Introduction

In the current rush for sustainable electrical transportation, lithium-based batteries will be the flagship for the coming years [1]. However, some concerns arise regarding their mass production in terms of safe usage, non-hazardous disposal and recycling of batteries and battery components. It has to be taken into account not only the ethical and environmental challenges of mining lithium, cobalt and other mineral ore resources, but also the small fraction of lithium-ion batteries that is currently recycled, exacerbating consequently the global material supply of strategic elements [2]. In order to overcome these relevant issues, new environmentally friendly strategies need to be developed.

Among the wide spectra of possible energy storage systems, fully organic radical batteries (ORBs), in which both cathode and anode are organic redox-active materials, are among the most promising ones due to their minimum use of metal compounds, opening up a new field of ubiquitous safety devices with full recyclability. Among the different energy storage systems, ORBs present objective advantages but also challenges that should be overcome (Fig. 1).

Additionally, polymer materials based ORBs allow a wider range of processing methods such as printing (e.g., screen printing, inkjet printing), doctor blading, or roll-to-roll manufacturing, leading, furthermore, to rapid upscaling of technologies and the production of flexible devices [3].

1.1. Requirements and limitations of ORBs

Conducting polymers, such as poly(3,4-ethylenedioxythiophene) (PEDOT), polyacetylene (PA), polypyrrole (PPy), and polyaniline (PAN), have been studied as a lithium battery cathode active material. However, they present limitations in the doping levels as the excitons generated by the electrochemical redox reactions are generally delocalized, interacting with one another. Additionally, the dependence of the redox potential on the state of charge led to a prompt abandonment of this approach [4]. On the other hand, the combination of conjugated polymers with stable organic radicals are among the most used types of active materials in organic batteries. They are mainly characterized by an unpaired electron that is stabilized through sterically demanding

* Corresponding author.

E-mail address: cmscosta@fisica.uminho.pt (C.M. Costa).

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substituents or electron resonance. As the redox process involves only the transfer of a single electron with barely not structural changes, they present a fast electron transfer kinetics, resulting in high-rate capability and good cycling stability when implemented into batteries [5]. Chemical groups such as nitroxyl, phenoxy, and hydrazyl are robust structures with less-reactive unpaired electrons in the uncharged state. In particular, the 2,2,6,6-tetramethyl-4-piperidiny-N-oxyl radical (TEMPO) is the most studied one [6].

Up to now, due to the design complexity of an efficient polymeric anode, the ORBs system entails a metal (mostly lithium, zinc, sodium, magnesium) electrode, its respective metal-ion-containing electrolyte and an organic cathode electrode. The metallic anode consists of a M^{n+}/M redox couple where the metal is deposited during the charge and dissolved in the form of cations during the discharge process [7]. For organic anodes, the mass of the used materials is an important parameter, as it influences the effective capacity of the ORB.

The design of the organic cathodes should fulfill four main characteristics such as:

- The backbone should have a good conductivity (preferably higher than $10^{-5} \text{ S.cm}^{-1}$).
- The potential coupling of the charge transfer needs to be reasonably high to allow an electronic interaction between the involved donor and acceptor states.
- The Gibbs energy (ΔG) of the charge transfer from the radical to the backbone needs to be positive.
- The activation energy of the charge transfer should be small.

The electron affinity, polarizability and steric accessibility affect the intrinsic reactivity of the organic electrode. Depending on the polymerization technique, it is possible to design complex architectures like branched, graft, star-shaped, and brush polymers as well as dendrimers. Nevertheless, as mention before, the redox-active material could limit the number of suitable and matching techniques for the synthesis [8]. Zhang et al. showed that increasing the number of radical pendant groups attached to the conducting backbone entails a decrease in the conductivity of the material. This can be attributed to a disruption of the crystalline domains of the backbone [9]. For example, a PEDOT backbone with nitroxide-based TEMPO pendants exhibited a conductivity of

$5.7 \times 10^{-2} \text{ S.cm}^{-1}$ [10].

One relevant parameter to consider when polymers and small organic molecules are used to designed cathodes is the molecular aggregation. As consequence of the charge/discharge processes, their molecular oxidation states change and therefore their conformation package and aggregation state. This has a strong impact on the electrochemical properties of a small-molecule organic cathode. In this context, Wang et al. designed phenothiazine derivatives (e.g. 1,4-di(10Hphenothiazin-10-yl) benzene (PM-2S), 10-(4-(10H-phenothiazin-10-yl) phenyl)-10Hphenoxazine (PM-SO), and 1,4-di(10H-phenoxazin-10-yl) benzene (PM-2O)) as cathodes in order to unravel the key role of molecular aggregation in the electrochemical properties of the cell. Fig. 2 summarizes the different crystal structures behavior when molecules are in the charge or discharge states [11].

Among them, PM-2S delivered the best performance due to its flexible conformation. Using this molecule as organic cathode, the battery exhibited a specific capacity of 77 mAh.g^{-1} at 5C after 500 cycles, and a high reversible capacity of 78 mAh.g^{-1} at 10C.

As aforementioned, the most prominent radical investigated as ORBs to date has been the nitroxide-based TEMPO and its methacrylate polymer-derivative, poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate) (PTMA), which provides a cell voltage of 3.58 V versus Li. However, adverse effects of TEMPO radicals on the charge transfer within the electrode material and incompatibilities with other components of the battery (e.g. degradation of the cellulose based separator) have also been reported. Consequently, further improvement needs to be addressed to develop efficient organic based batteries. Wang et al. have recently reported the use of anthraquinone (AQ) as an organic redox mediator to promote TEMPO reduction kinetics [12]. When the electrode composite was prepared P(TMA-co-AQ)/ Multi-walled carbon nanotubes (MWCNT), the charge transfer resistance (R_{ct}) was reduced from 1646Ω (pristine PTMA) to 473Ω , attributed to the π - π interaction resulted from the core-sheath structure formed with the polymer wrapping around the surface of MWCNTs. In addition, the modified PTMA presented higher specific capacities and discharge capacities as well as better cycling stability when compared to the pristine counterpart (Fig. 3).

Instead of modified TEMPO radicals, other approaches using another nitroxide motifs, in particular the isoindoline-based 1,1,3,3-

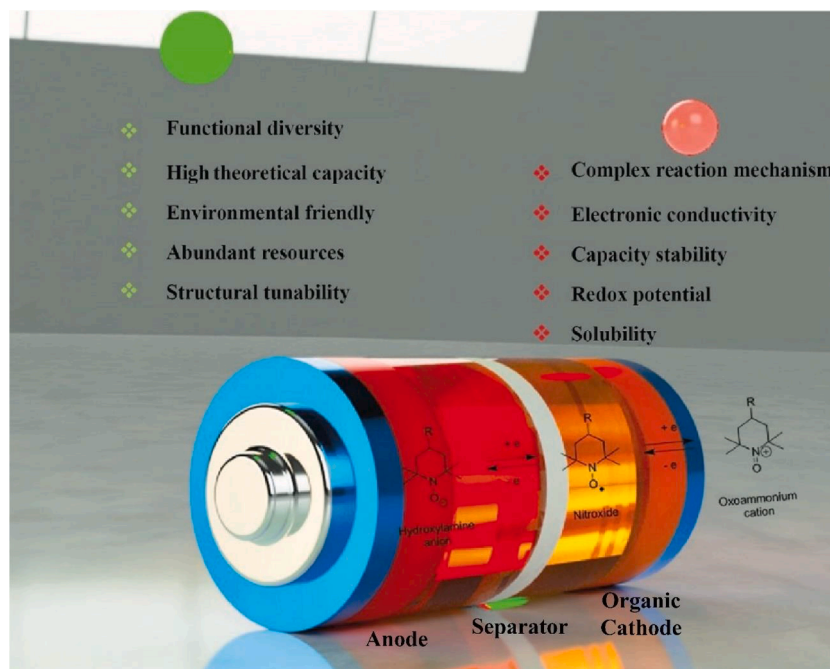


Fig. 1. Advantages and challenges of organic electrode materials for energy storage and representative structure of an organic battery.

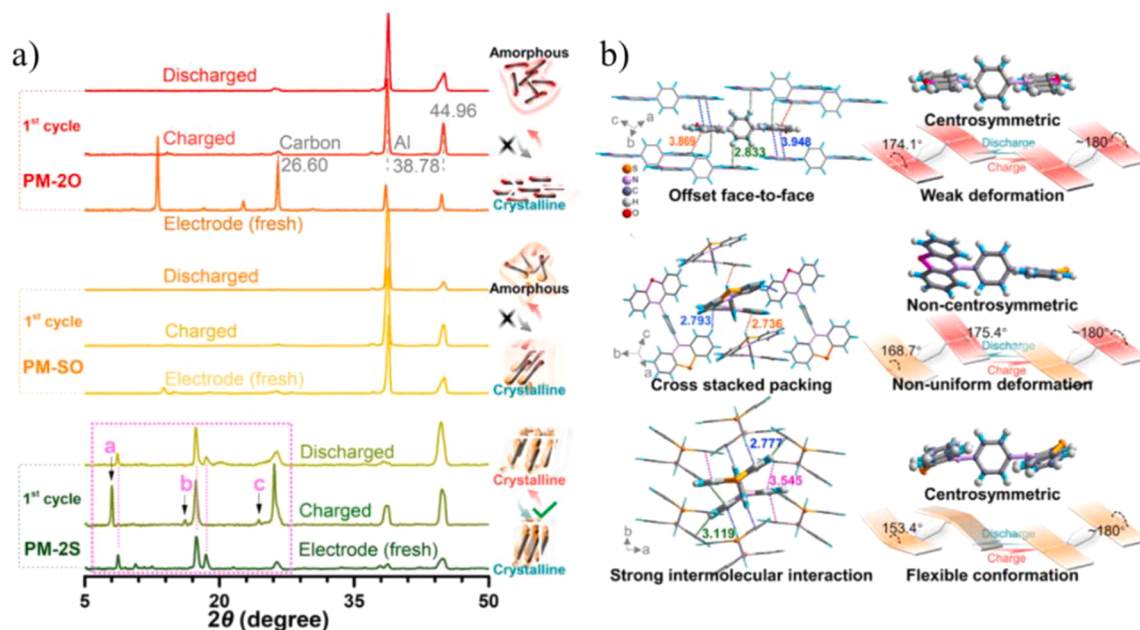


Fig. 2. (a) Ex situ grazing incidence X-ray diffraction (GIXD) patterns and (b) single crystal structure and stacking mode of the organic electrodes upon cycling. Reprinted with permission [11]. Copyright 2022, Elsevier.

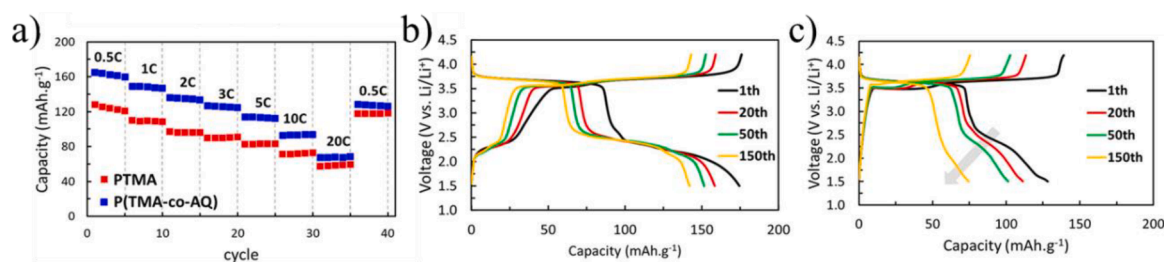


Fig. 3. (a) Specific capacities of PTMA and P(TMA-co-AQ) cathodes cycled from 0.5C to 20C at 25 °C. Typical charge/discharge profiles of (b) P(TMA-co-AQ) and (c) PTMA cathodes for the 1st, 20th, 50th, and 150th cycle at 0.5C. Reprinted with permission [11]. Copyright 2022, Elsevier.

tetramethylisoidolin-2-yloxy (TMIO) and poly(5-vinyl-1,1,3,3-tetramethylisoidoline-2-yloxy) (PVTMIO) have been developed for battery applications [13]. The electrochemical behaviors showed an improvement of 100–200 mV in the oxidation peaks with respect to PTMA (characteristic of the isoindoline nitroxides), entailing an increment of the energy density. Unfortunately, the low sublimation temperature of the small molecule (~50 °C) limits its use in battery applications. Nevertheless, PVTMIO exhibited quite impressive performance with a discharge voltage of 3.69 V, specific capacity of 104.7 mAh.g⁻¹ and excellent coulombic efficiency >99% after 100 cycles.

Although the concept of ORBs was introduced by Nakahar et al. in 2002, it was till 2009 when the first all-organic ORB featuring organic active materials for both electrodes was presented by Suga and Nishide et al. [14,15]. In this pioneering work, a combination based on poly(methacrylate)-combined TEMPO, poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate) as the cathode and the poly(galvinoxylstyrene) as anode was developed. The performance of the cell displayed a capacity of 45 mC.cm⁻² for the film with a thickness of 1 μm. Since then, other full organic systems have been explored, such as polytriphenylamine (PTPA) and 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA)-derived polyimide (PNTCDA) as cathode and anode, respectively [16]. Although this system uses an aqueous-electrolyte, it employs high salt concentration (21 M LiTFSI) “water-in-salt” solution in order to avoid water dissociation. The advantages of this system include an energy density of 52.8 Wh.kg⁻¹ and, more importantly, it can be designed from renewable and earth-abundant materials.

The majority of the works based on symmetric organic batteries (where both anode and cathode material have been investigated) have focused on quinones [17], terephthalic acids [18] or imides [19]. As an example, Casado et al. employed a phenothiazine and naphthalene-polyimide-based redox polymer for both anode and cathode [20]. This all-polymer battery delivered outstanding power density (1542 W.kg⁻¹) and excellent cycling stability (94% of capacity retention after 1000 cycles at 800 mA.g⁻¹). The same group reported also the use of P(TMA-co-AQ)/MWCNT cathodes in a fully organic battery with 2.8 V output voltage. This was achieved by using the most negative organic electrode material, terephthalate salts (e.g. Na₂TP and Ag₂TP), as anode and the aforementioned polymer as cathode. The full battery delivered a capacity of 43 mAh.g⁻¹ with an energy density of 157 Wh.kg⁻¹ at 0.5C. Regarding the stability, the battery still delivered a very stable capacity of 133 mAh.g⁻¹ for over 100 cycles even at 1C, showing only 0.02% loss per cycle with nearly 100% coulombic efficiency [21].

An all-organic battery concept was successfully achieved by fabricating a battery that do not rely on metals. For that, an all-polypeptide organic radical battery comprising redox-active amino-acid macromolecules was designed. The proposed battery reached a maximum charge capacity of 37.8 mAh.g⁻¹, being the theoretical capacity of 44.5 mAh.g⁻¹. More importantly, taking advantage of the polymer chemistry, the materials were designed for an on-demand polypeptide degradation (in the presence of acid) [22].

Although efficient fully organic batteries are still in an early stage, the stable cyclability, charge/discharge plateaus, and power density

obtained in these approaches makes this technology very suitable for an environmentally friendlier energy storage system. Moreover, it has also been demonstrated the great versatility of chemical modifications and the wide variety of novel material that can be employed in fully organic battery design.

Taking advantage of advanced Machine Learning (ML) tools, it is possible to predict the performance of rechargeable batteries as well as to find candidate polymer materials for batteries much more efficiently [23]. For instance, Li and Tabor [24] predicted molecules with high electron conductivity for the low potential components of organic radical polymer batteries. Using a Gaussian Process regression, a set of promising redox-active molecules and two Pareto-optimal molecules (both N-methylphthalimides) were identified. Another interesting approach consists of using materials with different redox potentials to predict novel polymers with ideal potentials by ML [25] (e.g. random forest - RF). After creating a data base from the screening of 600 previous experimental results and considering the redox potential, molecule structures and molecular fingerprints, RF was used to predict/generate new structures that were checked to prevent invalid structures. From the 47 structures obtained (most of them benzene rings and some specific functional groups and a nitrogen atom), a monomer bicarbazole-phenyl (BCz-pH) with high redox activity was successfully predicted. The battery performance was improved in terms of discharge voltage, cycle stability and high specific capacity when this molecule was used as cathode material. In addition to predict new candidate materials for organic batteries, molecular dynamical (MD) simulations can also provide an insight in the charge transfer kinetics in ORBs [26]. In particular, semiclassical Marcus theory and MD simulations were used to evaluate structure-property relationships in the frame of this new class of materials (e.g. TEMPO linked to thiophene units) as well as the (intramolecular) charge transfer kinetics among the redox-active units.

Consequently, organic batteries (OBs), and in particular ORBs, possess a great future ahead regarding their good electrochemical properties and cycle sustainability. However, much work needs to be carried out in order to be competitive with current technologies based on inorganic materials.

In the following, the composition of the different ORB components (Section 2), the current status on materials for organic batteries (Section 3), and the state of the art of the different types of organic batteries (Section 4) are comprehensively reviewed.

2. Composition of the main components of organic radical batteries

Organic batteries, similar to the typical batteries, are based on three main components: two electrodes (cathode and anode) and a separator, the latter being typically a porous membrane soaked in an electrolyte solution. Regarding the electrodes, they can be divided in three different constituents: active material, conductive material and polymer binder.

2.1. Active material

The core demand to a battery active material is the availability of at least one reversible electrochemical process with stable species in both the oxidized and the reduced form. The respective redox potential should be appropriate, i.e., as high (p-type material) or low (n-type material) as possible, but still manageable regarding the used electrolyte and current collector, to achieve a cell voltage that is as high as possible. Organic compounds offer a large pool of available structures and possibilities of functionalization, which enable the tuning of the redox processes of interest, in particular regarding the redox potentials (Table 1). Thus, compounds that can either serve as p-type or n-type material or even both (b-type) can be prepared, although most of the organic materials that have been developed up to now are more suited for applications as p-type material due to their relatively high redox

potentials. In addition, a high specific capacity, which leads, in combination with a high cell voltage, to a high specific energy, is likewise essential for active materials [27]. Furthermore, an appropriate (low) solubility in the used electrolyte system is required to impede shuttling effects, which lead to self-discharge and low cycling stability. This is often achieved through the introduction of polymerizable groups and the subsequent polymerization or crosslinking. In addition, polymerization improves the film-forming ability of the material, which facilitates the processing via additive manufacturing techniques (e.g., screen printing, inkjet printing). Regarding economic aspects, also a simple and straightforward synthetic route and cheap raw materials are desirable.

2.2. Conductive additive and binder

Most of the applied conductive additives are nanostructured carbon materials, e.g., carbon nanoparticles, mesoporous carbon, vapor-grown carbon fibers, graphene, and carbon nanotubes [27].

A binder material can be necessary to ensure intermixing of the active material and the carbon conductive additive, as well as to enhance the mechanical stability of the composite electrode. It has therefore an essential impact on the battery performance and stability. When organic solvents are applied in the electrode processing or the battery electrolyte, fluorinated polymers, e.g., poly(tetrafluoroethylene) (PTFE) and poly(vinylidene difluoride) (PVDF), are mostly used due to their electrochemical stability, binding capability, and electrolyte absorption ability. For water-based systems, carboxymethyl cellulose (CMC) is the most frequently used binder. Metal salts of CMC, poly(acrylate)s, or PEDOT:PSS represent alternatives that enhance the composite performance by the introduction of additional ions or semi conducting characteristics [27].

2.3. Electrolytes

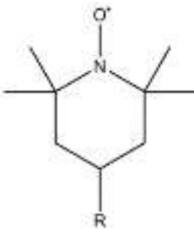
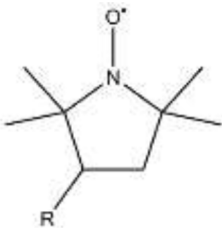
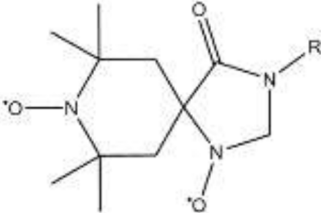
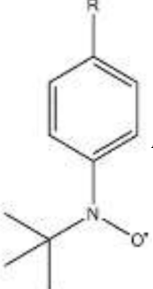
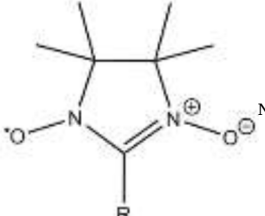
The electrolyte is essential for the maintenance of the charge balance during the redox processes in battery charging/discharging, using organic components both in the salts and solvents. Besides the fundamental requirement to provide ions of the necessary type and with a maximum mobility, the electrolyte must be electrochemically and chemically inert under the applied conditions and used materials. Furthermore, it must be stable regarding evaporation and flammability, show a low toxicity, and feature good swelling and affinity toward the composite electrode to ensure effective ion exchange [27]. The typical commercially available batteries already use organic components in their electrolytes, such as lithium hexafluorophosphate (LiPF_6) in different proportions of various carbonate solvents as ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC) [28]. Usually, these electrolytes use two combined solvents to meet the requirements of high fluidity and dielectric constant to promote ion dissociation [29]. Another approach for organic materials can be the use of different kinds of ionic liquids, due to their high viscosity and stability [30]. This approach is advantageous as ionic liquids promote the safety of the batteries due to their non-flammability and low toxicity. However, ionic liquids still lack the needed ionic conductivity to work properly as electrolyte, and still possess some compatibility issues with the other battery components [31]. The safety of organic batteries can be further improved by replacing the conventional electrolytes by solid electrolytes, similarly to the conventional batteries. This can represent an advantage, as many materials that are not suitable for conventional batteries can be more compatible when combined with organic electrodes [32]. In this particular case, solid polymer electrolytes are the most suitable candidates, due to their thermal and mechanical stability and good compatibility with organic electrodes [33].

3. Materials for organic radical batteries: organic radicals and polymer backbone combinations

Organic Radical Batteries (ORBs) can be classified based on the active material, a stable organic radical characterized by the presence of an unpaired electron within the molecule and able to form

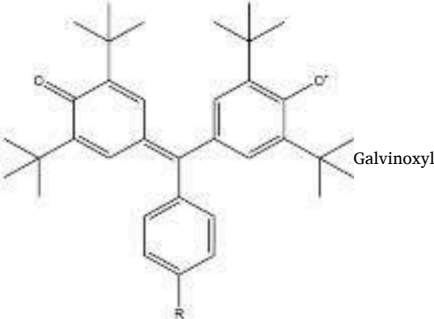
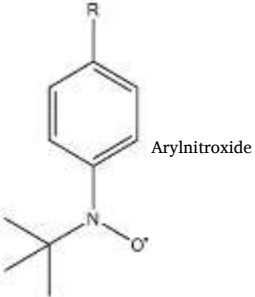
macroradicals [34] bearing polymers. In order to avoid stability problems, those radical entities are connected with substituents preventing the bond formation between radicals [35,36]. Different organic radicals have been used for ORBs, and as shown in Table 1, the most common organic radical motifs are the nitroxyl and the phenoxyl ones, such as, TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl) [37], PROXYL (2,2,5,

Table 1
Overview of the radical and polymer backbones used for ORBs.

	Radical	Polymer backbone	Ref.
p-type polymer	 <p>TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl)</p>	poly(methacrylate) (PMA) poly(acetylene) (PAC) poly(norbornene) (PNB) poly(vinylether) (PVE) poly(ethylene glycol) (PEG) poly(7-oxanorbornene) (PONM) poly(methyl siloxane) (PMS) poly(ethylene-alt-maleic anhydride) (PEM) Polyallene poly(β -ketoester) poly(acryl amide) poly(thiophene) (PT) poly(4-glycidyoxy) Polypyrrole Polyaniline (PANI) Cellulose DNA ionic liquids Porous organic framework (POF) Graphene poly(acetylene) (PAC) poly(norbornene) (PNB) poly(ethylene glycol), (PEG) Cellulose	[37,43-74] [75-79] [14,77,80-84] [85-88] [89-91] [92] [93] [94] [95] [96] [97,98] [99-101] [102] [103] [104] [105] [106] [107-111] [112] [113] [78,114] [114] [38,90] [105]
	 <p>PROXYL (2,2,5,5-tetramethyl-1-pyrrolidinyloxy)</p>		
	 <p>Spirobisnitroxide</p>	poly(acetylene) (PAC)	[39]
	 <p>Arylnitroxide</p>	poly(methacrylate) (PMA) poly(styrene) (PS)	[40,115] [116]
Bipolar polymer	 <p>Nitronylnitroxyl</p>	poly(styrene) (PS)	[41,117]

(continued on next page)

Table 1 (continued)

Radical	Polymer backbone	Ref.
n-type polymer	poly(styrene) (PS) poly(vinylphenol) (PVP)	[14,117] [42,118,119]
		
	poly(styrene) (PS)	[116]

5-tetramethyl-1-pyrrolidinyloxy) [38], Spirobisnitroxide [39], Arylnitroxide [40], Nitronylnitroxyl [41] and Galvinoxyl [42].

Among the nitroxyl radical materials, TEMPO is the most explored radical, being the use of poly(methacrylate) (PMA) as polymer backbone the most extended, reaching more than 40% of publications among all the polymers for this specific field (Fig. 4). In fact, since Nakahara et al. reported the first application of poly(2,2,6,6-tetramethylpiperidinyloxy methacrylate) (PTMA) as an organic radical cathode material for rechargeable batteries [55], most efforts have focused on developing materials based on nitroxyl radicals. PTMA has a theoretical capacity of $111 \text{ mAh}\cdot\text{g}^{-1}$ and during the last decade most of the studies were focused on the variation and optimization of established systems, reaching capacity values close to the theoretical one [43,46]. Other polymer backbones have been used in conjunction with TEMPO (Table 1), among which the work carried out in the last 5 years with poly(ethylene-alt-maleic anhydride) (PEM) by Chen et al. [94], poly(acryl amide) by Zhu et al. [97], poly(thiophene) (PT) by Aydin et al. [99], poly(4-glycidyl) by Sukegawa et al. [102] and polypyrrole by Xu et al. [103] stands out. Furthermore, a special interest has been focused on the development of TEMPO materials with ionic liquids [107–109] and Porous Organic Frameworks (POFs) [112]. Ionic conductivity and the contribution of stability to the system by ionic liquids and the advantages of low cost, excellent chemical stability, ultrahigh surface area, and facile synthesis of POF materials, opened a new way for designing functional promising materials for potential applications in electrochemistry-related fields.

Most of the further studied organic radicals for applications in ORB are also nitroxyl radicals, such as (2,2,5,5-tetramethyl-1-pyrrolidinyloxy) (PROXYL) based materials studied by Qu et al. [78,105,114] and Oyaizu et al. [38,90], Spirobisnitroxide [39], Arylnitroxide [40] and Nitronylnitroxyl [41]. Very few polymeric backbone compounds have been used with those radicals (Fig. 4), being poly(styrene) (PS) the most widely studied. Further, it has been no further investigation in recent years in these materials.

While p-type nitroxyl polymers (cathode) like PTMA can be easily synthesized, the preparation of n-type polymers (anode) potentially replacing lithium is a more challenging task [120]. First approaches focused on phenoxyl radicals, such as galvinoxyl bearing poly(styrene), were generally prepared by free radical polymerization processes by

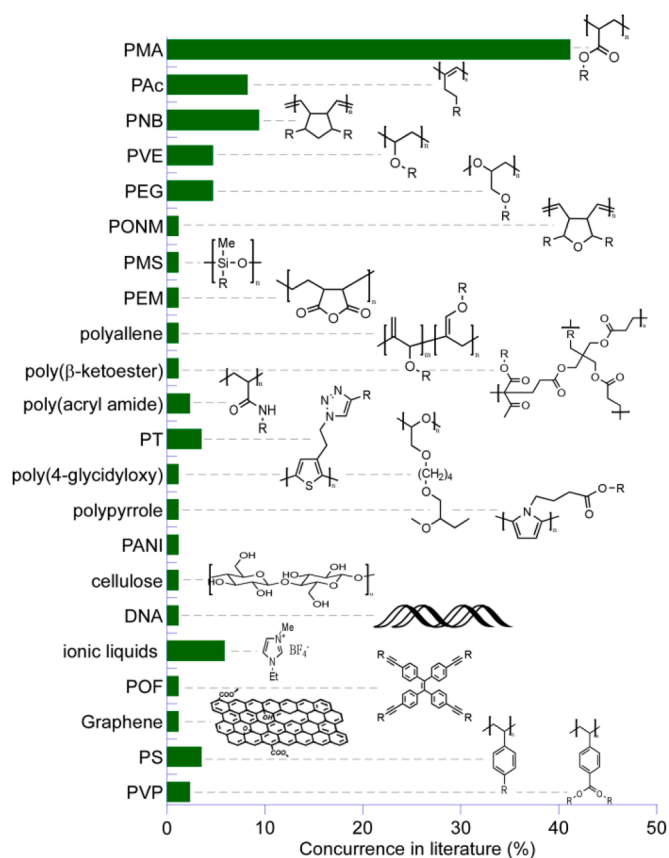


Fig. 4. Concurrence in literature of polymer backbones for organic radicals used as electrode materials in ORBs (source: Web of Science).

Suga et al. [14,117], and during the last years poly(vinylphenol) (PVP) backbones were introduced by Janhert et al. [42,119] and Kaneko et al. [118].

As TEMPO-containing polymers are the most widely tested, those

polymers were combined with conductive carbon materials in order to improve the electrochemical properties through enhanced electronic conductivities. Thus, carbon fibers [121], nanocarbons [51], graphene [65,113] and CNTs [102,108] were used, among others, either by in situ polymerization on the material [122], by co-dispersion [123], by encapsulation [124], or by grafting-on approaches [125].

The resulting materials often showed a sloping or multistep voltage, most likely due to an additional capacitive contribution by the high-surface area of the carbon material. On the other hand, a significantly improved rate capability, increased energy density and rapid electron transfer compared to simple composites of active material and conductive additive were achieved [36], showing great potential for energy storage devices.

To conclude, during the last years no new macroradicals with promising properties for ORBs have been developed. However, already established TEMPO (mainly PTMA) systems have been further studied and optimized in order to obtain an improved battery performance.

4. Current developments on organic radical batteries

Organic radical batteries can be applied in different kinds of battery systems, such as lithium-ion, sodium-ion and potassium-ion. These batteries can be fully organic or partially organic, and most of the research is focused on the electrode materials, mainly at the active materials level.

The reversibility of the electrochemical reaction (redox) of the active material serves as the basis, mainly, for the choice of an electrode material for a rechargeable battery, either as cathode or anode. According to the proposed classification of Hünig (Fig. 5), organic molecules present a redox chemistry based on the change of the state of charge of the molecule, which offers access to three different redox mechanisms [126]. Accordingly, n-type systems are characteristic of the organic molecules evolving from a neutral state to a negatively charged one accompanied by cation uptake (e.g. Quinones) while p-type systems are considered if the molecule is evolving from a neutral to a positively charged state, accompanied by anion uptake (e.g. conjugated amines and conductive polymers).

Bipolar systems combine both types of mechanisms. The same organic molecule or, eventually, the same redox center, can evolve from a neutral to a positive state and acts as a p-type system or a negative one and acts as a n-type system. Nitroxide radicals are the most typical here but are generally used as a p-type system due to its high redox potential (> 3.5 V vs. Li^+/Li) and better stability than n-type redox.

N-type systems for organic cathode materials are the most considered with carbonyl-based chemistries being by far the most used due to

their potential to achieve simultaneously high energy and high power densities, as well as by their cycling stability [126,127].

In general, organic molecules are divided into two main groups: carbonyl compounds [128–134] and organic polymers [36,120,132, 134–142].

Most carbonyl compounds are n-type organics in which one carbonyl undergoes a reversible one-electron reduction to form a monovalent anion. This is balanced by a metal-ion and stabilized by structural substituents [143]. Carbonyl compounds can be classified into three types according to the stabilization mechanism (Fig. 6a). Type I are compounds that use vicinal carbonyls to form stable enolates. For type II compounds, which include aromatic carboxylates (Fig. 6b), imides (Fig. 6c) and anhydrides (Fig. 6d), carbonyl groups are directly connected to an aromatic core that disperses the negative charge by delocalization. Type III compounds are mostly quinones (Fig. 6e) and ketones (Fig. 6f). These share some characteristics of type I and II compounds, however, the main stabilizing force comes from the formation of extra aromatic systems upon reduction. Due to their large structural variety, the redox behavior of carbonyl compounds can be adjusted by the inductive and resonant effect [143].

Regarding organic polymers (Fig. 7), they include conductive polymers (Fig. 7a) [144], conjugated microporous polymers (Fig. 7b), nitroxyl radical polymers (Fig. 7c–e) [145], organometallic polymers (Fig. 7f), Schiff bases (Fig. 7g) and pteridine derivatives (Fig. 7h).

At large, redox polymers include carbonyl polymers, nitroxyl radical polymers, sulfur containing polymers and conducting polymers. They have several advantages, such as flexibility, film forming ability, versatile chemical structures, tunable redox properties, abundant resources and recyclability. For different applications, they are attractive in a number of electrochemical devices, such as biosensors, biofuel cells, batteries or electrochromic devices [127].

Redox polymers reported cell voltages of up to 4.1 V, so, they are among the best organic cathode materials versus lithium as anode. Two classes of polymers have been mainly considered, as shown in Fig. 7: aliphatic redox polymers and conducting polymers.

In the first, to ensure their insolubility in battery electrolytes, redox-active groups are covalently attached to an aliphatic polymer backbone. Polymers containing stable nitroxyl radicals in the side group are typical examples of this class of polymers. These polymers are generally electronically insulating, and charge transport between redox-active side groups can only occur through hopping processes or self-exchange between redox centers, which limits their rate capability. Their main advantage is that they feature a stable redox potential, regardless of the charging state of the battery.

On the other hand, conducting polymers, possess intrinsic

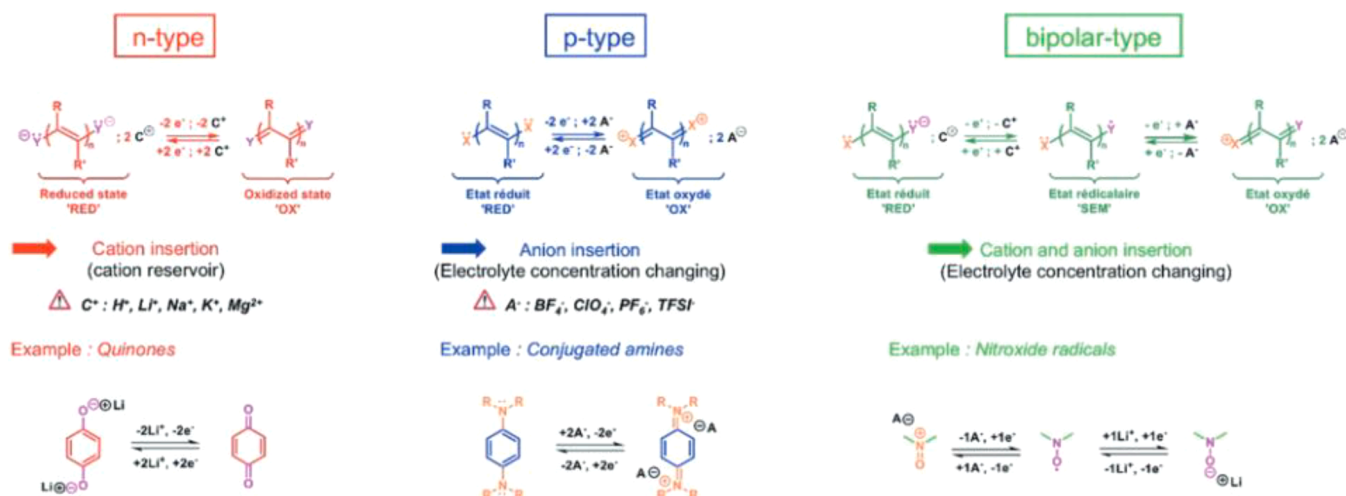


Fig. 5. Hünig classification of redox reactions of organic molecules. Reprinted with permission [126]. Copyright 2018, Chimie novell.

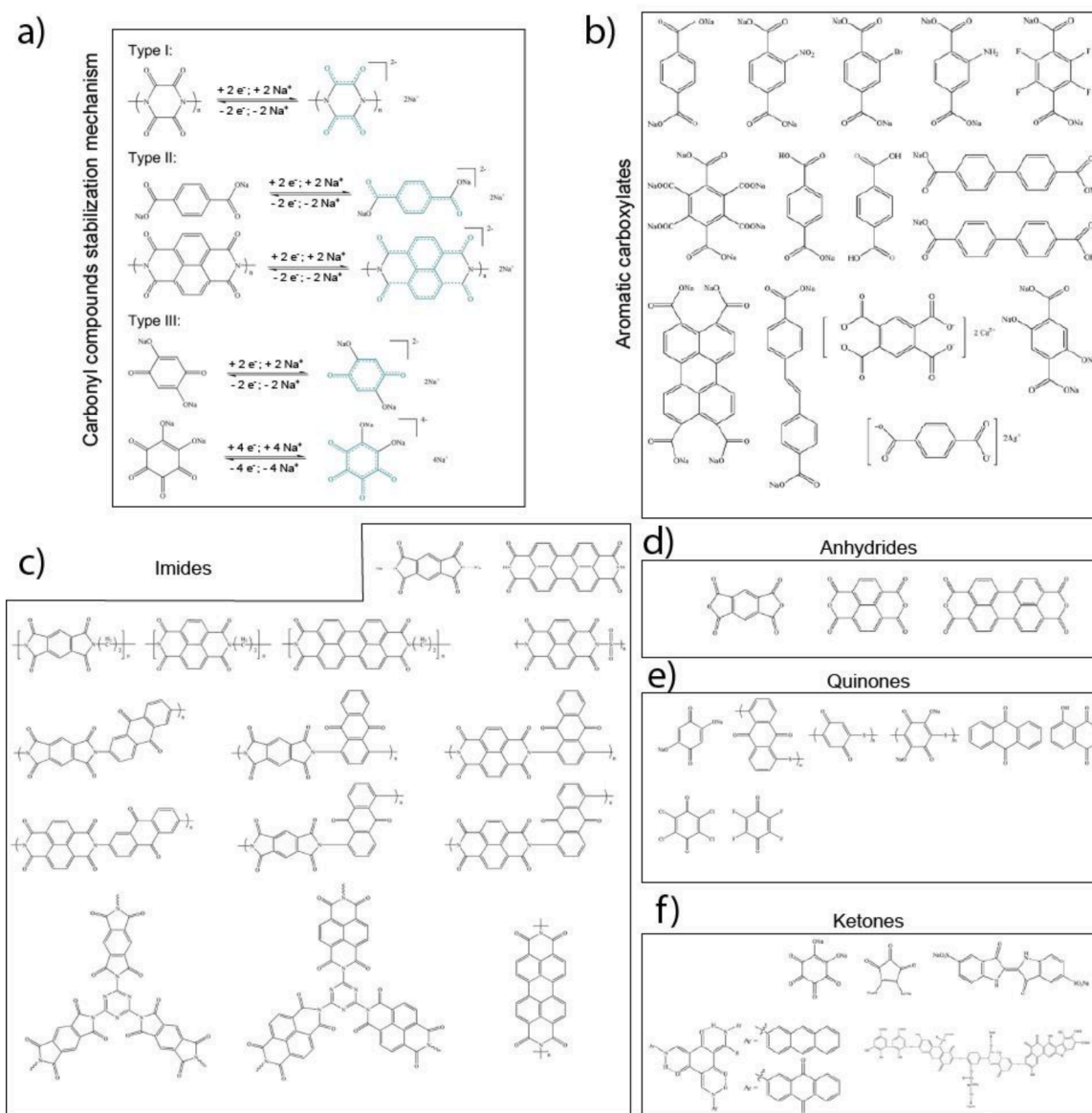


Fig. 6. (a) Carbonyl compounds stabilization mechanism, (b) Aromatic carboxylates, (c) imides, (d) anhydrides, (e) quinones, (f) ketones molecular structures. Reprinted with permission [143]. Copyright 2018, Elsevier.

conductivity in the doped state, but sloping charge/discharge potentials due to the extensive delocalization of charges. Moreover, frequently only low doping levels are available in a reversible fashion. A combination of designs by using π -conjugated redox polymers P1 and P2 as cathode-active materials in a lithium organic battery is presented in Fig. 8 [146].

Still on conducting polymers, they have been used in a variety of applications. These materials exhibit the ability to allow the passage of electric current, store charge or display redox activities. Common polymers are mostly dielectric and can be modified in order to conduct electric current by the addition of conducting fillers, as metal powders, carbon black and other conductive materials. These filled polymers are commonly called Extrinsic Conducting Polymers – ECP's and can be used as pressure sensors, actuators, or electromagnetic interference (EMI) shielding, among others [147].

Polymers formed by chains that contain conjugated chemical double bonds, with a minimal molecular size able to produce electrical conductivity, are usually called Intrinsically Conducting Polymers – ICP's or simply conducting polymers. These materials formed by organic molecules containing conjugated chemical bonds such as aromatic rings and/

or conjugated oligomeric or polymeric conjugated oligomeric/polymeric chains have attracted enormous attention because of the possibility of their utilization in the development of electronic devices.

As already mentioned, conjugated polymers are formed by a main backbone containing alternating single and double chemical bonds known as conjugation. Whereas a single bond (or sigma bond, σ) is strong and contains strongly localized electrons under a sp^3 orbital symmetry, a double bond (or pi bond, π) is weaker and electrons are less localized following a sp^2 orbital symmetry. This means that π electrons may exhibit higher mobility when compared to σ electrons and can move along the backbone since the conjugation leads to the formation of extended delocalized orbitals [147].

Conducting polymers (CPs) include polyaniline (PANI), polypyrrole (PPy), polythiophene (PTh), poly paraphenylene vinylene (PPV), and poly(3,4-ethylenedioxythiophene) (PEDOT) [148,149], among others. Electrochemically changing the oxidation state leads to the addition or removal of charge from the polymer backbone as well as a flux of ions to balance charges. This ion flux, often accompanied by solvent, induces swelling or contraction of the material. In addition, the conformation changes of the polymeric chain also take place. By these processes, the

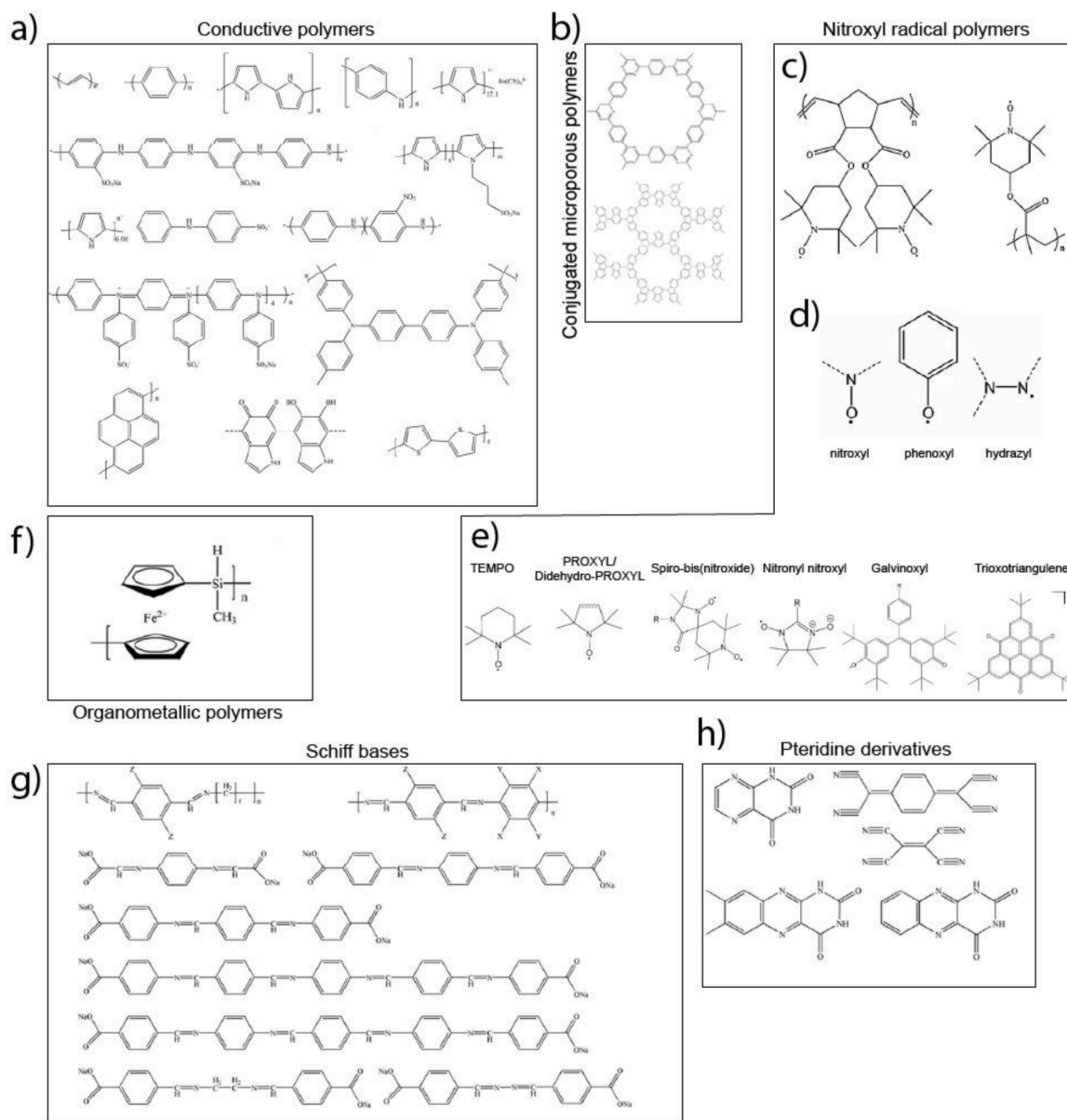


Fig. 7. Organic polymers chemical structures of (a) conductive polymers. Reprinted with permission [143]. Copyright 2018, Elsevier, (b) conjugated microporous polymers. Reprinted with permission [143]. Copyright 2018, Elsevier., (c-e) nitroxyl radical polymers. Reprinted with permission [27]. Copyright 2017, Springer Nature, (f) organometallic polymers. Reprinted with permission [143]. Copyright 2018, Elsevier (g) Schiff bases. Reprinted with permission [143]. Copyright 2018, Elsevier and (h) pteridine derivatives. Reprinted with permission [143]. Copyright 2018, Elsevier.

input electric energy changes into the mechanical work [148,150].

In conducting polymers, the neutral polymer chain can be oxidized or reduced to become either positively or negatively charged through doping process. Further, conducting polymers could not be perfectly conductive without using dopants and doping of π -conjugated polymers results in high conductivity. The doping process is influenced by different factors such as polaron length, chain length, charge transfer to adjacent molecules and conjugation length.

As an example, the existing dopants for PPy are CF_3SO_3^- and ClO_4^- [151]. The oxidants are $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and $\text{Fe}_2(\text{SO}_4)_3$ and the additives are sodium dodecylbenzene sulfonate, sodium alkylnaphthalene sulfonate, sodium alkylsulfonate, *p*-Nitrophenol, *m*-Nitrophenol and *p*-Cyanophenol [152,153].

Thus, conductive polymers such as PPy [153–191] and PANI [154, 192–204], have been extensively studied for a wide range of applications and for improving the properties of the materials. In particular, conductive polymers are experiencing strong research growth for

battery applications [205,206].

A strategy to improve the characteristics of organic polymers for battery application rely to their combination with carbonaceous materials. PPy, like polyaniline and most of the common conducting polymers, exchanges anions with the polymer backbone, which is sometimes described as a p-doping process [127].

The anion insertion reactions can lead to high reduction potentials over 3 V, but the batteries developed with those materials show a poor cycle life that must be overcome. The combination of inter-penetrating CNTs with a conducting polymer, like PPy, is useful because the strong interaction between carbon nanotubes and the NH-groups of PPy will result in improved mechanical strength and electrical conductivity from carbon contribution, especially when the polymer is in its reduced state. The bonding between the polymer and carbon depends on the chemical composition of the carbon surface. Bonding with PPy occurs by electronic π -stacking from the attraction of p-orbitals of the electron rich carbon aromatic rings with the electron-deficient orbitals of PPy for

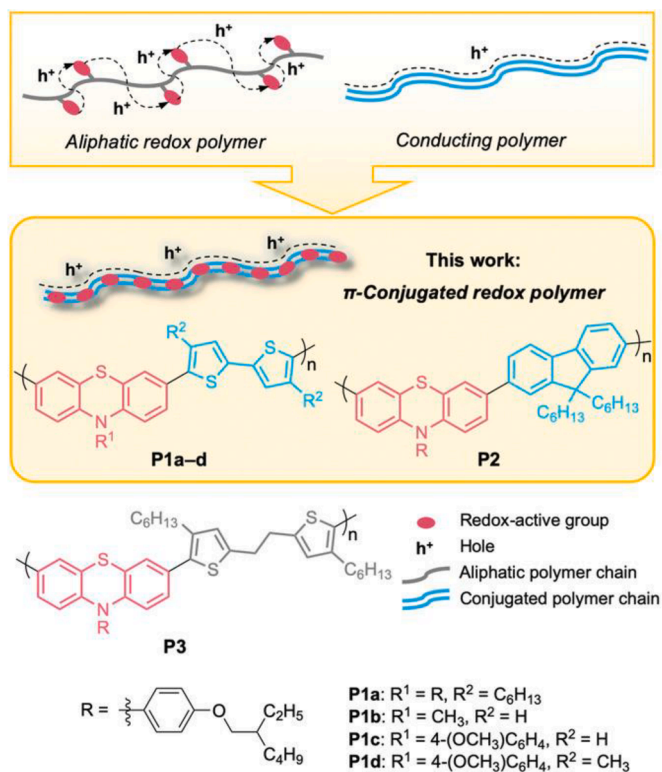


Fig. 8. Combination of two designs by using π -conjugated redox polymers P1 and P2 as cathode-active materials in a lithium organic battery. Reprinted with permission [146]. Copyright 2019, Wiley.

carbons that are highly graphitized and with minor surface functionalization [127].

On the other hand, with functionalized carbons, bonding occurs between the oxygen-containing functional groups on the carbon surface and the hydrogen from the $-NH$ groups of the PPy rings. However, the binding energy of π - π^* stacking for the large molecules is much greater than the energy of hydrogen bonds, which explains the very stable structure with SWCNT-PPy, and the very weak structure with carbon black (CB)-PPy [127].

4.1. Lithium batteries

The main results obtained in recent years regarding lithium batteries using organic materials are presented in Table 2.

Aimed at organic molecule-polymer hybridization, rather than using polymerization to stabilize organic molecules, an approach is to hybridize the active organic molecules with a conducting polymer, which has the additional beneficial effect of increasing the electrical conductivity [127]. High capacities were obtained with a sulfur heterocyclic quinone (dibenzo(b,i)thianthrene-5,7,12,14 tetraone = DTT) and the conductive polymer PEDOT:PSS used as a binder. PEDOT with π -conjugated thiophene rings carries positive charges that are balanced by the dissociated sulfonate groups in PSS. DTT and PEDOT:PSS interact with each other because of the electron transfer of extended π -conjugated configuration of DTT (electron donor) and cationic PEDOT (electron acceptor), which results in a non-covalent interaction [127], preventing the active DTT from dissolution. Moreover, the incorporation of the sulfur atom raises the initial reduction potential to 2.89 V, which is 0.3 V higher than that for its carbon counterpart 5,7,12,14-pentacenetetraone. DTT bends when lithium atoms are inserted and, in such geometry, every lithium atom coordinates with two oxygen atoms to strengthen the binding with DTT, so that DTT can efficiently take up four lithium ions [127].

The redox-active monomer 2-vinylbenzo[1,2-*b*:4,5-*b'*]-dithio-phen-4,8-dione was synthesized in high yields and polymerized using the free radical polymerization technique. The optimization of the polymerization to yield PVBTD insufficiently high molar masses, which allow its application as an active cathode material in Li-organic batteries. Thus, the use of lithium salts as supporting electrolyte leads to a shift of the redox process to more positive potentials and a merging of the two reoxidation signals to one, leading to a one staged charge/discharge behavior. Electrodes with a low amount of active material (10 wt.%) performed best and exhibited a capacity of 217 mAh·g⁻¹ (100% material activity) at an average cell voltage of 2.45 V for the first charge/discharge cycle. Upon cycling, the capacity dropped, possibly because the redox reaction was not completely side reaction free and after 100 cycles the battery exhibited 114 mAh·g⁻¹ (52% active material). Furthermore, the battery can be charged with negligible capacity loss at a fast charging speed of 10C. Batteries with higher active material content were also investigated but showed lower capacities due to poor material activity (Fig. 9a) [213].

Phenoxazine has been also incorporated into a linear and a cross-linked poly(vinylene) (PVMPO) and obtained polymers with high cycling performance and discharge potential of 3.52 V vs. Li/Li⁺ when tested in composite electrodes. Concerning battery application, phenoxazine derivatives have been proposed as redox shuttle candidates for overcharge protection and as mediators for redox targeting. Composite electrodes were prepared using 50 wt.% PVMPO or X-PVMPO, 45 wt.% carbon black and 5 wt.% binder (PVDF). Dry mixtures of PVMPO or X-PVMPO, carbon black and binder were dissolved/dispersed in NMP (1-methyl-2-pyrrolidinone) until a honey-like viscosity was obtained [223].

A conjugated copolymer design with phenothiazine as a redox-active group and a bithiophene co-monomer was presented, enabling ultra-high rate capability and cycling stability. After 30 000 cycles at a 100C rate, >97% of the initial capacity was retained. The composite electrodes feature defined discharge potentials at 3.6 V versus Li/Li⁺ due to the presence of separated phenothiazine redox centers. A comparison with three structurally related polymers demonstrated that changing the size, amount, or nature of the side groups led to a reduced cell performance. Composite electrodes were prepared using 60 wt.% polymer, 35 wt.% carbon black (Super C65), and 5 wt.% binder (PVDF) immersed in NMP [146].

1-(Bromomethyl)pyrene was used as a quaternizing agent to synthesize pyrene functionalized phosphaviologen: single-walled carbon nanotubes (PY₂PV:SWCNT) composites were dissolved in NMP. A PVDF solution was added to the PY₂PV:SWCNT solution to prepare a 20 wt.% PVDF 80 wt.% PY₂PV:SWCNT composite. A coin cell geometry was used with lithium reference and LiPF₆ in TEGDME as electrolyte. A lithium foil was used as the anode, a glass fiber separator (EL-cell) was used to prevent short circuiting, and carbon-coated copper (EL-cell) was used as the cathodic current collector. Thus, the battery architecture consisted of lithium foil: glass fiber impregnated with electrolyte: PY₂PV:SWCNT/PVDF on carbon-coated Cu foil [208].

Casado et al., presented dual redox-active polyimides based on phenothiazine and naphthalene tetracarboxylic dianhydride units. After only one optimization step, the electrodes based on these dual redox polymers can be applied simultaneously as anode and cathode in a symmetric all-organic battery (Fig. 9b). The phenothiazine functional polyimide shown two redox active voltages at around 2.5 and 3.7 V (vs. Li/Li⁺) with high discharge capacities of 160 mAh·g⁻¹. Moreover, the symmetric full battery delivered high power density up to 1542 W kg⁻¹ with stable cyclability for 1000 cycles. This work demonstrated an efficient strategy to develop dual redox active polymer electrodes for next generation all-polymer batteries. Coin cells were assembled in an Ar-filled glove box, the anode and cathode were composed of the same electrode, that was, 40 wt.% Polyimide homopolymer, 40 wt.% KB, and 20 wt.% PVDF. A glass fiber soaked with electrolyte (LiPF₆ in EC/DMC 1:1 with 2 wt.% vinylene carbonate) was placed between the two

Table 2

Organic materials developed for partial and all-organic Li-based batteries, including the characteristics of the different battery components and the main battery characteristics.

Organic material	Electrode composition	Reference electrode	Electrolyte	Voltage/ V vs. Li/ Li ⁺	Cyclability/ mAh·g ⁻¹	Ref.
PEDOT-conducting polymer backbone functionalized with hydroquinones and pyridines (1:2 ratio)	graphite	Lithium	1 M LiPF ₆ in EC/DEC 1:1 (v/v) (LP40, BASF); 0.1 M LiTFSI in PYR14TFSI; 0.2 M LiTFSI in PYR14TFSI	3.3	65 (50th cycle) /63 (100th cycle); 64 (50th cycle) /61 (100th cycle); 61 (50th cycle) /48 (100th cycle)	[207]
Conjugated copolymer with phenothiazine as a redox-active group and a bithiophene co-monomer	60 wt.% polymer, 35 wt.% carbon black (Super C65), and 5 wt.% binder (PVDF)	Lithium	1 M LiPF ₆ in EC/DMC: 1/1, BASF Selectilyte	3.6	30 000 cycles at a 100C rate, >97% of the initial capacity is retained	[146]
1-(Bromomethyl)pyrene was used as a quaternizing agent to synthesize pyrene-functionalized phosphaviologen (PY ₂ PV)	20 wt.% PVDF 80 wt.% PY ₂ PV: SWCNT composite	Lithium	1 M LiPF ₆ in TEGDME	1.95–3.5	53 at 1 C, and retain their capacity after 500 cycles	[208]
Dual redox polyimides based on phenothiazine and naphthalene moieties	40/80/85 wt.% polymer, 40/15/15 wt.% carbon black (Super C65), and 20/5/0 wt.% binder (PVDF) 40 wt.% polymer, 40 wt.% carbon black (Super C65), and 20 wt.% binder (PVDF)	Lithium 40 wt.% polymer, 40 wt.% carbon black (Super C65), and 20 wt.% binder (PVDF)	1 M LiPF ₆ in EC/DMC 1:1 with 2 wt.% vinylene carbonate	2.5 - 3.7	160	[209]
Carbon nanotubes modified with organosulfur molecule	Either purified or functionalized MWNTs	Lithium	Lithium bis (trifluoromethanesulfone) imide (LiTFSI) 1 M dissolved in 50/50 tetraethylene glycol dimethyl ether (TEGDME) / 1,3-dioxolane (DIOX)	2.3	Excellent stability over cycling as 95% of the Initial capacity is maintained after 50 cycles	[210]
Naphthalene dianhydride with (RR)- and (SS) trans-1,2-diaminocyclohexane (nanoporous molecular triangles (–)– and (+)–NDI- Δ)	The active material, carbon black and PVDF binder (300 mg in total) were mixed in a ratio of 5:4:1 (50 wt.% active material) or 7:2:1 (70 wt.% active material)	Lithium	1 M lithium bis (trifluoromethane-sulfonyl) imide (LiTFSI) and 0.2 M lithium nitrate in a mixed solvent system (1:1 v/v) of 1,3-dioxolane and 1,2-dimethoxyethane.	1.8–3	146.4 at 0.1 C; 58.1 at 100 C; 71.1 at 10 C for 300 cycles	[211]
Poly-5-vinyl-1,1,3,3-tetramethylisindolin-2-yloxy (PVTMIO)	10% of active material (TMIO or 4/Super P®/PVDF; 10/80/10 wt.%)	Lithium	0.1 M Solution of tetrabutylammonium hexafluorophosphate (TBAPF ₆) in dichloromethane (DCM)	3.7	104.7 (90% capacity retention after 100 cycles)	[13]
9,10-di(1,3-dithiol-2-ylidene)–9,10-dihydroanthracene (exTTF)	exTTF	Lithium	—	3.5	Theoretical capacity of 132, a lifetime exceeding more than 250 cycles	[212]
Poly(2-vinyl-4,8-dihydrobenzo [1,2- <i>b</i> :4,5- <i>b'</i>]-dithiophene-4,8-dione) (PVBTD)	PVBTD and PVDF in NMP to vapor-grown carbon fibers as conducting additives (ratio: 1/8/1 m/m/m)	Lithium	Ethylene carbonate, dimethyl carbonate 1/1 m/v, 1 M lithium perchlorate)	2.45	217 (for the first charge/discharge cycle)	[213]
AQ-ter-denpol	AQ-ter-denpol and carbon black with PVDF or PEDOT [poly(3,4-ethylenedioxythiophene)] as a binder (2:5:3 or 0.5 w/w)	Lithium	1 M LiPF ₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (5:5 v/v)	—	—	[214]
Bis(cyclohexyl)pyromellitic diimide (PMDI-Ref), the cyclic dimeric pyromellitic diimide ((–)–2PMDI), and the cyclic trimeric pyromellitic diimide ((–)–3PMDI- Δ)	PMDI derivative with carbon black and PVDF binder in a weight ratio of 60:30:10	Lithium	LiPF ₆ dissolved in a mixture of ethylene carbonate and dimethyl carbonate (EC:DMC, 1:1 v/v)	1.6–3.2	—	[215]

(continued on next page)

Table 2 (continued)

Organic material	Electrode composition	Reference electrode	Electrolyte	Voltage/ V vs. Li/ Li ⁺	Cyclability/ mAh·g ⁻¹	Ref.
Polyvinyl-based redox polymer with a methylphenothiazine side group (PVMPT)	50 wt.% PVMPT mixed with 47 wt.% conductive additive (Super C65) and 3 wt.% binder (PVdF-HFP)	Lithium	1 M LiPF ₆ in EC:DMC 1:1	3–4	—	[216]
2,3-diamino-1,4-Naphthoquinone (DANQ); 1H-naphtho[2,3-d]imidazole-4,9-dione (IMNQ)	DANQ (or IMNQ), Super P carbon and PVDF binder in a weight ratio of 60:30:10	Lithium	1 M lithium bis (trifluoromethane) sulfonimide (LiTFSI) in a mixture of dimethoxy ethane (DME) and 1,3-dioxolane (DIOX) in volume ratio of 1:2.	1.8–3	250 and 99% capacity retention of its initial capacity after 500 cycles at 0.2C	[217]
Dinickel 1,4-benzenediphosphate (Ni 2 BDP)	Active material was mixed with Super P and CMC in a 4:3:1 wt ratio	Lithium	0.8 M LiPF ₆ in a mixture of EC and DEC (1:1, v/v)	1.2–3	585	[218]
Organic sulfonate and multiwalled carbon nanotubes (NQS/MWNTs)	NQS/MWNTs and NQSI/MWNTs hybrid films were used as cathodes directly without any further addition of binder, additives, or a current collector; Pristine NQ, NQS and NQSI electrodes were prepared by mixing active materials (40 wt %), conductive carbon materials (Super P, 50 wt.%), PVDF binder (10 wt.%),	Lithium	2 M lithium bis-(trifluoromethanesulfonyl) imide dissolved in tetraethylene glycol dimethyl ether (2 M LiTFSI/TEGDME)	1.6–3.5	—	[219]
s-tetrazine derivatives	tetrazines, carbon black and PVDF in DMF were prepared in a vial with a weight ratio of 4:4:2	Lithium	—	2.3	—	[220]
Poly (naphthotriazolequinonestyrene) (pNTQS)	pNTQS, PVDF and SuperP (10/10/80)	Lithium	1,3-dioxolane (DOL)/ dimethoxyethane (DME) 1/1 with 1 M Lithium bis(trifluoromethane) sulfonimide (LiTFSI)	1.9–2.75	135	[221]
Nitroxide radical polymers	10 wt.% active cathode materials were fabricated by mixing 10:10:80 (wt.%) of active cathode material, poly (tetrafluoroethylene) (PTFE), and vapor-grown carbon fiber (VGCF).	Lithium	Mixture of ethylene carbonate (EC) (30 vol%) and diethyl carbonate (DEC) (70 vol%) containing 1 M LiPF ₆	2–4	—	[222]
Phenoxazine-based polymers	50 wt.% PVMPO or X-PVMPO, 45 wt.% carbon black and 5 wt.% binder PVDF	Lithium	1 M LiPF ₆ in EC:DMC 1:1	3.52	—	[223]
Polyanthraquinone sulfide (PAQS)	PAQS was mixed with conductive carbon. To this mixture a 5 wt.% solution of PVDF A ratio of 4:5:1 (by weight) of PAQS:C65:PVDF	Lithium	1 M LiTFSI	—	—	[224]
Two 3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA)-based polyimides, namely perylene diimide-Benzidine (PDI-Bz) and perylene diimide-Urea (PDI-Ur)	active materials (PDI-Bz and PDI-Ur), conductive carbon black and a polymer binder (PVDF) at the weight ratio of 60:30:10	Lithium	1 M LiPF ₆ in a mixture of ethylene carbonate (EC)/ dimethylcarbonate (DMC) (EC/DMC; 1:1 molar ratio)	1.5–3.5	120	[225]
Amorphous covalent triazine-based frameworks (ACTFs)	ACTFs	Lithium	1 M LiPF ₆ in ethylene carbonate/dimethyl carbonate (1:1)	1.5–4.5	—	[226]
Poly[N-(10-oxo-2-vinylanthracen-9(10H)-ylidene)cyanamide]	polymer/PVDF/MWCNT 1/1/8 (w/w/w)	Lithium	1 M LiClO ₄ in EC/DMC 1/4 (v/v)	2.3	137	[227]
Bio-derived redox polymer with a poly(norbornene) backbone and flavin pendant group	The nanoparticles of P3, CB, and PVDF were then mixed together in a ratio of 35:50:15	Lithium	1.0 M LiPF ₆ tetraethylene glycol dimethyl ether (TEGDME)	2.5	125	[228]
Poly(benzoquinonyl sulfide) (PBQS)	PBQS	Lithium	1 M LiTFSI/DOL + DME	2.67	275	[229]

(continued on next page)

Table 2 (continued)

Organic material	Electrode composition	Reference electrode	Electrolyte	Voltage/ V vs. Li/ Li ⁺	Cyclability/ mAh·g ⁻¹	Ref.
Poly(1,4-anthraquinone) (P14AQ) and poly(1,5-anthraquinone) (P15AQ)	AQ, PAQ, P14AQ, P15AQ	Lithium	1 M LiTFSI/ DOL + DME, 2:1, v/v	1.4–3	—	[230]
1,1'-Iminodianthraquinone (IDAQ)	AQ or IDAQ, conductive carbon, and polytetrafluoroethylene binder with weight ratio of 6:3:1	Lithium	1 M LiN(CF ₃ SO ₂) ₂ (LiTFSI) solution in a mixture of DOL and DME (1:1, v/v)	1.5–3	—	[231]
Naphthalene diimides	Electroactive material, acetylene black conductive additive, and PVDF binder (45:50:5)	Lithium	1 M LiClO ₄ in 1:1 v/v ethylene carbonate: dimethyl carbonate (EC/DMC)	2.3–2.9	121	[232]
Lithium 2,6-bis(ethoxycarbonyl)-3,7-dioxo-3,7-dihydro-s-indacene-1,5-bis(olate)	60% (by weight) Li _{2+x} C ₁₈ H ₁₂ O ₈ and 40% (by weight) carbon black	Lithium	1 M LiPF ₆ in a 1:1 (w/w) mixture of ethylene carbonate/dimethyl carbonate solution	1.67–1.96	125	[233]
Nanostructured freestanding conducting polymer composites [polypyrrole (PPy) and polyaniline (PANI)]	PPy-based paper and CCF-reinforced PANI@nanocellulose	Lithium	1 M LiPF ₆ in EC:DEC (1:1, v/v)	2–4	102	[234]
Hexaazatrinaphthalene framework (HATNPF)	mixing active material (HATNPF1 or HATNPF2) with graphene oxide and PVDF as a binder (ratio of 4:5:1 in weight)	Lithium	equimolar LiCF ₃ SO ₃ /G4 (tetraglyme) salt	—	309 (92% capacity retention after 1200 cycles)	[235]
Polytetra(2-Thienyl)ethylene (PTTE)	active material, acetylene black, and sodium alginate in a mass ratio of 5:4:1	Lithium	LiPF ₆ was 1 M in a mixture of ethylene carbonate, ethyl methyl carbonate, and dimethyl carbonate (1:1:1, v/v/v)	0–3	973	[236]
Polytriphenylamine/carbon nanotube (PTPA/CNT), poly(4-carbamoyl-N,N-diphenylaniline-2,2,5,5-tetramethyl-pyr-rolin-1-oxyl)/ carbon nanotube (PTPA-PO/CNT)	separately mixing PTPA and CNT, PTPA and acetylene black, and PTPA/CNT and PTPA-PO/CNT with 10 wt.% PVDF	Lithium	1 M LiPF ₆ dissolved in ethylene carbonate/dimethyl carbonate (EC/DMC, 1/1, v/v)	2–4.2	107.6 (PTPA/CNT), 128 (PTPA-PO/CNT)	[237]
N-Phenyl-p-phenylenediamine (N-PPDA) and pyrene (PYR) in a 1:1 molar/molar (PPDA-PYR) copolymers	poly-PPDA-PYR	Lithium	LiPF ₆ salt	3.2	113	[238]
3,4,9,10-perylene-tetracarboxylicacid-dianhydride (PTCDA, known as “red 224”); graphene aerogel (PGC)	Active material (PGCs or PTCDA, 80%), binder PVDF, 10%) and conductive material (acetylene black, 10%)	Lithium, graphite (80%), acetylene black (10%), and PVDF (10%)	1 M LiPF ₆ in ethylene carbonate/dimethyl carbonate (EC/DMC 1:1 Vol %)	—	—	[239]
Covalent triazine frameworks two-dimensional layered fluorinated Exfoliated (E-FCTF)	70 wt.% active material (E-CTF, FCTF or E-FCTF), 10 wt.% PVDF, and 20 wt.% acetylene black	Lithium	1 M LiPF ₆ in EC and DEC (1:1, v/v)	0–3	1035 after 300 cycles and 581 after 1000 cycles	[240]
Self-assembled graphene/poly (anthraquinonylsulfide) (PAQS) composite aerogel (GPA)	PAQS electrode was prepared by mixing pure PAQS, carbon black and PVDF at a weight ratio of 60:30:10	Lithium	1 M LiTFSI in 1,2-dimethoxyethane (DME)/1,3-dioxolane (DOL) (1:2 by volume ratio).	—	102 at 20 C	[241]
All-thiophene-based polymer of poly(3,3'-bithiophene)	Active material, acetylene black and sodium alginate in a mass ratio of 5:4:1	Lithium	1 M LiPF ₆ in a mixture of ethylene carbonate, ethyl methyl carbonate, and dimethyl carbonate (1:1:1, v/v/v)	0–3	1215 excellent rate capability, and outstanding cycling stability with a capacity retention of 663 after 1000 cycles	[242]
Ellagic acid (EA), Tannic acid (TA)	EA or TA was homogeneously mixed with super P and PVDF at a mass ratio of 55:35:10	Lithium	1 M LiPF ₆ in EC/DEC, 1:1 v/v	0–3	644, 364, 195, and 162 for EA and 297, 451, 465, and 265 for TA are obtained at the current densities of 0.1, 0.2, 0.5, and 1.0 after 150, 250, 500, 1000 cycles	[243]

(continued on next page)

Table 2 (continued)

Organic material	Electrode composition	Reference electrode	Electrolyte	Voltage/ V vs. Li/ Li ⁺	Cyclability/ mAh ⁻¹	Ref.
Two types of triazine-based covalent organic nanosheets (CONS): covalent imine network-1 (CIN-1) and Schiff base networks-1 (SNW-1), synthesized with carbon nanotubes (CNTs) and denoted as two composites of CIN-1/CNT and SNW-1/CNT, respectively.	The active material, conductive carbon black (Super P), and PVDF were mixed (weight ratio of 8:1:1)	Lithium	1 M LiPF ₆ in mixture of EC and DEC (w/w, 1/1)	—	—	[244]
All organic components Polyaniline nanowire-coated carbon nanotube (CNT/PANI@Li) in	PDHBQS/CNT (the weight ratio of PDHBQS to CNT was 7:3)	CNT/PANI@Li	1.0 M LiTFSI in DOL and DME (1:1 in weight)	1.5–3	120	[245]
flexible full cells was demonstrated by combining flexible organic poly(2,5-dihydroxyl-1,4-benzoquinonylsulfide)/carbon nanotube (PDHBQS/CNT)						
(2-vinylthianthrene) and poly(2-methacrylamide-TCAQ)	thianthrene polymer was prepared by adding a solution/dispersion of the polymer and PVDF; in NMP to Super P® as conducting additive (ratio: 40/5/55, m/m/m, polymer/PVDF/Super P®).	TCAQ-polymer was prepared by adding a solution/dispersion of the polymer and PVDF; in NMP to Super P® as conducting additive (ratio: 40/5/55, m/m/m, polymer/PVDF/Super P®).	1 M LiClO ₄ EC/DMC (3/7, v/v)	1.35	105	[246]
Lithium						
anthracene-9,10-bis[2-benzene-1,4-bis(olate)] (ABB4OLi)	ABB4OH/CMK-3/SP/polyacrylonitrile copolymer (La133, binder) electrode was 4:4:1:1	H ₂ TP/SP/polyacrylonitrile copolymer (La133, binder) electrode was 6:3:1	3 M bis(trifluoromethane)sulfonimide lithium salt in the mixture solvents of 1,3-dioxolane and 1,2-dimethoxyethane with the volume ratio of 1:1 “Water-in-salt”	0.5 - 3.8	70 (cathode during 200 Cycles)	[247]
Polytriphenylamine (PTPAN); 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA)-derived polyimide (PNTCDA)	polytriphenylamine (PTPAN), ketjen black (KB) as conductive agent, and polytetrafluoroethylene (PTFE) as binder in the mass ratio of 6:3:1.	1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA)-derived polyimide (PNTCDA), ketjen black (KB) as conductive agent, and polytetrafluoroethylene (PTFE) as binder in the mass ratio of 6:3:1.		2.1	Supercapacitor like, high power of 32,000 W kg ⁻¹ and a long cycle life (700 cycles with capacity retention of 85%)	[16]

electrodes [248].

Carbon nanotubes modified with organosulfur molecules have been used as positive electrode for lithium batteries. The electrode material presented disulfide bonds that can react with lithium during the discharge of the batteries. This study, demonstrated that the active material remains anchored to the carbon nanotubes, thus avoiding the problem of the active material dissolution in the electrolyte. Coin cells discharge/charge tests exhibited promising results with a specific capacity of 100 mAh·g⁻¹_{electrode}, an operating voltage around 2.3 V vs Li⁺/Li and a good stability over cycling as 95% of the initial capacity is maintained after 50 cycles. This method allowed to overcome the well-identified problem of the active material dissolution in Li/organic and Li/S batteries, preventing the system from an early loss of storage capacity (Fig. 9c,d) [210].

Ultrahigh rate capability for the nano porous molecular triangles redox-active naphthalenediimide (NDI) units (–)– and (+)–NDI-Δ in organic rechargeable lithium-ion batteries was demonstrated, which possess an ideal balance of electronic and molecular structural properties in the solid state for supporting electrode reactions in an efficient manner. A capacity of 146.4 mAh·g⁻¹ at a low current rate of 0.1 C and a capacity of 58.1 mAh·g⁻¹ at an ultrahigh rate of 100 C were achieved. Also, the battery is rechargeable, maintaining a capacity of 71.1 mAh·g⁻¹ after cycling at 10 C for 300 cycles. The ultrahigh rate performance displayed by the (–)– and (+)–NDI-Δ batteries constituted an

essential development for a new strategy involving small molecules for improving the properties of organic active materials. The active material, carbon black, and PVDF binder were mixed in a ratio of 5:4:1 (50 wt.% active material) or 7:2:1 (70 wt.% active material) in NMP. Lithium-ion half-cells were assembled under Ar atmosphere with lithium foil as the counter electrode and a separator based on Celgard 2400 that was treated on each side with an electrolyte solution containing lithium bis(trifluoromethane-sulfonyl)imide (LiTFSI) and lithium nitrate in a mixed solvent system (1:1 v/v) of 1,3-dioxolane and 1,2-dimethoxyethane [211].

The first organic based semi-solid lithium-redox flow batteries (Li-RFBs) were developed using 10-methylphenothiazine (MPT), delivering a high volumetric capacity (55 Ah L⁻¹) and energy density (190 Wh L⁻¹) with high coulombic efficiency (>98%) and cycling stability (>100 cycles) (Fig. 9e). The demonstrated volumetric capacity is 8-fold that of the liquid MPT RFB, achieving the highest energy density among Li-organic based RFBs. Lithium organic nanocomposite suspension (LIONS) is an universal approach to enable the use of low solubility organic materials in RFBs, providing a new direction for all insoluble organic active material to achieve low-cost and high-energy-density RFBs [249].

Ernould et al. showed that the strong solvation of lithium cations by organic phosphates, widely used as flame-retardant constituents, induced a negative redox potential shift by as much as 500 mV. It was

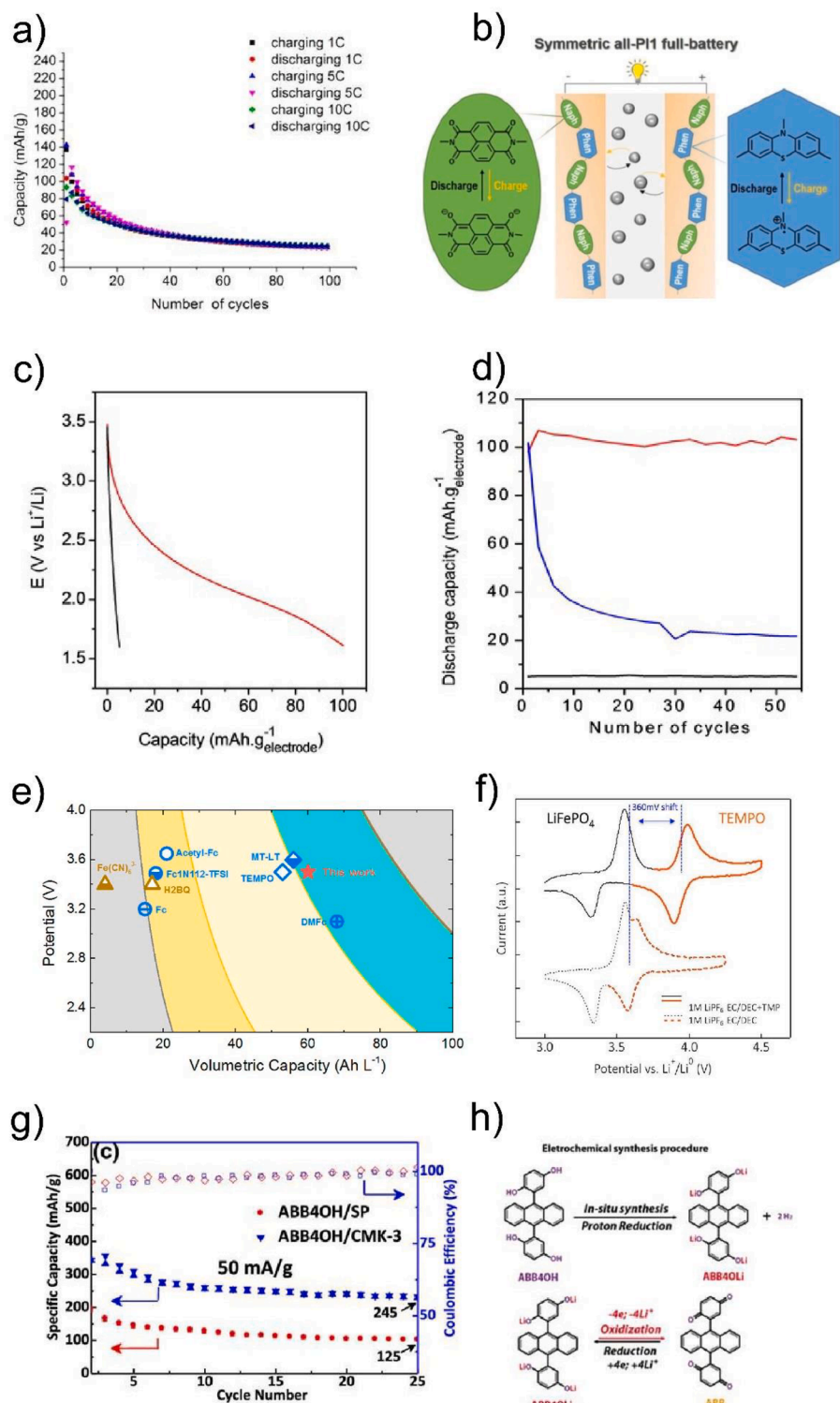


Fig. 9. Capacity development during extended charge/discharge cycling (100 cycles) of Li-organic batteries with composite electrodes of 4/MWCNT/PVdF 10/80/10 and 40/50/10 m/m/m in EC/DMC 1/1 m/v, 1 M LiClO₄. Reprinted with permission [213]. Copyright 2015, American Chemical Society (a); phenothiazine and naphthalene-polyimide-based redox polymer applied as both cathode and anode material to build a symmetric polymer-polymer battery with good cycling stability. Reprinted with permission [248]. Copyright 2020, Wiley (b); discharge curves for purified (black) and functionalized MWNTs (red) used as positive electrode materials in a lithium batteries (2mg samples, 5mA.g⁻¹ applied, third cycle given as an example) (c); capacity retention of samples with purified MWNTs (black), MWNTs mixed with the disulfide-containing molecule 8 derived from 4 (blue), MWNTs covalently functionalized with the thiolated molecule (red) used as a positive electrode material (d). Reprinted with permission [210]. Copyright 2018, Wiley. Comparison of achieved volumetric capacity versus cell potential of other reported Li-organic-based RFBs. Reprinted with permission [249]. Copyright 2018, American Chemical Society (e); Cyclic voltammetry of a hybrid PTMA/Li-FePO₄ electrode measured in a two-electrode cell configuration, vs lithium metal pseudoreference with two different electrolytes: 1 M LiPF₆ in EC/DEC and 1 M LiPF₆ in EC/DEC/TMP. Reprinted with permission [250]. Copyright 2019, American Chemical Society (f); Initial 25 cycles (except for first cycle) for the ABB4OH/SP electrode and ABB4OH/CMK-3 electrode, respectively (g); and detailed electrochemical mechanism of ABB4OH in Li-ion half cells. Reprinted with permission [247]. Copyright 2019, American Chemical Society (h).

demonstrated that the redox potential shift is characteristic of Li-cation (de)solvation processes whereas it is negligible for other processes. This has important consequences for high energy hybrid battery concepts such as high voltage dual-ion graphite or organic batteries, also sending a different light on the enhanced anodic stability of these nonconventional battery electrolyte formulations (Fig. 9f) [250].

A new electrochemical method for the in-situ synthesis of a novel lithium-rich organic cathode, namely lithium anthracene-9,10-bis[2-benzene-1,4-bis(olate)] (ABB4OLi, C_T = 256 mAh.g⁻¹), from its

phenol precursor of anthracene-9,10-bis(2-benzene-1,4-diol), was reported. The addition of anthracene moiety as the linking bridge had the function of increasing the molecular weight and simultaneously enhance the electronic conductivity for the designed organic molecule (ABB4OLi). In Li-ion half cells, Li₂TP was employed as the anode material, ABB4OLi could deliver average specific capacities of 194 mAh.g⁻¹ during 250 cycles (50 mA.g⁻¹) and 100 mAh.g⁻¹ during 400 cycles (2 A.g⁻¹). In the all-organic Li-ion full cells with the working voltage above 1 V, the ABB4OLi electrode could realize average capacities of 70

$\text{mAh}\cdot\text{g}^{-1}$ during 200 cycles (50 mA g^{-1}) (Fig. 9g). This work represents a significant step for the development of organic Li-ion full batteries [247].

Further, two similar small molecules of organosulfur acenes have been developed to investigate the structure-property relationships and their influence in battery performance, proving the molecular packing dependence of battery performance, the solubility, and stability. Tetra-thiotetracene (TTT) and hexathiapentacene (HTP) were two typical organosulfur acenes which contain four and six sulfur atoms, respectively. Therefore, TTT and HTP can react with four or six lithium/sodium atoms and hence possess a large theoretical capacitance ($28\text{ mAh}\cdot\text{g}^{-1}$ for TTT and $317\text{ mAh}\cdot\text{g}^{-1}$ for HTP), which makes them suitable candidates as cathodes in Li-ion batteries [137].

A dendronized polymer (denpol) containing multi-anthraquinone-terminated dendrons (AQ-ter-denpol) was investigated as an organic cathode material for rechargeable Li-ion batteries, with a view to its unique morphology. These methodologies established an opportunity for developing a new generation of organic electrodes based on denpols [214].

In fact, lithium-organic batteries have been developed with remarkable charge–discharge properties, for example, a high discharge capacity of $250\text{ mAh}\cdot\text{g}^{-1}$ (363 mAh cm^{-3}), discharge potential plateaus in the range of $2.3 - 2.5\text{ V}$, and 99% capacity retention after 500 cycles at 0.2C . In particular, the batteries had excellent rate performance up to 50C with reversible redox behavior, unlike most other organic cathode materials. The key to success was a simple molecular substitution, addition of amino groups at the 2- and 3- positions of the NQ ring, yielding 2,3-diamino-1,4-naphthoquinone (DANQ). DANQ has an exceptionally low band gap of 2.7 eV and a larger than 20-fold enhancement in the lithium diffusion rate compared to unmodified NQ. The main shortcoming of the organic molecules, i.e., their solubility in the electrolyte, was overcome by covalent linking of the amino groups to the surfaces of the cathode framework. The cyclization of amino groups in DANQ yielded 1H-naphtho[2,3-*d*]imidazole-4,9-dione (IMNQ), enabled to achieve a 0.15 V enhancement in the redox potential owing to the delocalized electron distribution in the heteroaromatic ring. This work suggested that NQ derivatives with modulated charge/ion transport properties are a viable alternative to the more widely studied lithium metal oxides. The organic cathodes were prepared with DANQ (or IMNQ), Super P carbon, and PVDF binder in a weight ratio of 60:30:10 [217].

The utilization of dinickel 1,4-benzenediphosphonate (Ni_2BDP) as a dual-functional electrode material for organic-based LIBs was disclosed. This molecular engineered electrode delivered a high capacity of $585\text{ mAh}\cdot\text{g}^{-1}$ through multi-electron redox processes. The electrode sample was fabricated by mixing active material, Super P, and cellulose sodium salt (CMC) binder in a 4:3:1 wt ratio [218].

Two types of triazine-based covalent organic nanosheets (CONs) were exfoliated and composited with carbon nanotubes: covalent imine network-1 (CIN-1) and Schiff base networks-1 (SNW-1) were synthesized in the presence of carbon nanotubes (CNTs) as CIN-1/CNT and SNW-1/CNT composites, respectively. The thin-layered 2D structure for the exfoliated CONs can activate more functional groups for lithium storage and boost the utilization efficiency of redox sites compared to its bulk counterpart. Large reversible capacities of above $1000\text{ mAh}\cdot\text{g}^{-1}$ can be achieved after 250 cycles, which was comparable to high-capacity inorganic electrodes. Moreover, the lithium-storage mechanism was determined to be an intriguing 11 and 16 electron redox reaction, associated with the organic groups (unusual triazine ring, piperazine ring, and benzene ring, and common $\text{C} = \text{N}$, $-\text{NH}-$ groups). The active material, conductive carbon black (Super P), and PVDF were mixed (weight ratio of 8:1:1) and deposited on copper foil. LiPF_6 in mixture of EC and DEC (w/w, 1/1) and the lithium foil were applied as the electrolyte and the reference electrode, respectively [244].

A symmetric solid-state battery based on organic porous electrodes was fabricated using scalable spray-printing. A symmetric all-organic

battery was then formed with the addition of another identical set of electrode and electrolyte layers. Both density functional theory calculations and charge-discharge profiles show that the potentials for the negative and positive electrode reactions were amongst the lowest ($\approx 2.0\text{ V}$ vs Li) and the highest ($\approx 3.5\text{ V}$ vs Li), respectively, for quinone-type molecules. Over the C-rate range 0.2 to 5 C , the battery has a discharge cell voltage of more than 1 V even up to 250 charge-discharge cycles and the obtained capacities are in the range $50\text{--}80\text{ mAh}\cdot\text{g}^{-1}$ at 0.5 C [251].

A series of electrochromic electron-accepting poly(chalcogenoviologens) with multiple, stable and reversible redox centers has been reported as anodic materials in organic radical Li-ion batteries (ORLIBs). Introduction of heavy atoms (S, Se, and Te) into viologen scaffolds significantly improved the capacity and cycling stability of the ORLIBs. Notably, the poly(Te-BnV) anode had an intercalation ability of 20 Li-ions and showed higher conductivity and insolubility in the electrolyte, hence contributing to a reversible capacity of $502\text{ mAh}\cdot\text{g}^{-1}$ at $100\text{ mA}\cdot\text{g}^{-1}$ when the Coulombic efficiency approached 100%. The poly(Te-BnV) anode had the highest reported capacity to date for a viologen-based electrode. Based on their unique electrochromic and redox properties, flexible electrochromic batteries were fabricated where the charged/discharged state could be visually monitored. This work presented a promising avenue for the development of organic polymer-based electrodes for flexible hybrid visual electronics [252].

Lu et al. described a dissolution-recrystallization method to prepare flexible, binder-free, and free-standing hybrid films of sodium 1,4-dioxonaphthalene-2-sulfonate and multiwalled carbon nanotubes (NQS/MWNTs) as high-performance cathode for rechargeable LIBs. The hybrid films demonstrated high utilization of NQS, stable cycling, and high-rate capability. The superior electrochemical performance was attributed to decreased size and high polarity of NQS and the three-dimensional intertwined conductive network formed by MWNTs. Furthermore, NQS/MWNTs exhibited high initial reduction potential at 2.97 V [219].

Azo compounds are firstly applied in all-solid-state lithium batteries (ASSLB) to suppress the dissolution challenge. Due to the high compatibility of azobenzene (AB) based compounds to Li_3PS_4 (LPS) solid electrolyte, the LPS solid electrolyte was used to prevent the dissolution and shuttle reaction of AB. To maintain the low interface resistance during the large volume change upon cycling, a carboxylate group was added into AB to provide 4-(phenylazo) benzoic acid lithium salt (PBALS), which could bond with LPS solid electrolyte via the ionic bonding between oxygen in PBALS and lithium ion in LPS. The ionic bonding between the active material and solid electrolyte stabilized the contact interface and enabled the stable cycle life of PBALS in ASSLB [253].

Min et al. prepared a series of s-tetrazine derivatives bearing various substituents including phenyl, alkoxy, and chlorine such as 3,6-dichloro-1,2,4,5-tetrazine (DCT), 3,6-dimethoxy-1,2,4,5-tetrazine (DMT) and 3-chloro-6-ethoxy-1,2,4,5-tetrazine (CET). The porous carbon CMK-3 was introduced to encapsulate the s-tetrazines, which allowed 100% utilization of the theoretical capacity and stable cycle performance of the s-tetrazines by preventing dissolution of the molecules into the electrolytes. It is stated that this class of redox-active group could pave the way for the next-generation of energy storage system. Slurries of the tetrazines, carbon black (Super P), and PVDF in dimethylformamide (DMF) were prepared in a vial with a weight ratio of 4:4:2. Coin type cells were assembled with the cathodes, a Li-metal anode, and a polypropylene separator [220].

Nishida et al. have focused on “closed-shell” organic electron acceptors and donors, such as 7,7,8,8-tetracyanoquinodimethane (TCNQ) derivatives, dibenzotetrathiafulvalene (DBTTF), and 1,6-dithiapyrene (DTPY), as active cathode materials. Cathode composites of coin-type cells containing 10 wt.% active cathode materials were fabricated by mixing 80:10:10 (wt.%) of active cathode material, poly(tetrafluoroethylene) (PTFE), and vapor-grown carbon fiber (VGCF). The electrolyte solution was a mixture of ethylene carbonate (EC) (30 vol%) and diethyl

carbonate (DEC) (70 vol%) containing LiPF_6 [222].

Phenothiazine-based polymers are attractive due to their redox potential of 3.5 V vs. Li/Li^+ and high cycling stabilities. Three types of poly (norbornene)s have been presented, functionalized with phenothiazine units through either a direct connection or ester linkages, as well as their cross-linked derivatives. The directly linked poly(3-norbornylphenothiazine)s demonstrated excellent rate capability and cycling stability with a capacity retention of 73% after 10 000 cycles at a C-rate of 100C rate for the crosslinked polymer. The polymer network structure of the crosslinked poly(3-norbornylphenothiazine) herein was beneficial for its rate performance [254].

Cross-linked poly(3-vinyl-N-methylphenothiazine) as cathode-active material was presented, which showed a remarkable rate capability (up to 10C) and cycling stability at a high and stable potential of 3.55 V versus Li/Li^+ and a specific capacity of $112 \text{ mAh} \cdot \text{g}^{-1}$. Its use in full cells with a high mass loading of 70 wt.% was demonstrated against lithium titanate as intercalation material as well as lithium metal, which both showed excellent performance. Through comparison with poly(3-vinyl-N-methylphenothiazine), it was shown that changing the structure of the redox-active polymer through cross-linking can lead to a change in charge/discharge mechanism and cycling behavior of the composite electrode. Poly(3-vinyl-N-methylphenothiazine) in its cross- and non-cross-linked form both showed good results as cathode-active materials with variable specifications regarding specific capacity, cycling stability, and rate capability. Composite electrodes were prepared using 50 wt.% X-PVMPT, 40 wt.% carbon black (Super C65), and 10 wt.% binder (PVDF) or 70 wt.% X-PVMPT, 20 wt.% carbon black, and 10 wt.% binder. PVMPT based electrodes contained 50 wt.% PVMPT, 47 wt.% carbon black, and 3 wt.% binder [255].

It has also been demonstrated that amorphous covalent triazine-based frameworks (ACTFs) can be successfully used as a cathode material. These frameworks undergo a unique Faradaic reaction, as they can be present in a p-doped and an n-doped state. During charging and discharging, the polymeric cathode changes its charge state through a continuous, linear bipolar redox mechanism. The outcome is a remarkably high specific energy of $1084 \text{ Wh} \cdot \text{kg}^{-1}$ combined with a high specific power of $13\,238 \text{ W} \cdot \text{kg}^{-1}$ based on the mass of the framework. The present finding could show a new route to improve the performance of lithium-based energy storage devices by employing artificial porous polymeric frameworks as electrode materials. These findings suggest that ACTF-1 is a promising metal-free porous polymeric framework with a new energy storage strategy, which used both p-doping and n-doping as a cathode material. Based on this energy storage concept, it was demonstrated an unusually high specific energy and specific power. The lithium organic system based on ACTFs reaches a performance comparable to other next-generation energy storage systems, such as lithium–air and lithium–sulfur systems [226].

A new anthraquinone-based monomer was synthesized and due to the mono-modification the redox behavior of the monomer can be tailored. The polymeric backbone as well as the conducting and binding materials (multi-walled carbon nanotubes and PVDF, respectively) revealed no significant influence on the electrochemical behavior and, as a consequence, the polymers were employed as active material in a composite electrode for lithium organic batteries. In contrast to the monomer, the polymers showed good cycle stability over 100 cycles [227].

The semi-synthesis of a pendant flavin polymer was presented and its use as the cathode in a lithium-ion battery described. Flavins, which can be derived from riboflavin (vitamin B2), are highly promising electrode materials due to their ability to accept two electrons per unit, high potential ($\approx 2.5 \text{ V}$), and high theoretical capacity ($\approx 142 \text{ mAh} \cdot \text{g}^{-1}$ for riboflavin). Furthermore, their ability to accept multiple electrons provided scope for materials with high capacity. This is the first polymer that used a pendant bio-derived redox unit for battery applications. It was shown that this polymer provided a capacity of $125 \text{ mAh} \cdot \text{g}^{-1}$ with a voltage of 2.5 V in a device using lithium metal as the anode material. It

was also demonstrated that this material has a much higher performance than the small molecule riboflavin [228].

Further, the application of an antiaromatic compound as an electrode-active material in rechargeable batteries has been reported. The performance of dimesityl-substituted norcorrole nickel(II) complex (NiNC) as a cathode-active material was examined with a Li metal anode. A maximum discharge capacity of about $207 \text{ mAh} \cdot \text{g}^{-1}$ was maintained after 100 charge/discharge cycles. Moreover, the bipolar redox property of NiNC enabled the construction of a Li metal free rechargeable battery. The high performance of NiNC batteries demonstrated a prospective feature of stable antiaromatic compounds as electrode-active materials [256].

A fluorinated covalent organic polymer (F-COP) as a template for high performance sulfur cathodes in Li – S batteries was described. The fluorination allowed facile covalent attachment of sulfur to a porous polymer framework via nucleophilic aromatic substitution reaction ($\text{S}_\text{N}\text{Ar}$), leading to high sulfur content, e.g., over 70 wt.%. The F-COP framework was microporous with 72% of pores within three well-defined pore sizes, 0.58, 1.19, and 1.68 nm, which effectively suppressed polysulfide dissolution via steric and electrostatic hindrance. As a result of the structural features of the F-COP, the resulting sulfur electrode exhibited high electrochemical performance of $1287.7 \text{ mAh} \cdot \text{g}^{-1}$ at 0.05C, 96.4% initial Coulombic efficiency, 70.3% capacity retention after 1000 cycles at 0.5C, and robust operation for a sulfur loading of up to $4.1 \text{ mg}_{\text{sulfur}} \cdot \text{cm}^{-2}$ (Fig. 10a). These findings suggest the F-COP family with the adaptability of $\text{S}_\text{N}\text{Ar}$ chemistry and well-defined microporous structures as useful frameworks for highly sustainable sulfur electrodes in Li – S batteries. The sulfur electrodes were prepared by dispersing S-COP-99 s with conductive agent (carbon black/CNT) and PVDF in NMP in the mass ratio 7:2:1. A polypropylene membrane was used as separator, and a solvent mixture of DOL/DME in 1:1 (v/v) containing LiTFSI and LiNO_3 was used as the electrolyte [257].

An ideal polymer electrode based on anthraquinone, namely, polyanthraquinone (PAQ), or specifically, poly(1,4-anthraquinone) (P14AQ) and poly(1,5-anthraquinone) (P15AQ) was identified. As a lithium-storage cathode, P14AQ showed exceptional performance, including reversible capacity almost equal to the theoretical value ($260 \text{ mAh} \cdot \text{g}^{-1}$; $> 257 \text{ mAh} \cdot \text{g}^{-1}$ for AQ), a very small voltage gap between the charge and discharge curves ($2.18\text{--}2.14 = 0.04 \text{ V}$), stable cycling performance (99.4% capacity retention after 1000 cycles), and fast-charge/discharge ability (release of 69% of the low-rate capacity or 64% of the energy in just 2 min) (Fig. 10b). Exploration of the structure-performance relationship between P14AQ and related materials also provided deeper understanding for the design of organic electrodes [230].

1,1'-Iminodianthraquinone (IDAQ), a novel organic cathode, was taken as an example to quantitatively investigate the function as separator. IDAQ was able to achieve strongly improved cycling stability with capacity retention of 76% after 400 cycles and Coulombic efficiency above 99.6%, which reached the highest level for reported soluble organic electrode materials. Besides Li–organic batteries, such kind of Nafion-based sandwich-type separators were also promising for Li–S batteries and other new battery designs involving dissolved electro-active species. Herein, they proposed a new utilization of Nafion, namely a polypropylene/Nafion/polypropylene sandwich-type separator. For simplicity, it was abbreviated as PNP (monolayer polypropylene and bilayer polypropylene were abbreviated as P and PP, respectively). Coin cell was used to test the battery performance, consisting of lithium foil anode, separator (P, PP, or PNP) soaked with the electrolyte, and the cathode. The cathode film was prepared by manually mixed active material (AQ or IDAQ), conductive carbon, and polytetrafluoroethylene binder with weight ratio of 6:3:1. The cathode current collector was aluminum mesh. The electrolyte was $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (LiTFSI) solution in a mixture of DOL and DME (1:1, v/v) (Fig. 10c,d) [231].

Phosphaviologens P-MV and P-BnV have been incorporated into electrode materials in a hybrid organic/Li-ion battery setting. These

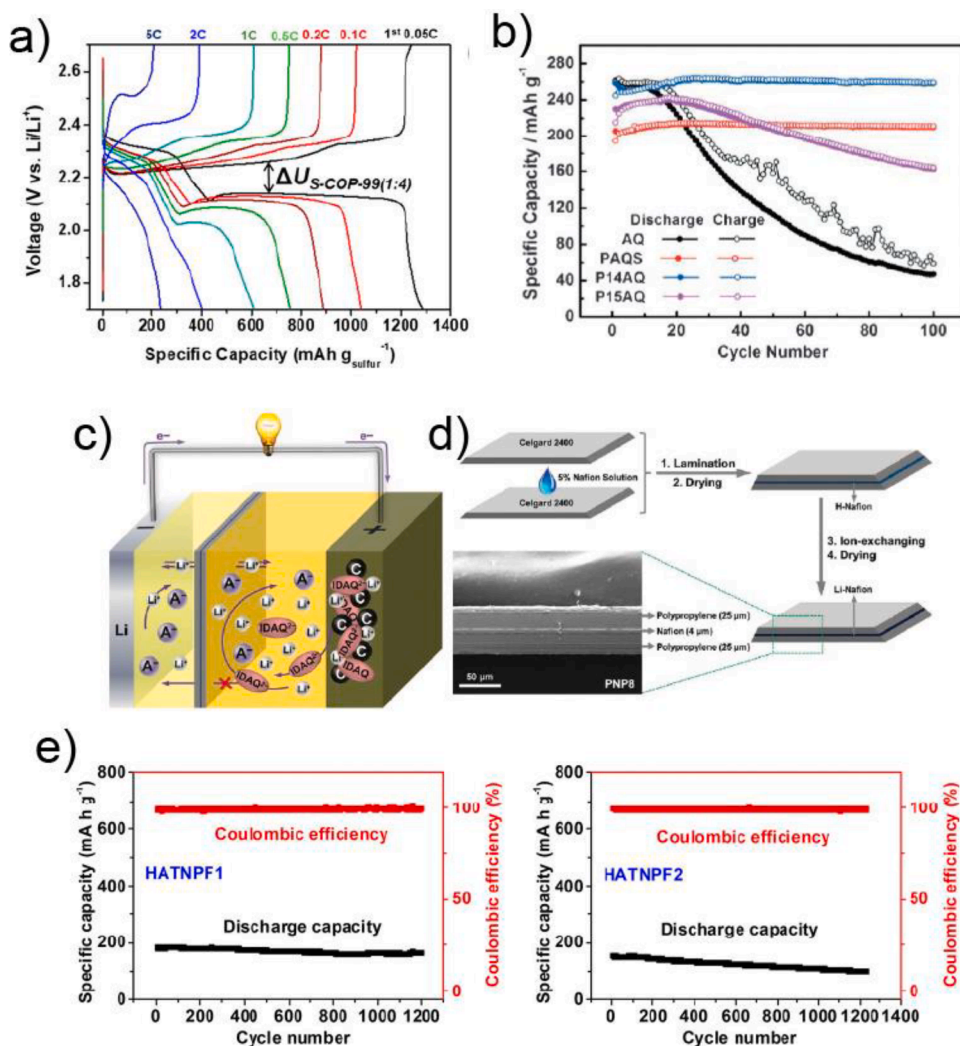


Fig. 10. S-COP-99(1:4) evaluated at various C-rates in the voltage range 1.7–2.7 V. Reprinted with permission [257]. Copyright 2019, American Chemical Society (a); cycling profiles at a current rate of 0.2C, with a cutoff voltage of 1.5–3.0 V. Reprinted with permission [230]. Copyright 2015, Wiley (b); Supposed cell configuration and operation mechanism of a Li-IDAQ battery using a PNP separator. A⁻ is the anion of electrolyte salt and C⁺ is the conductive carbon in the electrode (c); the fabrication process of a PNP separator and the cross-section SEM image of PNP8. Reprinted with permission [231]. Copyright 2016, Wiley (d); HATNPF1 demonstrated a better cycling stability than HATNPF2 (500 mA.g⁻¹). Reprinted with permission [235]. Copyright 2018, American Chemical Society (e).

initial studies focused on using the synthesized materials to test their viability as electrode materials in proof-of-concept devices via half-cell measurements versus Li-metal. While they did not provide large leaps in terms of overall capacity, the phosphaviologens (PV) used two redox steps in the charging/discharging cycles, allowing to double the electron capacity per molecule compared to that of conventional viologens used as electrode materials. In an attempt to improve performance and stability, new synthetic methods were developed to access phosphaviologen dimers, along with polymeric species that can be solution-processed as electrode materials in proof-of-concept batteries [258].

Application and investigation of porous composite electrodes for organic batteries fabricated by an ice-templating method were reported. The possibility to produce polymer composite electrodes with highly aligned, parallel pores was demonstrated and electrochemical investigations were presented to examine their suitability for application in organic batteries. The performance of such ice-templated porous electrodes was experimentally compared with planar electrodes of similar composition against zinc and lithium counter electrodes, respectively. Fundamental properties limiting the performance of ice templated porous electrodes were discussed and further means to overcome those limitations were proposed [259].

A family of naphthalene diimide derivatives was synthesized and their redox properties explored with the intent of unveiling structures with reduction potentials that are higher than those encountered in previous organic redox processes. Changes in the electronic characteristics of the aryl substituents resulted in materials with discharge potentials that

vary from 2.3 to 2.9 V vs Li/Li⁺, with discharge capacities as high as 121 mAh.g⁻¹ [232].

Synthesis, characterization, and device performance of an organic salt, lithium 2,6-bis(ethoxycarbonyl)-3,7-dioxo-3,7-dihydro-s-indacene-1,5-bis(olate), capable of reversibly intercalating with minimal polarization 1.8 Li per unit formula over two main voltage plateaus located at ~ 1.96 and ~ 1.67 V (vs. Li/Li⁺), lead to an overall capacity of 125 mAh.g⁻¹. Proton NMR and in situ XRD analyses of battery cycling versus Li at room temperature revealed that the insertion - deinsertion process was fully reversible with the dips in the voltage - composition traces associated with changes in the 3D structural packing of the electrochemically active molecules [233].

Nanostructured freestanding conducting polymer composites [e.g., PPy and PANI] can be used to circumvent the shortcomings associated with poor cycling stability, rapid self-discharge, and low energy and power densities. Freestanding and binder-free PPy and cellulose-based composites can straightforwardly be used as versatile organic cathode materials for LIBs. The composite, reinforced with chopped carbon filaments (CCFs), exhibit a large active mass loading of approximately 10 mg.cm⁻², an area capacity of 1.0 mAh.cm⁻² (corresponding to 102 mAh.g⁻¹), and stable cycling. With an active mass loading of 4.4 mg.cm⁻², a capacity of 0.22 mAh cm⁻² (corresponding to 58 mAh.g⁻¹) was found for current densities of 5 A.g⁻¹ yielding discharge times of approximately 40 s, and a capacity retention of 91% over 100 cycles was obtained at 0.2 A.g⁻¹. The present method constituted a straightforward approach for the manufacturing of high-performance freestanding

electroactive conducting-polymer-based paper-like electrodes for inexpensive and sustainable, high-performance organic LIBs [234].

Two new porous organic frameworks as cathode materials for lithium-ion battery (LIB) using hexaazatrinaphthalene (HATN) cores with high theoretical capacities were designed. The polymer materials were synthesized in a facile and scalable manner with different structural features ranging from a rigid conjugated framework (HATNPF1) to a flexible non-conjugated framework (HATNPF2). HATNPF polymers demonstrated a high specific capacity (309 mAh.g^{-1}), excellent long-term cycling stability (92% capacity retention after 1200 cycles) (Fig. 10e) and rate capability (65% capacity retention at 2 A.g^{-1} as compared to capacity at 0.2 A.g^{-1}), which represents an improvement over previously reported porous organic polymers and the HATN monomer [235].

An all-organic battery consisting of two redox-polymers, namely poly(2-vinylthianthrene) and poly(2-methacrylamide-TCAQ) was assembled. This all-organic battery showed good performance characteristics, namely flat discharge plateaus, an output voltage exceeding 1.3 V, and theoretical capacities of both electrodes higher than 100 mAh.g^{-1} . Both organic electrode materials were synthesized in two respective three synthetic steps using the free-radical polymerization technique. Li-organic batteries manufactured from these polymers proved their suitability as organic electrode materials. The cathode material poly(2-vinylthianthrene) displayed a discharging plateau at 3.95 V versus Li^+/Li and a discharge capacity of 105 mAh.g^{-1} , corresponding to a specific energy of about 415 mWh.g^{-1} . The anode material poly(2-methacrylamide-TCAQ) exhibited an initial discharge capacity of 130 mAh.g^{-1} , corresponding to 94% material activity. The combination of both materials resulted in an all-organic battery with a discharge voltage of 1.35 V and an initial discharge capacity of 105 mAh.g^{-1} (95% material activity) [246].

Composites of polytriphenylamine (PTPA), its novel derivative poly(4-carbamoyl-N,N-diphenylaniline-2,2,5,5-tetramethyl-pyr-rolin-1-oxyl) (PTPA-PO) and multiwalled carbon nanotubes (MWNTs) were synthesized by in situ polymerization. It was demonstrated that the as-synthesized polytriphenylamine derivative, PTPA-PO, with a CNT cathode presented two well-defined plateaus and an enhanced discharge capacity of 139.3 mAh.g^{-1} . Additionally, the PTPA-PO/CNT electrodes showed superior cycling performance and remained above 90% of the initial capacity after 100 cycles. The enhanced electrochemical performance of PTPA-PO was due to its combination of the conducting polymer PTPA and free radical active site pendant PO, which increased its electrochemical reaction rate, the composite being a promising material for high-performance polymer-based organic batteries. Cathode electrodes were obtained by separately mixing PTPA and CNT, PTPA and acetylene black, and PTPA/CNT and PTPA-PO/CNT with 10 wt.% PVDF in NMP. The electrolyte solution was LiPF_6 dissolved in ethylene carbonate/dimethyl carbonate (EC/DMC, 1/1, v/v) [237].

A novel conjugated copolymer based on aniline and pyrene units has been synthesized and employed as an organic cathode material in rechargeable Lithium-ion batteries (LIBs). Due to the synergistic effects from conducting aniline and pyrene units, the resultant batteries based on the as-obtained copolymer can deliver a promising reversible specific capacity of 113 mAh.g^{-1} with a high voltage output of 3.2 V and a remarkable 75.2% capacity retention after 180 cycles. Moreover, an excellent rate performance was also achieved with a fast recovery of the capacity at different current densities [238].

A structure-design strategy is reported for thiophene-containing conjugated microporous polymers (CMPs) with extraordinary electrochemical performance as anode materials in LIBs. The comparative study of the electrochemical performance of the structure-designed thiophene-containing CMPs revealed that high redox-active thiophene content, highly crosslinked porous structure, and improved surface area plays significant roles for enhancing electrochemical performances of the resulting CMPs. The all-thiophene-based polymer of poly(3,3'-bithiophene) with crosslinked structure and a high surface area of 696

$\text{m}^2.\text{g}^{-1}$ exhibited a discharge capacity as high as 1215 mAh.g^{-1} at 45 mA.g^{-1} , excellent rate capability, and outstanding cycling stability with a capacity retention of 663 mAh.g^{-1} at 500 mA.g^{-1} after 1000 cycles. The structure-performance relationships revealed in this work offer a fundamental understanding in the rational design of CMPs anode materials for high performance LIBs [242].

A vertical polyaniline nanowire-coated carbon nanotube (CNT/PANI) composite flexible electrode on which Li could be homogeneously deposited to obtain a CNT/PANI@Li anode was reported [245]. In the composite, CNT/PANI acted as a host matrix with well-distributed Li ion flux attributed to high electroactive surface area, thereby effectively suppressing the Li dendrite. Compared with the pure CNT electrode, the CNT/PANI electrode presented low overpotential and stable long-term cycling with much less fluctuant stripping/plating profiles. The potential application of CNT/PANI@Li in all-flexible full cells was demonstrated by combining flexible organic poly(2,5-dihydroxyl-1,4-benzoquinonyl sulfide)/carbon nanotube (PDHBQS/CNT) composite films, in which the cathode achieved an performance of 120 mAh.g^{-1} at 50 mA.g^{-1} . Besides, pouch batteries with suitable flexibility were tested successfully, which demonstrated a promising future for all-flexible and high-performance Li-metal batteries [245].

4.2. Other battery types

Even though the majority of the research is focused on lithium technology, some recent literature also approached different battery types, such as sodium, potassium, magnesium or nickel. These types are approached in the following sections. Finally, there are other materials that can be applied in multiple battery types.

4.2.1. Sodium batteries

Quinone derivative ($\text{C}_6\text{R}_4\text{O}_2$) containing electron-withdrawing elements ($\text{R}=\text{Cl}$) as a novel, high-energy organic cathode for sodium-ion batteries (NIBs), was proposed. The introduction of electronegative elements lowered the LUMO energies of the quinone derivatives, which in turn increased their Na storage potential. A rationally designed cathode ($\text{C}_6\text{R}_4\text{O}_2$) exhibited an average voltage of $\sim 2.72 \text{ V}$ (vs. Na/Na^+), which was considerably higher than those of reported organic cathode materials. Experimentally, the $\text{C}_6\text{R}_4\text{O}_2$ electrode could deliver a capacity of 161 mAh.g^{-1} and an energy density of 420 Wh.kg^{-1} with a theoretical energy density of 580 Wh.kg^{-1} , which was the highest value yet attained with quinone-derived cathode materials. Overcoming the degradation of capacity coming from the dissolution of the electrode material into the surrounding electrolyte will make $\text{C}_6\text{R}_4\text{O}_2$ electrodes a promising low-cost, high-energy alternative for NIBs [260].

A series of dianhydride-based PIs, which bear various commercially available dianhydrides such as pyromellitic dianhydride (PMDA), 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA), and perylene 3,4,9,10-tetracarboxylic dianhydride (PTCDA), were proposed for battery applications and synthesized by a facile one-pot reaction. Specifically, the synthesis of PTCDA-based PIs was carried out and the excellent electrochemical performance as cathode materials for rechargeable NIBs demonstrated, which was attributed to their unique polymer structure composed of an alkyl chain interconnecting the electrochemically active centers. Among the developed polymers, PTCDA-based PI shows a high specific power of 20.99 kW.kg^{-1} , specific energy of 285 Wh.kg^{-1} , and over 5000 cycle life, retaining 87.5% of its initial capacity in half-cells and thus showing superiority over PMDA and NTCDA-based PI analogues due to its low solubility and the lowest unoccupied molecular orbital (LUMO) energy, which reveals a versatile yet unexplored strategy for the design of organic materials for NIBs. The electrodes were prepared by mixing active material (60 wt.%), acetylene black (30 wt.%), and PVDF (10 wt.%) in NMP. For the optimization of the electrochemical performance of the PI2, the electrode composition was changed to active material (30 wt.%), acetylene black (60 wt.%), and PVDF (10 wt.%) [261].

The first use of highly porous azo-linked polymers (ALPs) as a new redox-active electrode material for rechargeable sodium-ion batteries was reported. ALPs are highly cross-linked polymers and therefore eliminate the solubility issue of organic electrodes in common electrolytes, which is prominent in small organic molecules and leads to fast capacity fading. Moreover, the high surface area coupled with the π -conjugated microporous nature of ALPs facilitated electrolyte adsorption in the pores and assisted in fast ionic transport and charge transfer rates. An average specific capacity of 170 mAh.g^{-1} at 0.3 C rate was obtained while maintaining 96% Coulombic efficiency over 150 charge/discharge cycles [262].

4.2.2. Potassium batteries

A highly reversible phase transformation of the organic cathode during potassiation/depotassiation is a key factor for capacity retention. Consequently, a potassium-organic battery has been developed with a high-power density of 9796 W.kg^{-1} , a remarkable energy efficiency of 89%, a long cycle stability for 1000 cycles, a superior areal capacity around 2 mAh.cm^{-2} , and a long-term cycling time over 8 months. Besides, the full cells also exhibited a superior rate performance and good cycle stability over 3000 cycles. This work provided new insight into the stabilization of the organic cathode and demonstrated the enormous potential of organic cathodes for application in high-power potassium-ion batteries (PIBs), which may bring PIBs to new heights. The PTCDA@450 °C cathode, pristine PTCDA cathode, and SC anode were prepared by mixing the active materials with carbon black, and carboxyl methyl cellulose at a weight ratio of 8:1:1. Assembled using coin cells with a potassium foil as the counter electrode, PTCDA@450 °C as the work electrode, and several kinds of electrolyte. The separators were glass fibers [263].

4.2.3. Magnesium batteries

The use of non-nucleophilic electrolytes in combination with carefully chosen organic active materials is a very promising strategy for the further development of Mg batteries. Capacities between 150 and 200 mAh.g^{-1} at a voltage from 1.5 to 2.0 V can be obtained, with the possibility of achieving high-rate capabilities that are inherent to organic batteries. All Mg-battery electrochemical tests were performed in cells with graphite discs acting as cathode current collectors and GF/A glass fiber separators. Cathode composites were prepared by mixing active material, poly(antraquinoyl) sulfide (PAQS), Printex XE2 carbon, and PTFE binder in the ratio 50:35:15. For counter electrode, Mg foil was used and Mg powder was synthesized. In cases where Mg powder was utilized, it was simply added on the anode side and slightly hand pressed using a stainless steel disk and spring to ensure good contact between electrodes and current collectors, as in the case of Mg foil, upon assembly Mg powder did not pelletize [264].

A Mg-organic battery based on renewable rhodizonate salt (e.g. $\text{Na}_2\text{C}_6\text{O}_6$) activated by Mg-Li dual-salt electrolyte was proposed. The nanostructured organic system could achieve a high reversible capacity of $350\text{--}400 \text{ mAh.g}^{-1}$ due to the existence of high-density carbonyl groups ($\text{C}=\text{O}$) as redox sites. Nanocrystalline wired $\text{Na}_2\text{C}_6\text{O}_6$ by reduced graphene oxide enabled a high-rate performance with 200 and 175 mAh.g^{-1} at 2.5 (5 C) and 5 A.g^{-1} (10 C) respectively, which also benefited from high intrinsic diffusion coefficient ($10^{-12}\text{--}10^{-11} \text{ cm}^2.\text{s}^{-1}$) and pseudocapacitance contribution ($> 60\%$) of $\text{Na}_2\text{C}_6\text{O}_6$ for Li-Mg co-intercalation. The suppressed exfoliation of C_6O_6 layers by a firmer non-Li pinning via Na-O-C or Mg-O-C and dendrite resistive Mg anode led to a long-term cycling for at least 600 cycles. Such an excellent capacity/rate performance endows $\text{Na}_2\text{C}_6\text{O}_6$ system high energy and power densities up to 525 Wh.kg^{-1} and 4490 W.kg^{-1} (based on active cathode material) respectively, exceeding the level of high-voltage insertion cathodes with typical inorganic structures [265].

4.2.4. Nickel batteries

The work reported by Clausen et al. was an initial investigation of the

possible use of redox active anthraquinone as anode material in combination with $\text{Ni}(\text{OH})_2$ in a secondary battery with aqueous KOH electrolyte. The redox active materials were mixed with graphite and carbon black, adding poly(vinylalcohol) and ZEON binder suspensions, followed by homogenization and drying. Three different anode materials were investigated: an anthraquinone monomer and two different anthraquinone based oligomers. Batteries based on one of the oligomerized anthraquinones (oligo[benzene-1,4-dithiol-alt-(1,5-dichloroanthraquinone)] anode) shown the best performance and retains almost 50% of the discharge capacity after 100 cycles [266].

4.2.5. Advanced approaches for various battery systems

Fluorine atoms were introduced into the covalent triazine frameworks (CTF) to obtain two-dimensional layered fluorinated CTF (FCTF) and its exfoliated few-layered product (E-FCTF), and used as anodes of Li, Na and K organic batteries. Exfoliated E-FCTF electrode delivers high reversible capacities, as well as excellent cycle life for alkali organic batteries (1035 mAh.g^{-1} at 100 mA.g^{-1} after 300 cycles and 581 mAh.g^{-1} at 2 A.g^{-1} after 1000 cycles for lithium organic batteries [240].

4,4'-(phenazine-5,10-diyl)dibenzoate anion (denoted as PZDB) can be used as a bipolar active material for organic symmetric cell. PZDB can be regarded as a cathode-active phenazine moiety covalently sandwiched between two conjugated anode-active benzoate moieties (Fig. 11a,b). Such a strategy by integrating cathode-active moiety into the dilithium or disodium salts of conjugated carboxylates, which are easily accessible and almost insoluble in common aprotic electrolytes, is highly promising for battery application [267].

New organic and hybrid organic-inorganic functional derivatives of closo dodecaborane dianion, namely $\text{B}_{12}\times\text{I}_2^{2-}$ ($\text{X} = -\text{C}\equiv\text{CH}$, $-\text{C}\equiv\text{C}-\text{CN}$, and $-\text{C}\equiv\text{C}-\text{BO}$), have been proposed for battery applications based on density functional theory. The second excess electron in B_{12} ($\text{C}\equiv\text{C}-\text{CN}$) $_{12}^{2-}$ and B_{12} ($\text{C}\equiv\text{C}-\text{BO}$) $_{12}^{2-}$ has a very strong bound with an ΔE_2 value of 4.90 and 5.14 eV, respectively, in the gas phase, which is almost six-times higher than that of $\text{B}_{12}\text{H}_{12}^{2-}$ (0.81 eV). The implications of these stable dianions as electrolytes in the Li and Mg ion batteries, and the results are found to be highly promising. Among all the dianions considered, B_{12} ($\text{C}\equiv\text{C}-\text{BO}$) $_{12}^{2-}$ and B_{12} ($\text{C}\equiv\text{C}-\text{CN}$) $_{12}^{2-}$ are the most suitable choices as electrolytes for the Li and Mg ion batteries, as the $\text{Li}^+/\text{Mg}^{2+}$ salt of these two dianion require much less energy to dissociate into the corresponding cation and anion. In addition, the oxidation potential of B_{12} ($\text{C}\equiv\text{C}-\text{BO}$) $_{12}^{2-}$ and B_{12} ($\text{C}\equiv\text{C}-\text{CN}$) $_{12}^{2-}$ dianions versus Mg^{2+}/Mg is very high (12.91 and 12.58 V, respectively) (Fig. 11c). The present work reveal that it is possible to design multiple charged stable anions for battery applications through suitable organic-inorganic functionalization [268].

A novel polymer cathode material, poly(benzoquinonylsulfide) (PBQS), was reported, for either rechargeable Li or Na battery. Remarkably, PBQS showed a high energy density of 734 Wh.kg^{-1} ($2.67 \text{ V} \times 275 \text{ mAh.g}^{-1}$) in Li battery, or 557 Wh.kg^{-1} ($2.08 \text{ V} \times 268 \text{ mAh.g}^{-1}$) in Na battery, which exceeded those of most inorganic Li or Na intercalation cathodes. Besides, PBQS also demonstrated excellent long-term cycling stability (1000 cycles, 86%) and superior rate capability (5000 mA.g^{-1} , 72%) in Li battery. The research on the structure-property relationship between benzoquinone (BQ) and PBQS, and the electrochemical behavior difference between Li-PBQS battery and Na-PBQS batteries, also provide significant insights into developing improved Li-organic and Na-organic batteries beyond conventional Li-ion batteries [229].

A novel, thiophene-rich conjugated microporous polymer of polytetra(2-thienyl)ethylene (PTTE) was synthesized via FeCl_3 -catalyzed oxidative polymerization and applied as an anode material for lithium-ion batteries (LIBs) and sodium-ion batteries (NIBs). Owing to the high surface area, high redox-active thiophene content, and the plentiful nano porous structures in PTTE, the assembled LIBs exhibit a high specific capacitance of 973 mAh.g^{-1} at 100 mA.g^{-1} with excellent rate performance, and the NIBs showed a capacitance as high as 370

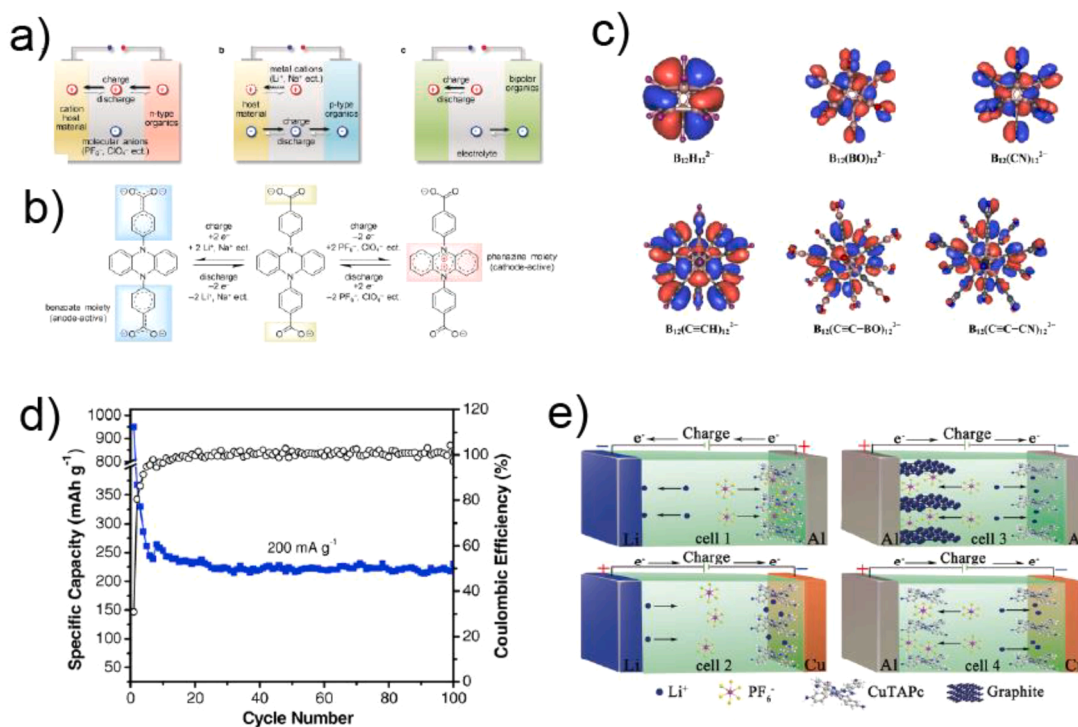


Fig. 11. Schematic demonstration of the charge and discharge process inside a full cell using n-type organics and p-type organics as the cathode, and bipolar organics as both the cathode and anode (a); redox mechanism of the PZDB anion (b). Reprinted with permission [267]. Copyright 2019, Wiley; Highest occupied molecular orbital (HOMO) pictures of $B_{12} \times 122^-$ dianions ($X = -H, -BO, -CN, -C\equiv CH, -C\equiv C-BO, -C\equiv C-CN$) obtained using B3LYP/DEF method. Reprinted with permission [268]. Copyright 2018, American Chemical Society (c); Cycling stability of PTTE. Reprinted with permission [236]. Copyright 2018, Wiley (d); various cell configurations for using CuTAPc as a bipolar electrode material. Reprinted with permission [269]. Copyright 2019, Wiley (e).

$mAh\ g^{-1}$ at a current density of $50\ mA\ g^{-1}$, excellent rate capability, and outstanding cycling stability with a capacity retention of $230\ mAh\ g^{-1}$ at $200\ mA\ g^{-1}$ after 100 cycles (Fig. 11d). These results demonstrated this thiophene-rich conjugated microporous polymer as a promising electrode material for next-generation energy storage devices [236].

A strategy to screen a variety of phthalocyanine-based bipolar organics was proposed. The self-polymerizable bipolar Cu tetraaminephthalocyanine (CuTAPc) showed multifunctional applications in various energy storage systems, including lithium-based dual-ion batteries (DIBs) using CuTAPc as the cathode material, graphite-based DIBs using CuTAPc as the anode material and symmetric DIBs using CuTAPc as both the cathode and anode materials (Fig. 11e). Notably, in lithium-based DIBs, the use of CuTAPc as the cathode material results in a high discharge capacity of $236\ mAh\ g^{-1}$ at $50\ mA\ g^{-1}$ and a high reversible capacity of $74.3\ mAh\ g^{-1}$ after 4000 cycles at $4\ A\ g^{-1}$. Most importantly, a high energy density of $239\ Wh\ kg^{-1}$ and power density of $11.5\ kW\ kg^{-1}$ could be obtained in all organic symmetric DIBs [269].

The green and natural gallic acid derivatives, ellagic acid (EA, dimer) and tannic acid (TA, oligomer) are suitable anode materials for Li and Na ion batteries due to their π - π conjugated structures and abundant carbonyl, carboxyl, phenolic groups. $644, 364, 195$, and $162\ mAh\ g^{-1}$ for EA and $297, 451, 465$, and $265\ mAh\ g^{-1}$ for TA are obtained for Li ion batteries (LIBs) at the current densities of $0.1, 0.2, 0.5$, and $1.0\ A\ g^{-1}$ after 150, 250, 500, 1000 cycles, respectively. The specific capacities of EA and TA LIBs were higher than those of organic LIBs and could be comparable with the metal oxide LIBs, and the cycling stabilities of EA and TA LIBs were better. Meanwhile, EA and TA were used as anode materials which enabled the construction of Na ion batteries, which showed the specific capacity of $105\ mAh\ g^{-1}$ for EA and $46\ mAh\ g^{-1}$ for TA at $50\ mA\ g^{-1}$ after 350 cycles. This work provided important inspirations for exploring organic materials from nature which were applied in the development of green and high-performance energy

storage devices. For the working electrode preparation, ellagic acid was homogeneously mixed with super P and PVDF at a mass ratio of 55:35:10 with NMP as a solvent. For Li ion batteries, the counter electrode is Li metal, and the electrolyte contains $LiPF_6$ in EC/DEC, 1:1 v/v. In NIBs, Na metal, Whatman-1825 and $NaPF_6$ in EC/DMC, 1:1 v/v were used as the counter electrode, separator, and electrolyte, respectively [243].

A novel all-plastic-electrode based Li-ion battery with a single flexible bi-functional ladderized heterocyclic poly(quinone), $(C_6O_2S_2)_n$, as both cathode and anode was demonstrated. Benefiting from its unique ladder-like quinone and dithioether structure, the as-prepared polymer cathode showed a high energy density of $624\ Wh\ kg^{-1}$ (vs lithium anode) and a stable battery life of 1000 cycles. Moreover, the as-fabricated symmetric full-battery delivered a large capacity of $249\ mAh\ g^{-1}$ (at $20\ mA\ g^{-1}$), a good capacity retention of $119\ mAh\ g^{-1}$ after 250 cycles (at $1.0\ A\ g^{-1}$) and a noteworthy energy density up to $276\ Wh\ kg^{-1}$. The superior performance of poly(2,3-dithiino-1,4-benzoquinone) based electrode rivals most of the state-of-the-art demonstrations on organic-based metal ion shuttling batteries. The study provided an effective strategy to develop stable bifunctional electrode materials toward the next-generation of high performance all plastic batteries [270].

An effective strategy to prepare nanoengineered ultralight materials is based on organic electroactive material/graphene aerogels, in which aromatic carbonyl compounds were confined in a three-dimensional hybrid architecture and used cathode materials for LIBs and NIBs. As a representative example of aromatic carbonyl compounds, 3,4,9,10-perylene-tetracarboxylic acid dianhydride (PTCDA, known as "red 224", is a red color pigment with an aromatic core and two electroactive conjugated anhydride groups. A stable composite structure could be formed by the π - π interactions between the aromatic core and graphene, and the conjugated anhydride groups were electroactive for Li^+ / Na^+ ions. As expected, the PTCDA/graphene aerogel (PGC) as the cathode material

for LIBs can display a high initial capacity of $202.2 \text{ mAh}\cdot\text{g}^{-1}$ at a current density of $50 \text{ mA}\cdot\text{g}^{-1}$, long cycle performance without any decay after 200 cycles and excellent rate performance ($64 \text{ mAh}\cdot\text{g}^{-1}$ even at $2000 \text{ mA}\cdot\text{g}^{-1}$). Moreover, the PGC also displays high initial capacity of $\sim 98 \text{ mAh}\cdot\text{g}^{-1}$ at $25 \text{ mA}\cdot\text{g}^{-1}$ and good cycle performance with capacity retention of 90% after 100 cycles as the cathode material for NIBs [239].

Zhang et al. reported the synthesis of self-assembled graphene/poly (anthraquinonylsulfide) (PAQS) composite aerogel (GPA) with efficient integration of three-dimensional (3D) graphene framework with electroactive PAQS particles via a novel dispersion-assembly strategy, which can be used as a free-standing flexible cathode upon mechanical pressing. The entire GPA cathode could deliver a highest capacity of $156 \text{ mAh}\cdot\text{g}^{-1}$ at 0.1 C ($1 \text{ C} = 225 \text{ mAh}\cdot\text{g}^{-1}$) with an ultrahigh utilization (94.9%) of PAQS and exhibited an excellent rate performance with $102 \text{ mAh}\cdot\text{g}^{-1}$ at 20 C in LIBs. Furthermore, the flexible GPA film has also been tested as cathode for SIBs and demonstrated a high-rate capability with $72 \text{ mAh}\cdot\text{g}^{-1}$ at 5 C and an ultralong cycling stability (71.4% capacity retention after 1000 cycles at 0.5 C) which has been rarely achieved before. Such excellent electrochemical performance of GPA as cathode for both LIBs and SIBs can be ascribed to the fast-redox kinetics and electron transportation within GPA, resulting from the interconnected conductive framework of graphene and the intimate interaction between graphene and PAQS through an efficient wrapping structure. This approach opened up an universal way to develop cathode materials for powerful batteries with different metal-based counter electrodes [241].

4.3. Fully organic batteries

To achieve a fully organic battery, it is necessary to develop other materials than organic electrodes. In this regard, the production of organic materials as electrolytes and conductive materials is also

critical.

The solubility properties of a polyvinyl-based redox polymer with a methylphenothiazine side group (PVMPT) in organic solvent-based battery electrolytes were evaluated, generating new insights into the mechanism of the re-deposition process of dissolved active material. The composition of the electrodes was 50 wt.% PVMPT mixed with 47 wt.% conductive additive (Super C65) and 3 wt.% binder (PVDF-HFP). During cycling, the polymer was re-deposited and dissolved repeatedly until a stable surface film had formed (Fig. 12a). This surface film kept ionically and electronically conductive even after 1000 cycles and was able to withstand 10,000 cycles and high C-rates (10C) [216].

The use of ILs as electrolytes has been reported with the view of increasing redox potentials of nitroxide radicals. A series of imidazolium, phosphonium, and pyrrolidinium-based ILs coupled with widely used anions were chosen to predict redox potentials of the TEMPO radical using state-of-the-art quantum chemical calculations using one and two ion pairs to describe ILs. Some ILs showed a significant increase in the redox potential of this radical to reach as much as 5.5 eV, compared to the previously measured value of 2.2 eV in aqueous media (Fig. 12b). In particular, ILs were shown to stabilize the aminoxy anion, the reduced form of the nitroxide radical, which has not been achieved previously in traditional solvents. Although a simple model consisting of one and two ion pairs was used in the current study, these findings clearly demonstrated that ILs had a huge potential in improving redox potentials of nitroxide radicals [6].

A sulfonate-functionalized viologen molecule, 1,1'-bis(3-sulfonatopropyl)-4,4'-bipyridinium, (SPr)2 V, as an anolyte in neutral aqueous organic redox flow batteries (AORFBs) working through a cation charge-transfer mechanism was described. (SPr)2 V/KI AORFBs manifested high current performance from 40 to $100 \text{ mA}\cdot\text{cm}^{-2}$ with up to 71% energy efficiency. In extended cycling studies, the (SPr)2 V/KI redox flow battery delivered stable cycling performance at $60 \text{ mA}\cdot\text{cm}^{-2}$,

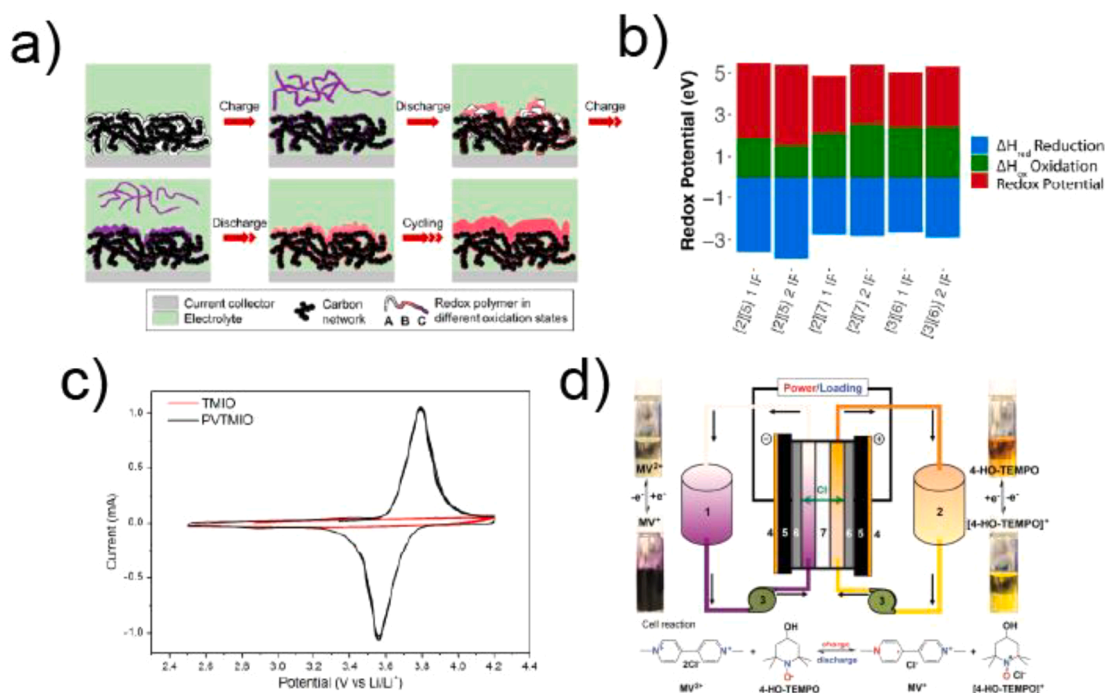


Fig. 12. Mechanism of charge/discharge of a PVMPT-based electrode. Reprinted with permission [216]. Copyright 2018, American Chemical Society (a); predicted potentials of TEMPO in one- and two-ion-paired systems. Reprinted with permission [6]. Copyright 2019, American Chemical Society (b); cyclic voltammograms of the assembled lithium-ion coin cells from TMIO (red) and PVTMIO (black): (10/80/10 wt.% TMIO or PVTMIO/Super P/poly(vinylidene difluoride) (PVDF)), 1 M LiPF₆/EC/DEC; scan rate: 5 mV s^{-1} . Reprinted with permission [13]. Copyright 2018, American Chemical Society (c); schematic representation of the MV/4-HO-TEMPO organic aqueous redox flow battery (OARFB), illustrations of discharged and charged states of MV 4-HO-TEMPO, and cell reactions. Arrows indicate electrolyte flow directions. Cell components: 1. MV anolyte reservoir; 2. 4-HO-TEMPO catholyte reservoir; 3. pump; 4. copper current collector; 5. carbon end plate; 6. graphite electrode; 7. anion exchange membrane (AEM). Reprinted with permission [276]. Copyright 2016, Wiley (d).

up to 7% energy efficiency, and 99.99% capacity retention per cycle. Density functional theory modeling of the electrostatic charge surface of (SPR)2 V and its charged state, [(SPR)2 V]^{−1}, suggests that charge repulsion and size exclusion enable their compatibility with a cation exchange membrane. These represent an attractive RFB technology for sustainable and benign renewable energy storage [271].

An all-radical battery with sulfur anions as the cathode and silyl radicals as the anode exhibited a practical discharge potential of approximately 1.8 V and stable cycle performance, demonstrating the potential of these materials for use in metal-free batteries that can replace conventional Li-ion batteries [272].

An aqueous-electrolyte all-organic rechargeable battery with a maximum operating voltage of 2.1 V has been developed based on polytriphenylamine (PTPA) and 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA)-derived polyimide (PNTCDA) as cathode and anode material, respectively. A key feature of the design was the use of a “water in-salt” electrolyte to bind “free” water; this impeded the side reaction of water oxidation, thereby enabling excellent reversibility in aqueous solution. The battery could deliver a maximum energy density of 52.8 Wh.kg^{−1}, which was closed to most of the all-organic batteries with organic electrolytes. The battery exhibited a supercapacitor-like high power of 32,000 W.kg^{−1} and a long cycle life (700 cycles with capacity retention of 85%), due to the kinetics not being limited by ion diffusion at either electrode. The polymer-based electrode (PTPA cathode or PNTCDA anode) was obtained by mixing active material, ketjen black (KB) as conductive agent, and polytetrafluoroethylene (PTFE) as binder in the mass ratio of 6:3:1 [16].

2,6-dihydroxyanthrahydroquinone (DHAQ) tends to form an anthrone intermediate that is vulnerable to subsequent irreversible dimerization, a decomposition pathway responsible for the loss of battery capacity based on those materials. The conditions minimizing anthrone formation and avoiding anthrone dimerization have been demonstrated [273], allowing to slow the capacity loss rate by over an order of magnitude. It has been anticipated that this mitigation strategy can be readily extended to other anthraquinone-based flow batteries, being therefore an important step towards realizing renewable electricity storage through long-lived organic flow batteries.

The first example of the 1,1,3,3-tetramethylisindolin-2-yloxy (TMIO)-class of nitroxides as an organic electrode material and the synthesis and application of a novel styrenic nitroxide polymer, poly-5-vinyl-1,1,3,3-tetramethylisindolin-2-yloxy (PVTMIO) was reported. The polymer was synthesized from the precursor monomer 2-methoxy-5-vinyl-1,1,3,3-tetramethylisindoline (VTMIO) and subsequent oxidative deprotection yielded the electroactive radical species. The suitability of PVTMIO for utilization in a high voltage organic radical battery was confirmed with a discharge capacity of 104.7 mAh.g^{−1}, high-rate performance and stability under cycling conditions (90% capacity retention after 100 cycles), making it one of the highest reported organic p-dopable cathode materials (Fig. 12c) [13].

Hydrophilic redox-active polymer nanoparticles with different redox potentials and radii were synthesized via the dispersion polymerization to yield their stable dispersion in aqueous electrolyte media as promising catholytes and anolytes in redox flow batteries. Despite the small physical diffusion coefficient (10^{−9} cm² s^{−1}) of the nanosized particles, the sufficiently large coefficient for charge transfer within the polymer particle dispersion (10^{−7} cm² s^{−1}) was observed as a result of the fast electron propagation throughout the polymer particles. Redox flow cells were fabricated using TEMPO-, viologen-, or diazaanthraquinone-substituted polymer nanoparticles as active materials. The reversible charge/discharge over 50 cycles was achieved even at a high concentration of the redox units (1.5 M), which exceeded the limitation of the solubility of the corresponding dissolved species [274].

A comprehensive analysis on the energy density of various kinds of organic batteries, with focus on the study of cathode and electrolyte formulation, theoretical and practical capacity, average discharge voltage and cycle life, using both liquid and solid electrolytes was

demonstrated, providing insights on the materials design and cell engineering for building competitive and high-energy density organic batteries [275].

Further, specific NSPILs were designed and evaluated as electrolytes for the all-organic proton battery. The NSPILs were based on either 1,2,4-triazole or 1-methyl-1,2,4-triazole partially protonated with bis(trifluoromethylsulfonyl)imide (TFSI) to produce a range of NSPILs with different degrees of protonation. Both types of NSPIL investigated leading to a maximum conductivity of 1.2 S.cm^{−1} at 120 °C, the eutectic composition of 1-methyl-1,2,4-triazolium TFSI also having a high conductivity of 24.9 mS.cm^{−1} at 25 °C, superior to, e.g., imidazolium TFSI NSPILs. Quinone functionalized PEDOT electrodes exhibited reversible, fast, and stable redox conversion in these electrolytes, and a model is suggested to determine proton activities of NSPILs based on the quinone formal potential. An all-organic proton battery cell was assembled to demonstrate the usefulness of these electrolytes in devices. Fast and complete redox conversion with a cell potential of 0.45 V was demonstrated, even up to scan rates corresponding to 140C. Compared to the pyridine based electrolytes used for the all-organic proton battery up until now, the present electrolytes display several advantages including lower melting temperature, lower toxicity, and compatibility with plastic materials [30].

A series of three compounds - namely, bis(cyclohexyl)pyromellitic diimide (PMDI-Ref), the cyclic dimeric pyromellitic diimide ((−)−2PMDI), and the cyclic trimeric pyromellitic diimide ((−)−3PMDI-Δ), were synthesized for battery electrodes. The battery electrode slurry was repaired by mortar and pestle, mixing each PMDI derivative with carbon black and PVDF binder in a weight ratio of 60:30:10 using in NMP as the solvent. It was demonstrated that controlling the relative conformational dispositions of redox-active units in macrocycles are key to achieving high energy density and long cycle-life electrodes for organic rechargeable batteries [215].

A total organic aqueous redox flow battery (OARFB) was reported, using low-cost and sustainable methyl viologen (MV, anolyte) and 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (4-HO-TEMPO, catholyte), and benign NaCl supporting electrolyte (Fig. 12d). The MV/4-HO-TEMPO aqueous redox flow battery (ARFB) has an exceptionally high cell voltage, 1.25 V. Prototypes of the organic ARFB can be operated at high current densities ranging from 20 to 100 mA cm² and deliver stable capacity for 100 cycles with nearly 100% Coulombic efficiency. The MV/4-HO-TEMPO ARFB displays attractive technical merits and thus represents a major advance in ARFBs [276].

Poly(naphthotriazolequinonestyrene) (pNTQS), the first redox-active polymer bearing naphthotriazoleiones, was developed and demonstrated its promising characteristics for an application in organic batteries. Coin cells comprising pNTQS as active electrode material revealed an excellent capacity of 135 mAh.g^{−1}, which exceeded most of the commonly applied polymer-based materials, while a capacity loss of only 30% over 1000 cycles was observed [221].

Dibenzothiophenesulfone has been also proposed as potential candidate as anode-active material with high-energy density. In addition, radical polymerization of vinyl dibenzothiophenesulfone yielded poly(vinyl dibenzothiophenesulfone) with a high molecular weight. A rechargeable device was fabricated with only organic compounds; poly(vinyl dibenzothiophenesulfone) as the anode, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-substituted poly(methacrylate) as the cathode, and tetraethylammonium salt and organic solvent as the electrolyte. This device yielded a maximum output voltage of 2.6 V in these organic devices, and the active component of the anode displayed a very high-energy density of >500 mWh.g^{−1} [277].

The effect of solvent nature on the electrochemical reversibility and capacity retention of polyanthraquinone sulfide (PAQS) was compared and contrasted. To prepare the electrodes, the appropriate quantity of PAQS was mixed with conductive carbon (C65) in a mortar and pestle. To this mixture a 5 wt.% solution of PVDF in NMP was added to obtain a final ratio of 4:5:1 (by weight) of PAQS:C65:PVDF. Overall, it has been

shown that although the problem of PAQS solubility is at the core of the capacity retention and must dictate the electrolyte solvent selection, it was equally important to consider the kinetic aspect and the reversibility of the redox reaction, which was also intricately linked to the solvent used in the electrolyte [224].

Expanded porphyrins, which are porphyrin analogues with more than five pyrrolic subunits, have attracted much attention because of their interesting optical, electrochemical, and coordination properties. In particular, hexaphyrin (1.1.1.1.1.1) exhibits multi-redox behavior in which two stable oxidation states, namely [26] hexaphyrin 1 and [28] hexaphyrin 2, were interconvertible through two electron oxidation and reduction. They isolated a delocalized π -radical on a doubly twisted hexaphyrin π system, which was stable towards air and moisture. The high stability can be accounted for by effective delocalization of the unpaired electron and steric and electronic effects of pentafluorophenyl substituents [278].

A nitroxide radical-substituted polyether, poly(TEMPO-substituted glycidyl ether) (PTGE), was synthesized using a potassium tert-butoxide/18-crown-6 initiator. The presence of 18-crown-6 lead to a significant improvement in the reactivity of the chain end, thus allowing the polymerization to proceed at moderate temperatures to suppress the deactivation of the pendant nitroxide group. Poly(TEMPO-substituted glycidyl ether) (PTGE) was synthesized using potassium tert-butoxide/18-crown-6 initiator in a high conversion (99%), suppressing the deactivation of the radical moieties, and it was demonstrated the PTGE/VGCF composite electrode as an excellent organic cathode material. The PTGE/VGCF composite electrodes demonstrated a fast (60 °C) charge/discharge capability with significant durability (> 1000 cycles) owing to the swellable and yet insoluble properties of PTGE [279].

The synthesis and the electrochemical characterization of a new redox-active monomer based on N,N-dicyanoanthraquinone diimine (DCAQI) has been presented. The monomers could be incorporated into a polymeric environment by free radical polymerization and Rh-catalyzed polymerization of the introduced vinyl and ethynyl substituted monomers, respectively [280].

Finally, a new class of stable and electrically conductive organic electrodes based on metal porphyrins with functional groups that were capable of electrochemical polymerization were presented, rendering the materials promising for electrochemical applications. Their structural flexibility and the unique highly conjugated macrocyclic structure allow the produced organic electrodes to act as both cathode and anode materials giving access to fast charging as well as high cycling stability. The extreme thermal and chemical stability of the porphyrin-based organic electrodes and their chemical versatility suggest an important role for these molecular systems in the further development of novel electrochemical energy storage applications [281].

5. Main conclusions and future trends

The main state of the art and current developments in the field of organic radical batteries (ORBs) has been presented. It is demonstrated that this energy storage system shows great potential for the next generation of sustainable energy storage, aimed to overcome the current more hazardous and environmental impactful lithium-ion batteries that dominate the market nowadays. The replacing of the metals used in the current technology, such as cobalt or nickel, with their extraction, processing and recycling drawbacks, with organic redox active materials is a promising strategy to be further explored. Most research is currently focus on materials for lithium-ion batteries, but there are also increasing approach towards beyond lithium alternatives, such as sulfur or even phosphor-based batteries. The most studied radical in ORBs is the p-type polymer TEMPO due to its outstanding characteristics. These studies are focused on the combination of this radical with several types of polymer backbones allowing an increase in performance and stability. In general, most of the developed materials present exceptional longevity in cycle life tests, being able to sustain a high number of cycles without losing

their capacity. Also, they seem to be advantageous regarding high discharge rates, with some materials delivering interesting capacities at rates up to 100C. These properties add up to the previously mentioned sustainability and recyclability ones. Several ORBs work use p- and n-type organic polymers and more recently b-type (both n- and p-type) to improve their stability. The combination of ORBs is also very extended once each one of the different connected molecules can provide different properties. The use of artificial intelligence and machine learning tools should be further addressed in order to accelerate the discovery of high-performance ORBs by theoretical chemistry studies and predict the properties of materials. In this way, new solutions to research flow, prediction, synthesis and analysis will be created. Furthermore, the necessity to test each combination in the laboratory will be reduced allowing a fast increase in ORBs performance and reducing the number of options providing fundamental insights. Some limitations that shall be overcome include the low discharge capacities of the organic batteries when compared to the reference values, as well as the low voltage outputs obtained, which limits the organic batteries utilization to low voltage operation systems. Thus, future efforts must be placed on the development of conformations that allow to increase the overall capacity of ORBs, improved lifecycles and allow higher discharge rates, in order to expand the applicability of these batteries. Furthermore, more work must be developed to further improve the sustainability of these batteries by studying architectures with more environmentally friendly materials. However, these systems can still be effectively used in applications that do not require high outputs such as low power wearable devices, and the advances in the field are promising to improve the performance of organic batteries in the medium term, making them excellent candidates for wide implementation as sustainable energy storage devices.

CRedit authorship contribution statement

J.C. Barbosa: Writing – original draft, Writing – review & editing. **A. Fidalgo-Marijuan:** Writing – original draft, Writing – review & editing. **J.C. Dias:** Writing – original draft, Writing – review & editing. **R. Gonçalves:** Writing – original draft, Writing – review & editing. **M. Salado:** Writing – original draft, Writing – review & editing. **C.M. Costa:** Writing – original draft, Writing – review & editing, Funding acquisition. **S. Lanceros-Méndez:** Writing – original draft, Writing – review & editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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References

- [1] M. Slattery, J. Dunn, A. Kendall, Transportation of electric vehicle lithium-ion batteries at end-of-life: a literature review, *Resour. Conserv. Recycl.* 174 (2021), 105755.
- [2] M. Salado, E. Lizundia, I. Oyarzabal, D. Salazar, The Role of Critical Raw Materials for Novel Strategies in Sustainable Secondary Batteries, *Phys. Status. Solidi* 219 (2022), 2100710.
- [3] R.S. Pinto, R. Gonçalves, S. Lanceros-Méndez, C.M. Costa, Three-Dimensional Printing for Solid-State Batteries, in: *Solid State Batteries, 2, Materials and Advanced Devices*: American Chemical Society, 2022, pp. 331–350.
- [4] V.V. Kondratiev, R. Holze, Intrinsically conducting polymers and their combinations with redox-active molecules for rechargeable battery electrodes: an update, *Chem. Pap.* 75 (2021) 4981–5007.
- [5] S. Dworakowska, F. Lorandi, A. Gorkczyński, K. Matyjaszewski, Toward Green Atom Transfer Radical Polymerization: current Status and Future Challenges, *Advanced. Science* 9 (2022), 2106076.
- [6] L. Wylie, K. Oyaizu, A. Karton, M. Yoshizawa-Fujita, E.I. Izgorodina, Toward Improved Performance of All-Organic Nitroxide Radical Batteries with Ionic Liquids: a Theoretical Perspective, *ACS. Sustain. Chem. Eng.* 7 (2019) 5367–5375.
- [7] Friebe C., Schubert U.S. High-Power-Density Organic Radical Batteries. In: Eichel R-A, editor. *Electrochemical Energy Storage: Next Generation Battery Concepts*. Cham: Springer International Publishing; 2019. p. 65–99.
- [8] P. Rohland, E. Schröter, O. Nolte, G.R. Newkome, M.D. Hager, U.S. Schubert, Redox-active polymers: the magic key towards energy storage – a polymer design guideline progress in polymer science, *Prog. Polym. Sci.* 125 (2022), 101474.
- [9] Y. Zhang, A.M. Park, S.R. McMillan, N.J. Harmon, M.E. Flatté, G.D. Fuchs, et al., Charge Transport in Conjugated Polymers with Pendent Stable Radical Groups, *Chem. Mater.* 30 (2018) 4799–4807.
- [10] N. Casado, G. Hernández, A. Veloso, S. Devaraj, D. Mecerreyes, M. Armand, PEDOT Radical Polymer with Synergetic Redox and Electrical Properties, *ACS. Macro. Lett.* 5 (2016) 59–64.
- [11] Y. Wang, W. Zhang, J. Yang, Y. Gong, J. Zhang, M. Fang, et al., The key role of molecular aggregation in rechargeable organic cathodes, *Matter* (2022).
- [12] Y. An, X. Han, Y. Liu, A. Azhar, J. Na, A.K. Nanjundan, et al., Progress in Solid Polymer Electrolytes for Lithium-Ion Batteries and Beyond, *Small* 18 (2022), 2103617.
- [13] K.A. Hansen, J. Nerker, K. Thomas, S.E. Bottle, A.P. O'Mullane, P.C. Talbot, et al., New Spin on Organic Radical Batteries—An Isoindoline Nitroxide-Based High-Voltage Cathode Material, *ACS. Appl. Mater. Interfaces* 10 (2018) 7982–7988.
- [14] T. Suga, H. Ohshiro, S. Sugita, K. Oyaizu, H. Nishide, Emerging N-Type Redox-Active Radical Polymer for a Totally Organic Polymer-Based Rechargeable Battery, *Adv. Mater.* 21 (2009) 1627–1630.
- [15] H. Nishide, K. Oyaizu, Toward Flexible Batteries, *Science* 319 (2008) 737–738.
- [16] X. Dong, H. Yu, Y. Ma, J.L. Bao, D.G. Truhlar, Y. Wang, et al., All-Organic Rechargeable Battery with Reversibility Supported by “Water-in-Salt” Electrolyte, *Chemistry* 23 (2017) 2560–2565.
- [17] P. Hu, H. Wang, Y. Yang, J. Yang, J. Lin, L. Guo, Renewable-Biomolecule-Based Full Lithium-Ion Batteries, *Adv. Mater.* 28 (2016) 3486–3492.
- [18] C. Wang, W. Tang, Z. Yao, Y. Chen, J. Pei, C. Fan, Using an organic acid as a universal anode for highly efficient Li-ion, Na-ion and K-ion batteries, *Org. Electron* 62 (2018) 536–541.
- [19] N. Patil, A. Mavrandakis, C. Jérôme, C. Detrembleur, N. Casado, D. Mecerreyes, et al., High-performance all-organic aqueous batteries based on a poly(imide) anode and poly(catechol) cathode, *J. Mater. Chem. A* 9 (2021) 505–514.
- [20] D. Casado, D. Mantione, D. Shanmukaraj, D. Mecerreyes, Symmetric All-Organic Battery Containing a Dual Redox-Active Polymer as Cathode and Anode Material, *ChemSusChem* 13 (9) (2020) 2464–2470.
- [21] S. Jiang, W. Li, Y. Xie, X. Yan, K. Zhang, Z. Jia, An All-Organic battery with 2.8V output voltage, *Chem. Eng. J.* 434 (2022), 134651.
- [22] T.P. Nguyen, A.D. Easley, N. Kang, S. Khan, S.M. Lim, Y.H. Rezenom, et al., Polypeptide organic radical batteries, *Nature* 593 (2021) 61–66.
- [23] H. Hatcher, Game changer for batteries, *Nat. Rev. Chem.* 6 (2022) 597.
- [24] C.H. Li, D.P. Tabor, Discovery of lead-low-potential radical candidates for organic radical polymer batteries with machine-learning-assisted virtual screening, *J. Mater. Chem. A* 10 (2022) 8273–8282.
- [25] S. Xu, J. Liang, Y. Yu, R. Liu, Y. Xu, X. Zhu, et al., Machine learning-assisted discovery of high-voltage organic materials for rechargeable batteries, *J. Phys. Chem. C* 125 (2021) 21352–21358.
- [26] Zens C., Friebe C., Schubert U., Richter M., Kupfer S. Tailored charge transfer kinetics in organic radical batteries - a joint synthetic-theoretical approach. 2022.
- [27] C. Friebe, U.S. Schubert, High-power-density organic radical batteries, *Top. Curr. Chem* 375 (2017) 19.
- [28] Z. Chen, N. Xu, W. Li, R. Zhao, Y. Dong, J. Liu, et al., Effect of trace hydrofluoric acid in a LiPF₆ electrolyte on the performance of a Li-organic battery with an N-heterocycle based conjugated microporous polymer as the cathode, *J. Mater. Chem. A* 7 (2019) 16347–16355.
- [29] C.M. Costa, Y.H. Lee, J.H. Kim, S.Y. Lee, S. Lanceros-Méndez, Recent advances on separator membranes for lithium-ion battery applications: from porous membranes to solid electrolytes, *Energy Storage Mater* 22 (2019) 346–375.
- [30] C. Karlsson, C. Strietzel, H. Huang, M. Sjödén, P. Jannasch, Nonstoichiometric Triazolium Protic ionic liquids for all-organic batteries, *ACS. Appl. Energy. Mater.* 1 (2018) 6451–6462.
- [31] H. Niu, L. Wang, P. Guan, N. Zhang, C. Yan, M. Ding, et al., Recent advances in application of ionic liquids in electrolyte of lithium ion batteries, *J. Energy. Storage* 40 (2021), 102659.
- [32] J. Heiska, M. Nisula, M. Karppinen, Organic electrode materials with solid-state battery technology, *J. Mater. Chem. A* 7 (2019) 18735–18758.
- [33] J.C. Barbosa, R. Gonçalves, C.M. Costa, Zea de, V. Bermudez, A. Fidalgo-Marijuan, Q. Zhang, et al., Metal-organic frameworks and zeolite materials as active fillers for lithium-ion battery solid polymer electrolytes, *Mater. Advan* 2 (2021) 3790–3805.
- [34] A.D. Jenkins, P. Kratochvil, R.F.T. Stepto, U.W. Suter, Glossary of basic terms in polymer science (the 1996 IUPAC Recommendations), *Polimery* 68 (1996) 2287–2311.
- [35] H. Nishide, K. Oyaizu, Materials science - toward flexible batteries, *Science* 319 (2008) 737–738.
- [36] C. Friebe, A. Lex-Balducci, U.S. Schubert, Sustainable energy storage: recent trends and developments toward fully organic batteries, *ChemSusChem* 12 (2019) 4093–4115.
- [37] S.Y. Wang, F. Li, A.D. Easley, J.L. Lutkenhaus, Real-time insight into the doping mechanism of redox-active organic radical polymers, *Nat. Mater* 18 (2019) 69–75.
- [38] K. Oyaizu, T. Kawamoto, T. Suga, H. Nishide, Synthesis and charge transport properties of redox-active nitroxide polyethers with large site density, *Macromolecules* 43 (2010) 10382–10389.
- [39] P. Nesvadba, L. Bugnon, P. Maire, P. Novak, Synthesis of A novel spirobisnitroxide polymer and its evaluation in an organic radical battery, *Chem. Mater.* 22 (2010) 783–788.
- [40] Z.C. Zhu, G.R. Shan, P.J. Pan, Nitroxide-mediated polymerization of methyl methacrylate by 4,4'-dimethoxydiphenyl-based alkoxyamine, *RSC. Adv* 6 (2016) 73842–73847.
- [41] T. Koizumi, H. Ohfuji, S. Tanaka, S. Shigematsu, N. Akutagawa, M. Satoh, et al., Charge-discharge behavior of secondary organic radical battery using 2-Aryl nitronyl nitroxides as the cathode active material, *Chem. Lett* 43 (2014) 1092–1094.
- [42] T. Jahnert, M.D. Hager, U.S. Schubert, Application of phenolic radicals for antioxidants, as active materials in batteries, magnetic materials and ligands for metal-complexes, *J. Mater. Chem. A* 2 (2014) 15234–15251.
- [43] K.A. Hansen, L.C. Chambers, M. Eing, C. Barner-Kowollik, K.E. Fairfull-Smith, J. P. Blinco, A methoxyamine-protecting group for organic radical battery materials—an alternative approach, *ChemSusChem* (2020).
- [44] A. Gopinath, A.S. Nasar, Electroactive six arm star poly(2,2,6,6-tetramethylpiperidinyloxy methacrylate): synthesis and application as cathode material for rechargeable Li-ion batteries, *Polymer. (Guildf)* 178 (2019), 121601.
- [45] A.A. Vereshchagin, P.S. Vlasov, A.S. Konev, P.X. Yang, G.A. Grechishnikova, O. V. Levin, Novel highly conductive cathode material based on stable-radical organic framework and polymerized nickel complex for electrochemical energy storage devices, *Electrochim. Acta* 295 (2019) 1075–1084.
- [46] S. Iwasa, T. Nishi, S. Nakamura, Enhancement of rapid charging capability of organic radical battery using ethylene carbonate-based electrolyte containing LiFSI, *J. Power. Sources* 402 (2018) 157–162.
- [47] H.J. Martin, B.K. Hughes, W.A. Braunecker, T. Gennett, M.D. Dadmun, The impact of radical loading and oxidation on the conformation of organic radical polymers by small angle neutron scattering, *J. Mater. Chem. A* 6 (2018) 15659–15667.
- [48] H. Tokue, T. Murata, H. Agatsuma, H. Nishide, K. Oyaizu, Charge Discharge with Rocking-Chair-Type Li⁺ Migration Characteristics in a Zwitterionic Radical Copolymer Composed of TEMPO and Trifluoromethanesulfonylimide with Carbonate Electrolytes for a High-Rate Li-Ion Battery, *Macromolecules* 50 (2017) 1950–1958.
- [49] F. Lederle, E.G. Hubner, Radical polymerization of styrene in presence of poly(2,2,6,6-tetramethylpiperidine-N-oxyl-4-yl methacrylate) - formation of polymer brushes, *Polymer. (Guildf)* 111 (2017) 258–264.
- [50] O. Bertrand, B. Ernould, F. Boujioui, A. Vlad, J.F. Gohy, Synthesis of polymer precursors of electroactive materials by SET-LRP, *Polym. Chem* 6 (2015) 6067–6072.
- [51] A. Vlad, J. Rolland, G. Hauffman, B. Ernould, J.F. Gohy, Melt-Polymerization of TEMPO methacrylates with nano carbons enables superior battery materials, *ChemSusChem* 8 (2015) 1692–1696.
- [52] S. Komaba, T. Tanaka, T. Ozeki, T. Taki, H. Watanabe, H. Tachikawa, Fast redox of composite electrode of nitroxide radical polymer and carbon with polyacrylate binder, *J. Power. Sources* 195 (2010) 6212–6217.
- [53] L. Bugnon, C.J.H. Morton, P. Novak, J. Vetter, P. Nesvadba, Synthesis of poly(4-methacryloyloxy-TEMPO) via group-transfer polymerization and its evaluation in organic radical battery, *Chem. Mater.* 19 (2007) 2910–2914.
- [54] H. Nishide, S. Iwasa, Y.J. Pu, T. Suga, K. Nakahara, M. Satoh, Organic radical battery: nitroxide polymers as a cathode-active material, *Electrochim. Acta* 50 (2004) 827–831.

- [55] K. Nakahara, S. Iwasa, M. Satoh, Y. Morioka, J. Iriyama, M. Suguro, et al., Rechargeable batteries with organic radical cathodes, *Chem. Phys. Lett* 359 (2002) 351–354.
- [56] K. Nakahara, J. Iriyama, S. Iwasa, M. Suguro, M. Satoh, E.J. Cairns, Cell properties for modified PTMA cathodes of organic radical batteries, *J. Power. Sources* 165 (2007) 398–402.
- [57] K. Nakahara, J. Iriyama, S. Iwasa, M. Suguro, M. Satoh, E.J. Cairns, Al-laminated film packaged organic radical battery for high-power applications, *J. Power. Sources* 163 (2007) 1110–1113.
- [58] K. Nakahara, J. Iriyama, S. Iwasa, M. Suguro, M. Satoh, E.J. Cairns, High-rate capable organic radical cathodes for lithium rechargeable batteries, *J. Power. Sources* 165 (2007) 870–873.
- [59] J.K. Kim, G. Cheruvally, J.W. Choi, J.H. Ahn, D.S. Choi, C.E. Song, Rechargeable organic radical battery with electrospun, fibrous membrane-based polymer electrolyte, *J. Electrochem. Soc* 154 (2007) A839–A843.
- [60] L.F. Deng, H.X. Li, L.X. Xiao, Y.H. Zhang, Synthesis and electrochemical properties of polyradical cathode material for lithium second batteries, *J. Cent. South. Univ. Technol* 10 (2003) 190–194.
- [61] J.K. Kim, G. Cheruvally, J.W. Choi, J.H. Ahn, S.H. Lee, D.S. Choi, et al., Effect of radical polymer cathode thickness on the electrochemical performance of organic radical battery, *Solid. State. Ion* 178 (2007) 1546–1551.
- [62] J.K. Kim, G. Cheruvally, J.H. Ahn, Y.G. Seo, D.S. Choi, S.H. Lee, et al., Organic radical battery with PTMA cathode: effect of PTMA content on electrochemical properties, *J. Ind. Eng. Chem* 14 (2008) 371–376.
- [63] J.K. Kim, J.H. Ahn, G. Cheruvally, G.S. Chauhan, J.W. Choi, D.S. Kim, et al., Electrochemical properties of rechargeable organic radical battery with PTMA cathode, *Met. Mater-Int* 15 (2009) 77–82.
- [64] C.M. Liu, J. Chen, F.Q. Wang, B.L. Yi, Improvement of electrochemical properties of PTMA cathode by using carbon blacks with high specific surface area, *Russ. J. Electrochem.* 48 (2012) 1052–1057.
- [65] Q. Chen, Y.N. Nuli, W. Guo, J. Yang, J.L. Wang, Y.G. Guo, PTMA/Graphene as a novel cathode material for rechargeable magnesium batteries, *Acta. Phys-Chim. Sin* 29 (2013) 2295–2299.
- [66] J.K. Kim, J. Scheers, J.H. Ahn, P. Johansson, A. Matic, P. Jacobsson, Nano-fibrous polymer films for organic rechargeable batteries, *J. Mater. Chem. A* 1 (2013) 2426–2430.
- [67] W. Guo, Y.X. Yin, S. Xin, Y.G. Guo, L.J. Wan, Superior radical polymer cathode material with a two-electron process redox reaction promoted by graphene, *Energy. Environ. Sci* 5 (2012) 5221–5225.
- [68] Y. Kim, C. Jo, J. Lee, C.W. Lee, S. Yoon, An ordered nanocomposite of organic radical polymer and mesocellular carbon foam as cathode material in lithium ion batteries, *J. Mater. Chem* 22 (2012) 1453–1458.
- [69] H.C. Lin, C.C. Li, J.T. Lee, Nitroxide polymer brushes grafted onto silica nanoparticles as cathodes for organic radical batteries, *J. Power. Sources* 196 (2011) 8098–8103.
- [70] C.H. Lin, W.J. Chou, J.T. Lee, Three-dimensionally ordered macroporous nitroxide polymer brush electrodes prepared by surface-initiated atom transfer polymerization for organic radical batteries, *Macromol. Rapid. Commun* 33 (2012) 107–113.
- [71] M.K. Hung, Y.H. Wang, C.H. Lin, H.C. Lin, J.T. Lee, Synthesis and electrochemical behaviour of nitroxide polymer brush thin-film electrodes for organic radical batteries, *J. Mater. Chem* 22 (2012) 1570–1577.
- [72] Y.H. Wang, M.K. Hung, C.H. Lin, H.C. Lin, J.T. Lee, Patterned nitroxide polymer brushes for thin-film cathodes in organic radical batteries, *Chem* 47 (2011) 1249–1251.
- [73] H.A. Lopez-Pena, L.S. Hernandez-Munoz, J. Cardoso, F.J. Gonzalez, I. Gonzalez, C. Frontana, Electrochemical and spectroelectrochemical properties of nitroxyl radical species in PTMA, an organic radical polymer. Influence of the microstructure, *Electrochem. commun* 11 (2009) 1369–1372.
- [74] Y.R. Zhang, A. Park, A. Cintora, S.R. McMillan, N.J. Harmon, A. Moehle, et al., Impact of the synthesis method on the solid-state charge transport of radical polymers, *J. Mater. Chem* 6 (2018) 111–118.
- [75] L.C. Cao, S. Sadaf, S.M. Beladi-Mousavi, L. Walder, PolyTEMPO and polyviologen on carbon nanotubes: syntheses, structures and organic battery applications, *Eur. Polym. J* 49 (2013) 1923–1934.
- [76] B. Bilgic, C. Kilic, B. Esat, First-principles study of polyacetylene derivatives bearing nitroxide radicals, *Phys. Rev. B* 84 (2011), 115207.
- [77] T. Katsumata, M. Satoh, J. Wada, M. Shiotsuki, F. Sanda, T. Masuda, Polyacetylene and polynorbornene derivatives carrying TEMPO. Synthesis and properties as organic radical battery materials, *Macromol. Rapid. Commun* 27 (2006) 1206–1211.
- [78] J.Q. Qu, T. Fujii, T. Katsumata, Y. Suzuki, M. Shiotsuki, F. Sanda, et al., Helical polyacetylenes carrying 2,2,6,6-tetramethyl-1-piperidinyloxy and 2,2,5,5-tetramethyl-1-pyrrolidinyloxy moieties: their synthesis, properties, and function, *J. Polym. Sci. Pol. Chem* 45 (2007) 5431–5445.
- [79] J. Qu, T. Katsumata, M. Satoh, J. Wada, J. Igarashi, K. Mizoguchi, et al., Synthesis and charge/discharge properties of polyacetylenes carrying 2,2,6,6-tetramethyl-1-piperidinyloxy radicals, *Chemistry* 13 (2007) 7965–7973.
- [80] C. Carlsson, T. Suga, H. Nishide, Quantifying TEMPO redox polymer charge transport toward the organic radical battery, *ACS. Appl. Mater. Interfaces* 9 (2017) 10692–10698.
- [81] T. Suga, H. Konishi, H. Nishide, Photocrosslinked nitroxide polymer cathode-active materials for application in an organic-based paper battery, *Chem* (2007) 1730–1732.
- [82] T. Katsumata, J.Q. Qu, M. Shiotsuki, M. Satoh, J. Wada, J. Igarashi, et al., Synthesis, characterization, and charge/discharge properties of polynorbornenes carrying 2,2,6,6-tetramethylpiperidine-1-oxyl radicals at high density, *Macromolecules* 41 (2008) 1175–1183.
- [83] K. Oyaizu, Y. Ando, H. Konishi, H. Nishide, Nernstian adsorbate-like bulk layer of organic radical polymers for high-density charge storage purposes, *J. Am. Chem. Soc* 130 (2008) 14459–14461.
- [84] Y. Dai, Y.X. Zhang, L. Gao, G.F. Xu, J.Y. Xie, Electrochemical performance of organic radical cathode with ionic liquid based electrolyte, *J. Electrochem. Soc* 158 (2011) A291–A5.
- [85] M. Suguro, S. Iwasa, Y. Kusachi, Y. Morioka, K. Nakahara, Cationic polymerization of poly(vinyl ether) bearing a TEMPO radical: a new cathode-active material for organic radical batteries, *Macromol. Rapid. Commun* 28 (2007) 1929–1933.
- [86] M. Suguro, S. Iwasa, K. Nakahara, Fabrication of a practical and polymer-rich organic radical polymer electrode and its rate dependence, *Macromol. Rapid. Commun* 29 (2008) 1635–1639.
- [87] K. Koshika, N. Sano, K. Oyaizu, H. Nishide, An ultrafast chargeable polymer electrode based on the combination of nitroxide radical and aqueous electrolyte, *Chem* (2009) 836–838.
- [88] K. Koshika, N. Sano, K. Oyaizu, H. Nishide, An aqueous, electrolyte-type, rechargeable device utilizing a hydrophilic radical polymer-cathode, *Macromol. Chem. Phys* 210 (2009) 1989–1995.
- [89] T. Suga, K. Yoshimura, H. Nishide, Nitroxide-substituted polyether as a new material for batteries, *Macromol. Symp* 245 (2006) 416–422.
- [90] K. Oyaizu, T. Suga, K. Yoshimura, H. Nishide, Synthesis and characterization of radical-bearing polyethers as an electrode-active material for organic secondary batteries, *Macromolecules* 41 (2008) 6646–6652.
- [91] K. Sato, T. Sukegawa, K. Oyaizu, H. Nishide, Synthesis of Poly(TEMPO-Substituted Glycidyl Ether) by Utilizing t-BuOK/18-Crown-6 for an Organic Cathode-Active Material, *Macromol. Symp* 351 (2015) 90–96.
- [92] J.Q. Qu, T. Katsumata, M. Satoh, J. Wada, T. Masuda, Poly(7-oxanorbornenes) carrying 2,2,6,6-tetramethylpiperidine-1-oxyl radicals: synthesis and charge/discharge properties, *Polymer. (Guildf)* 50 (2009) 391–396.
- [93] M. Suguro, A. Mori, S. Iwasa, K. Nakahara, K. Nakano, Syntheses and electrochemical properties of TEMPO radical substituted silicones: active material for organic radical batteries, *Macromol. Chem. Phys* 210 (2009) 1402–1407.
- [94] Y.G. Chen, Y.F. Zhang, X. Liu, X.L. Fan, B. Bai, K. Yang, et al., Long-life and high-power binder-free cathode based on one-step synthesis of radical polymers with multi-pendant groups, *Macromol. Rapid. Commun* 39 (2018), 1800195.
- [95] X.H. Zhang, H.Q. Li, L.T. Li, G.L. Lu, S. Zhang, L.N. Go, et al., Polyallene with pendant nitroxyl radicals, *Polymer. (Guildf)* 49 (2008) 3393–3398.
- [96] T. Ibe, R.B. Frings, A. Lachowicz, S. Kyo, H. Nishide, Nitroxide polymer networks formed by Michael addition: on site-cured electrode-active organic coating, *Chem* 46 (2010) 3475–3477.
- [97] J.F. Zhu, T. Zhu, H. Tuo, W.B. Zhang, Synthesis of a TEMPO-substituted polyacrylamide bearing a sulfonate sodium pendant and its properties in an organic radical battery, *Polymers. (Basel)* 11 (2019) 2076.
- [98] K. Koshika, N. Chikushi, N. Sano, K. Oyaizu, H. Nishide, A TEMPO-substituted polyacrylamide as a new cathode material: an organic rechargeable device composed of polymer electrodes and aqueous electrolyte, *Green. Chem* 12 (2010) 1573–1575.
- [99] M. Aydin, B. Esat, A polythiophene derivative bearing two electroactive groups per monomer as a cathode material for rechargeable batteries, *J. Solid. State. Electrochem* 19 (2015) 2275–2281.
- [100] M. Aydin, B. Esat, C. Kilic, M.E. Kose, A. Ata, F. Yilmaz, A polythiophene derivative bearing TEMPO as a cathode material for rechargeable batteries, *Eur. Polym. J* 47 (2011) 2283–2294.
- [101] T.K. Kunz, M.O. Wolf, Electrodeposition and properties of TEMPO functionalized polythiophene thin films, *Polym. Chem* 2 (2011) 640–644.
- [102] T. Sukegawa, K. Sato, K. Oyaizu, H. Nishide, Efficient charge transport of a radical polyether/SWCNT composite electrode for an organic radical battery with high charge-storage density, *RSC. Adv* 5 (2015) 15448–15452.
- [103] L.H. Xu, F. Yang, C. Su, L.L. Ji, C. Zhang, Synthesis and properties of novel TEMPO-contained polypyrrole derivatives as the cathode material of organic radical battery, *Electrochim. Acta* 130 (2014) 148–155.
- [104] W. Guo, Y.X. Yin, H.J. Yan, Y.G. Guo, Synthesis and electrochemical properties of poly-[2,5-di-N-(2,2,6,6-tetramethyl-4-piperidine-n-oxyl) benzamide] aniline as a cathode material for lithium-ion batteries, *J. Mol. Eng. Mater.* 1 (2013), 1340019.
- [105] J.Q. Qu, F.Z. Khan, M. Satoh, J. Wada, H.Y. Hayashi, K.J. Mizoguchi, et al., Synthesis and charge/discharge properties of cellulose derivatives carrying free radicals, *Polymer. (Guildf)* 49 (2008) 1490–1496.
- [106] J.Q. Qu, R. Morita, M. Satoh, J. Wada, F. Terakura, K. Mizoguchi, et al., Synthesis and properties of DNA complexes containing 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) moieties as organic radical battery materials, *Chemistry* 14 (2008) 3250–3259.
- [107] Y. Maruyama, K. Nagamine, A. Nomura, S. Iwasa, S. Tokito, Electrochemical characterization of TEMPO radical in ionic liquids, *Electrochemistry* 88 (2020) 34–38.
- [108] M. Aqil, F. Ouhib, A. Aqil, A. El Idrissi, C. Detrembleur, C. Jerome, Polymer ionic liquid bearing radicals as an active material for organic batteries with ultrafast charge-discharge rate, *Eur. Polym. J* 106 (2018) 242–248.
- [109] K. Kim, J.K. Kim, Organic di-radical rechargeable battery with an ionic liquid-based gel polymer electrolyte, *Korean. J. Chem. Eng* 33 (2016) 858–861.
- [110] J.K. Kim, A. Matic, J.H. Ahn, P. Jacobsson, C.E. Song, Preparation and application of TEMPO-based di-radical organic electrode with ionic liquid-based polymer electrolyte, *RSC. Adv* 2 (2012) 10394–10399.

- [111] S.H. Lee, J.K. Kim, G. Cheruvally, J.W. Choi, J.H. Ahn, G.S. Chauhan, et al., Electrochemical properties of new organic radical materials for lithium secondary batteries, *J. Power. Sources* 184 (2008) 503–507.
- [112] B.L. Zhou, X. Hu, G. Zeng, S.W. Li, Z.H. Wen, L. Chen, Bottom-up construction of porous organic frameworks with built-in TEMPO as a Cathode for Lithium-Sulfur Batteries, *ChemSusChem* 10 (2017) 2955–2961.
- [113] Z.Z. Du, W. Ai, L.H. Xie, W. Huang, Organic radical functionalized graphene as a superior anode material for lithium-ion batteries, *J. Mater. Chem. A* 2 (2014) 9164–9168.
- [114] J.Q. Qu, T. Katsumata, M. Satoh, J. Wada, T. Masuda, Synthesis and properties of polyacetylene and polynorbornene derivatives carrying 2,2,5,5-tetramethyl-1-pyrrolidinyloxy moieties, *Macromolecules* 40 (2007) 3136–3144.
- [115] Z.C. Zhu, G.R. Shan, Kinetics of Methyl Methacrylate Polymerization Mediated by 4,4'-Dimethoxydiphenyl Nitroxide, *Gaofenzi. Xuebao* (2017) 930–936.
- [116] T. Suga, Y.J. Pu, S. Kasatori, H. Nishide, Cathode- and anode-active poly (nitroxylstyrene)s for rechargeable batteries: p- and n-type redox switching via substituent effects, *Macromolecules* 40 (2007) 3167–3173.
- [117] T. Suga, S. Sugita, H. Ohshiro, K. Oyaizu, H. Nishide, p- and n-type bipolar redox-active radical polymer: toward totally organic polymer-based rechargeable devices with variable configuration, *Adv. Mater* 23 (2011) 751–754.
- [118] T. Kaneko, H. Tatsumi, T. Aoki, E. Oikawa, H. Yoshiki, N. Yoshioka, et al., Polymerization of (p-vinylphenyl)hydrogalvinoxyl and formation of a stable polyradical derivative, *J. Polym. Sci. Pol. Chem* 37 (1999) 189–198.
- [119] T. Jahnert, B. Häupler, T. Janoschka, M.D. Hager, U.S. Schubert, Synthesis and charge-discharge studies of poly(ethynylphenyl)galvinoxyls and their use in organic radical batteries with Aqueous Electrolytes, *Macromol. Chem. Phys* 214 (2013) 2616–2623.
- [120] T. Janoschka, M.D. Hager, U.S. Schubert, Powering up the future: radical polymers for battery applications, *Adv. Mater.* 24 (2012) 6397–6409.
- [121] S. Yoshihara, H. Isozumi, M. Kasai, H. Yonehara, Y. Ando, K. Oyaizu, et al., Improving charge/discharge properties of radical polymer electrodes influenced strongly by current collector/carbon fiber interface, *J. Phys. Chem. B* 114 (2010) 8335–8340.
- [122] T.S. Kim, J.E. Lim, M.S. Oh, J.K. Kim, Carbon conductor- and binder-free organic electrode for flexible organic rechargeable batteries with high energy density, *J. Power. Sources* 361 (2017) 15–20.
- [123] K. Zhang, Y.X. Hu, L.Z. Wang, M.J. Monteiro, Z.F. Jia, Pyrene-functionalized PTMA by NRC for greater pi-pi stacking with rGO and enhanced electrochemical properties, *ACS. Appl. Mater. Interfaces* 9 (2017) 34900–34908.
- [124] J.K. Kim, Y. Kim, S. Park, H. Ko, Encapsulation of organic active materials in carbon nanotubes for application to high-electrochemical-performance sodium batteries, *Energy. Environ. Sci* 9 (2016) 1264–1269.
- [125] B. Ernoult, O. Bertrand, A. Minoia, R. Lazzaroni, A. Vlad, J.F. Gohy, Electroactive polymer/carbon nanotube hybrid materials for energy storage synthesized via a "grafting to" approach, *RSC. Adv* 7 (2017) 17301–17310.
- [126] VLAD AELAA, Organic batteries - the route towards sustainable electrical energy storage technologies. *Chimie nouvelle LA REVUE DE CONTACT DE LA SOCIÉTÉ ROYALE DE CHIMIE_CN* 127. 2018.
- [127] A. Mauger, C. Julien, A. Paoletta, M. Armand, K. Zaghib, Recent progress on organic electrodes materials for rechargeable batteries and supercapacitors, *Materials* 12 (2019) 1770.
- [128] B. Häupler, A. Wild, U.S. Schubert, Carbonyls: powerful organic materials for secondary batteries, *Adv. Energy. Mater* 5 (2015), 1402034.
- [129] K. Amin, L. Mao, Z. Wei, Recent progress in polymeric carbonyl-based electrode materials for Lithium and Sodium ion batteries, *Macromol. Rapid. Commun* 40 (2019), 1800565.
- [130] K.C. Kim, Design strategies for promising organic positive electrodes in Lithium-Ion batteries: quinones and carbon materials, *Ind. Eng. Chem. Res* 56 (2017) 12009–12023.
- [131] H. Oubaha, J.F. Gohy, S. Melinte, Carbonyl-based π -Conjugated Materials: from synthesis to applications in Lithium-Ion batteries, *Chempluschem* 84 (2019) 1179–1214.
- [132] A. Wang, H. Xu, F. Liu, X. Liu, S. Wang, Q. Zhou, et al., Polyimide-based self-standing polymer electrolyte membrane for Lithium-Ion Batteries, *Energy. Technology* 6 (2018) 326–332.
- [133] Q. Zhao, C. Guo, Y. Lu, L. Liu, J. Liang, J. Chen, Rechargeable lithium batteries with electrodes of small organic carbonyl salts and advanced electrolytes, *Ind. Eng. Chem. Res* 55 (2016) 5795–5804.
- [134] Q. Zhao, Y. Lu, J. Chen, Advanced organic electrode materials for rechargeable sodium-ion batteries, *Adv. Energy. Mater* 7 (2017), 1601792.
- [135] S. Lee, G. Kwon, K. Ku, K. Yoon, S.K. Jung, H.D. Lim, et al., Recent progress in organic electrodes for Li and Na rechargeable batteries, *Adv. Mater* 30 (2018), 1704682.
- [136] Y. Liang, Z. Tao, J. Chen, Organic electrode materials for rechargeable Lithium batteries, *Adv. Energy. Mater* 2 (2012) 742–769.
- [137] J. Luo, B. Hu, M. Hu, Y. Zhao, T.L. Liu, Status and prospects of organic redox flow batteries toward sustainable energy storage, *ACS. Energy. Lett* 4 (2019) 2220–2240.
- [138] K.N. Oyaizu, Hiroyuki Mesoscale, Radical polymers: bottom-up fabrication of electrodes in organic polymer batteries, *Advan. Nanomater* (2010) 319–332.
- [139] S. Muench, A. Wild, C. Friebe, B. Häupler, T. Janoschka, U.S. Schubert, Polymer-based organic batteries, *Chem. Rev.* 116 (2016) 9438–9484.
- [140] J. Winsberg, T. Hagemann, T. Janoschka, M.D. Hager, U.S. Schubert, Redox-flow batteries: from metals to organic redox-active materials, *Angew. Chem. Int. Ed.* 56 (2017) 686–711.
- [141] J. Xie, P. Gu, Q. Zhang, Nanostructured conjugated polymers: toward high-performance organic electrodes for rechargeable batteries, *ACS. Energy. Lett* 2 (2017) 1985–1996.
- [142] J. Xie, Q. Zhang, Recent progress in multivalent Metal (Mg, Zn, Ca, and Al) and metal-ion rechargeable batteries with organic materials as promising electrodes, *Small* 15 (2019), 1805061.
- [143] Y. Xu, M. Zhou, Y. Lei, Organic materials for rechargeable sodium-ion batteries, *Mater. Today* 21 (2018) 60–78.
- [144] X. Cao, J. Liu, L. Zhu, L. Xie, Polymer electrode materials for high-performance Lithium/Sodium-ion batteries: a Review, *Energy Technol.* 7 (2019), 1800759.
- [145] T.N. Suga, Hiroyuki Rechargeable Batteries Using Robust but Redox Active Organic Radicals, *Stable. Radicals* (2010) 507–519.
- [146] P. Acker, L. Rzesny, C.F.N. Marchiori, C.M. Araujo, Esser B. π -Conjugation Enables Ultra-High Rate Capabilities and Cycling Stabilities in Phenothiazine Copolymers as Cathode-Active Battery Materials, *Adv. Funct. Mater* 29 (2019), 1906436.
- [147] Paulo H.S. Picciani ESM, William J. Orts and Luiz H.C. Mattoso Advances in Electroactive Electrospun Nanofibers. In: Tong Lin, editor. *Nanofibers - Production, Properties and Functional Applications*: Intechweb; 2011. p. 85–116.
- [148] Asaka K. Soft Actuators. *Stretchable Electronics*: Wiley-VCH Verlag GmbH & Co. KGaA; 2012. p. 305–24.
- [149] H. Peng, L. Zhang, C. Soeller, Travas-Sejdic J. Conducting polymers for electrochemical DNA sensing, *Biomaterials* 30 (2009) 2132–2148.
- [150] Asaka K. Actuators. *Electrochemical Aspects of Ionic Liquids*: John Wiley & Sons, Inc.; 2011. p. 271–8.
- [151] N.K. Guimard, N. Gomez, C.E. Schmidt, Conducting polymers in biomedical engineering, *Prog. Polym. Sci* 32 (2007) 876–921.
- [152] L.X. Wang, X.G. Li, Y.L. Yang, Preparation, properties and applications of polypyrroles, *React. Funct. Polym* 47 (2001) 125–139.
- [153] H. Wang, L. Bian, P. Zhou, J. Tang, W. Tang, Core-sheath structured bacterial cellulose/polypyrrole nanocomposites with excellent conductivity as supercapacitors, *J. Mater. Chem. A* 1 (2013) 578–584.
- [154] H.S. Abdulla, A.I. Abbo, Optical and electrical properties of thin films of polyaniline and polypyrrole, *Int. J. Electrochem. Sci* 7 (2012) 10666–10678.
- [155] D.O. Carlsson, M. Sjödin, L. Nyholm, M. Stromme, A comparative study of the effects of rinsing and aging of polypyrrole/nanocellulose composites on their electrochemical properties, *J. Phys. Chem. B* 117 (2013) 3900–3910.
- [156] Y. Fang, Y. Ni, G. Zhang, C. Mao, X. Huang, J. Shen, Biocompatibility of CS-PPy nanocomposites and their application to glucose biosensor, *Bioelectrochemistry* 88 (2012) 1–7.
- [157] N. Fekri, J.D.W. Madden, N.Y.J. Lee, F. Ko, C.A. Michal, Influence of porosity on charging speed of polypyrrole, *Synth. Met* 187 (2014) 145–151.
- [158] C. Keplinger, J.Y. Sun, C.C. Foo, P. Rothemund, G.M. Whitesides, Z. Suo, Stretchable, transparent, ionic conductors, *Science* 341 (2013) 984–987.
- [159] R. Kiefer, R. Temmer, N. Aydemir, J. Travas-Sejdic, A. Aabloo, T. Tamm, Electrochemistry of interlayer supported polypyrrole tri-layer linear actuators, *Electrochim. Acta* 122 (2014) 322–328.
- [160] A. Kumar, R.K. Singh, H.K. Singh, P. Srivastava, R. Singh, Enhanced capacitance and stability of p-toluenesulfonate doped polypyrrole/carbon composite for electrode application in electrochemical capacitors, *J. Power. Sources* 246 (2014) 800–807.
- [161] J.G. Martinez, T.F. Otero, Mechanical awareness from sensing artificial muscles: experiments and modeling, *Sens. Actuators. B* 195 (2014) 365–372.
- [162] T.F. Otero, M. Alfaro, V. Martinez, M.A. Perez, J.G. Martinez, Biomimetic structural electrochemistry from conducting polymers: processes, charges, and energies. coulometric results from films on metals revisited, *Adv. Funct. Mater* 23 (2013) 3929–3940.
- [163] T.F. Otero, J.G. Martinez, Artificial muscles: a tool to quantify exchanged solvent during biomimetic reactions, *Chem. Mater.* 24 (2012) 4093–4099.
- [164] T.F. Otero, J.G. Martinez, J. Arias-Pardilla, Biomimetic electrochemistry from conducting polymers. A review: artificial muscles, smart membranes, smart drug delivery and computer/neuron interfaces, *Electrochim. Acta* 84 (2012) 112–128.
- [165] T. Sandu, A. Sarbu, F. Constantin, C.I. Spataru, R.A. Gabor, R. Somoghi, et al., Characterization of functionalized polypyrrole, *Rev. Roum. Chim.* 57 (2012) 177–185.
- [166] V. Sencadas, D.M. Correia, A. Areias, G. Botelho, A.M. Fonseca, I.C. Neves, et al., Determination of the parameters affecting electrospun chitosan fiber size distribution and morphology, *Carbohydr. Polym* 87 (2012) 1295–1301.
- [167] T. Tian, J. Deng, Z. Xie, Y. Zhao, Z. Feng, X. Kang, et al., Polypyrrole hollow fiber for solid phase extraction, *Analyst* 137 (2012) 1846–1852.
- [168] Y. Xie, Y. Zhao, Electrochemical biosensing based on polypyrrole/titanium nanotube hybrid, *Mater. Sci. Eng. C* 33 (2013) 5028–5035.
- [169] X. Yuan, X.L. Ding, C.Y. Wang, Z.F. Ma, Use of polypyrrole in catalysts for low temperature fuel cells, *Energy Environ. Sci* 6 (2013) 1105–1124.
- [170] T.V. Vernitskaya, O.N. Efimov, Polypyrrole: a conducting polymer (synthesis, properties, and applications), *Usp. Khim* 66 (1997) 502–505.
- [171] K.T. Song, J.Y. Lee, H.D. Kim, D.Y. Kim, S.Y. Kim, C.Y. Kim, Solvent effects on the characteristics of soluble polypyrrole, *Synth. Met* 110 (2000) 57–63.
- [172] Saville PDR, Development Atlantic D. Polypyrrole, Formation and use. Ft. Belvoir: defense technical information center; 2005.
- [173] J. Rubio Retama, E. López Cabarcos, D. Mecerreyes, B. López-Ruiz, Design of an amperometric biosensor using polypyrrole-microgel composites containing glucose oxidase, *Biosens. Bioelectron.* 20 (2004) 1111–1117.
- [174] A.J.F. Romero, J.J.L. Cascales, T.F. Otero, Perchlorate interchange during the redox process of PPy/PVS films in an acetonitrile medium. A voltammetric and EDX study, *J. Phys. Chem. B* 109 (2005) 907–914.

- [175] Ramelow US, J.H. Ma, R. Darbeau, Electrical conductivities of polypyrrole reacted with dopant solutions, *Mater. Res. Innovations* 5 (2001) 40–49.
- [176] T.F. Otero, J. Padilla, Anodic shrinking and compaction of polypyrrole blend: electrochemical reduction under conformational relaxation kinetic control, *J. Electroanal. Chem.* 561 (2004) 167–171.
- [177] T.F. Otero, I. Cantero, H. Grande, Solvent effects on the charge storage ability in polypyrrole, *Electrochim. Acta* 44 (1999) 2053–2059.
- [178] M. Nikpour, H. Chaouk, A. Mau, D.J. Chung, G. Wallace, Porous conducting membranes based on polypyrrole-PMMA composites, *Synth. Met* 99 (1999) 121–126.
- [179] T. Mirfakhrai, J.D.W. Madden, R.H. Baughman, Polymer artificial muscles, *Mater. Today* 10 (2007) 30–38.
- [180] T.D. Licona-Sanchez, G.A. Alvarez-Romero, M. Palomar-Pardave, C.A. Galan-Vidal, M.E. Paez-Hernandez, M.T.R. Silva, et al., Influence of the cation nature of the sulphate salt on the electrochemical synthesis of sulfate-doped polypyrrole, *Int. J. Electrochem. Sci* 6 (2011) 1537–1549.
- [181] J.Y. Lee, C.A. Bashur, A.S. Goldstein, C.E. Schmidt, Polypyrrole-coated electrospun PLGA nanofibers for neural tissue applications, *Biomaterials* 30 (2009) 4325–4335.
- [182] Y. Kudoh, K. Akami, Y. Matsuya, Properties of chemically prepared polypyrrole with an aqueous solution containing Fe₂(SO₄)₃, a sulfonic surfactant and a phenol derivative, *Synth. Metals* 95 (1998) 191–196.
- [183] Y. Kudoh, Properties of polypyrrole prepared by chemical polymerization using aqueous solution containing Fe₂(SO₄)₃ and anionic surfactant, *Synth. Metals*. *Synth. Metals* 79 (1996) 17–22.
- [184] M. Kotal, S.K. Srivastava, B. Paramanik, Enhancements in conductivity and thermal stabilities of Polypyrrole/Polyurethane Nanoblends, *J. Phys. Chem. C* 115 (2011) 1496–1505.
- [185] B.J. Hwang, J.Y. Yang, C.W. Lin, Microscopic gas-sensing model for ethanol sensors based on conductive polymer composites from polypyrrole and poly(ethylene oxide), *J. Electrochem. Soc* 146 (1999) 1231–1236.
- [186] G. Han, G. Shi, Porous polypyrrole/polymethylmethacrylate composite film prepared by vapor deposition polymerization of pyrrole and its application for ammonia detection, *Thin. Solid. Films* 515 (2007) 6986–6991.
- [187] H. Dong, W.E. Jones Jr., Preparation of submicron polypyrrole/poly(methyl methacrylate) coaxial fibers and conversion to polypyrrole tubes and carbon tubes, *Langmuir* 22 (2006) 11384–11387.
- [188] G.J. Cruz, M.G. Olayo, O.G. López, L.M. Gómez, J. Morales, R. Olayo, Nanospherical particles of polypyrrole synthesized and doped by plasma, *Polymer. (Guildf)* 51 (2010) 4314–4318.
- [189] R. Ansari, Polypyrrole Conducting Electroactive Polymers: synthesis and Stability Studies, *E-J. Chem.* 3 (2006) 186–201.
- [190] M.E. Achour, A. Droussi, S. Zoulef, F. Gmati, A. Fattoum, A.B. Mohamed, et al., Electrical conductivity of polypyrrole-polymethylmethacrylate composites determined by impedance spectroscopy, *Spectr. Lett* 41 (2008) 299–304.
- [191] J.C. Dias, D.M. Correia, G. Botelho, S. Lancers-Méndez, V. Sencadas, Electrical properties of intrinsically conductive core-shell polypyrrole/poly(vinylidene fluoride) electrospun fibers, *Synth. Met* 197 (2014) 198–203.
- [192] J.Z. Wang, C.O. Too, G.G. Wallace, A highly flexible polymer fibre battery, *J. Power. Sources* 150 (2005) 223–228.
- [193] M. Wan, M. Li, J. Li, Z. Liu, Transparent and conducting coatings of polyaniline composites, *Thin. Solid. Films* 259 (1995) 188–193.
- [194] Q. Tang, J. Wu, X. Sun, Q. Li, J. Lin, F. Fan, Polyacrylamide-controlled growth of centimeter-scaled polyaniline fibers, *Polymer. (Guildf)* 50 (2009) 752–755.
- [195] P. Santhosh, K.M. Manesh, S.H. Lee, S. Uthayakumar, A.I. Gopalan, K.P. Lee, Sensitive electrochemical detection of superoxide anion using gold nanoparticles distributed poly(methyl methacrylate)-polyaniline core-shell electrospun composite electrode, *Analyst* 136 (2011) 1557–1561.
- [196] M.E. Nicho, M. Trejo, A. Garcia-Valenzuela, J.M. Saniger, J. Palacios, H. Hu, Polyaniline composite coatings interrogated by a nulling optical-transmittance bridge for sensing low concentrations of ammonia gas, *Sens. Actuators. B* 76 (2001) 18–24.
- [197] E.A. Menshikov, A.V. Bol'shakova, I.V. Yaminskii, Analysis of the structure of block copolymer films by atomic force microscopy, *Mosc. Univ. Phys. Bull* 64 (2009) 166–171.
- [198] Q. Lin, Y. Li, M. Yang, Investigations on the sensing mechanism of humidity sensors based on electrospun polymer nanofibers, *Sens. Actuators. B* 171–172 (2012) 309–14.
- [199] T. Jeevananda, M. Begum, Siddaramaiah, Studies on polyaniline filled PU/PMA interpenetrating polymer networks, *Eur. Polym. J* 37 (2001) 1213–1218.
- [200] H. Hu, J.M. Saniger, J.G. Bañuelos, Thin films of polyaniline-polyacrylic acid composite by chemical bath deposition, *Thin. Solid. Films* 347 (1999) 241–247.
- [201] A.K. Himanshu, S.K. Bandyopadhyay, R. Bahuguna, D.K. Ray, T.P. Sinha, Synthesis and Dielectric Studies of Polyaniline-Polyacrylamide Conducting Polymer composites. PART A ed, 2011, pp. 204–205.
- [202] E.M. Geniès, M. Lapkowski, J.F. Penneau, Cyclic voltammetry of polyaniline: interpretation of the middle peak, *J. Electroanal. Chem.* 249 (1988) 97–107.
- [203] S.J. Fan, Q.W. Tang, J.H. Wu, D. Hu, H. Sun, J.M. Lin, Two-step synthesis of polyacrylamide/poly(vinyl alcohol)/polyacrylamide/graphite interpenetrating network hydrogel and its swelling, conducting and mechanical properties, *J. Mater. Sci* 43 (2008) 5898–5904.
- [204] B. Das, S. Kar, S. Chakraborty, D. Chakraborty, S. Gangopadhyay, Synthesis and characterization of polyacrylamide-polyaniline conductive blends, *J. Appl. Polym. Sci* 69 (1998) 841–844.
- [205] P. Sengodu, A.D. Deshmukh, Conducting polymers and their inorganic composites for advanced Li-ion batteries: a review, *RSC. Adv* 5 (2015) 42109–42130.
- [206] Y. Shi, L. Peng, Y. Ding, Y. Zhao, G. Yu, Nanostructured conductive polymers for advanced energy storage, *Chem. Soc. Rev* 44 (2015) 6684–6696.
- [207] L. Åkerlund, R. Emanuelsson, G. Hernández, F. Ruipérez, N. Casado, D. Brandell, et al., In situ investigations of a proton trap material: a PEDOT-based copolymer with hydroquinone and pyridine side groups having robust cyclability in organic electrolytes and ionic liquids, *ACS. Appl. Energy. Mater.* 2 (2019) 4486–4495.
- [208] C.R. Bridges, M. Stolar, T. Baumgartner, Phosphaviologen-based pyrene-carbon nanotube composites for stable battery electrodes, *Batteries. Supercaps* 3 (2020) 268–274.
- [209] N. Casado, D. Mantione, D. Shanmukaraj, D. Mecerreyes, Symmetric all-organic battery containing a dual redox-active polymer as cathode and anode material, *ChemSusChem* (2019) n/a.
- [210] G. Charrier, H. Kamaledine, C. Barchasz, R. Cornut, B. Jousselm, S. Campidelli, Sulfur-containing molecules grafted on carbon nanotubes as highly cyclable cathodes for Lithium/organic batteries, *ChemElectroChem* 5 (2018) 1732–1737.
- [211] D. Chen, A.J. Avestro, Z. Chen, J. Sun, S. Wang, M. Xiao, et al., A rigid Naphthalenediimide triangle for organic rechargeable Lithium-Ion batteries, *Adv. Mater* 27 (2015) 2907–2912.
- [212] B. Häupler, R. Burges, C. Friebe, T. Janoschka, D. Schmidt, A. Wild, et al., Poly(exTTF): a novel redox-active polymer as active material for Li-organic batteries, *Macromol. Rapid. Commun* 35 (2014) 1367–1371.
- [213] B. Häupler, T. Hagemann, C. Friebe, A. Wild, U.S. Schubert, Dithiophenedione-containing polymers for battery application, *ACS. Appl. Mater. Interfaces* 7 (2015) 3473–3479.
- [214] J. Kim, J. Kim, J. Lee, H.K. Song, C. Yang, Synthesis of a redox-active denpol as a potential electrode in rechargeable organic batteries, *ChemElectroChem* 1 (2014) 1618–1622.
- [215] D.J. Kim, K.R. Hermann, A. Prokofjevs, M.T. Otley, C. Pezzato, M. Owczarek, et al., Redox-active macrocycles for organic rechargeable batteries, *J. Am. Chem. Soc* 139 (2017) 6635–6643.
- [216] M. Kolek, F. Otteny, J. Becking, M. Winter, B. Esser, P. Bieker, Mechanism of charge/discharge of poly(vinylphenothiazine)-based Li-Organic batteries, *Chem. Mater.* 30 (2018) 6307–6317.
- [217] J. Lee, H. Kim, M.J. Park, Long-life, high-rate lithium-organic batteries based on naphthoquinone derivatives, *Chem. Mater.* 28 (2016) 2408–2416.
- [218] H.H. Lee, D. Nam, C.K. Kim, K. Kim, Y. Lee, Y.J. Ahn, et al., Molecular engineered safer organic battery through the incorporation of flame retarding organophosphonate moiety, *ACS. Appl. Mater. Interfaces* 10 (2018) 10096–10101.
- [219] Y. Lu, Q. Zhao, L. Miao, Z. Tao, Z. Niu, J. Chen, Flexible and free-standing organic/carbon nanotubes hybrid films as cathode for rechargeable Lithium-Ion batteries, *J. Phys. Chem. C* 121 (2017) 14498–14506.
- [220] D.J. Min, F. Miomandre, P. Audebert, J.E. Kwon, S.Y. Park, s-Tetrazines as a new electrode-active material for secondary batteries, *ChemSusChem* 12 (2019) 503–510.
- [221] S. Muench, J. Winsberg, C. Friebe, A. Wild, J.C. Brendel, A. Lex-Balducci, et al., pNTQS: easily accessible high-capacity redox-active polymer for organic battery electrodes, *ACS. Appl. Energy. Mater.* 1 (2018) 3554–3559.
- [222] S. Nishida, Y. Yamamoto, T. Takui, Y. Morita, Organic rechargeable batteries with tailored voltage and cycle performance, *ChemSusChem* 6 (2013) 794–797.
- [223] F. Otteny, V. Perner, D. Wassy, M. Kolek, P. Bieker, M. Winter, et al., Poly(vinylphenoxazine) as fast-charging cathode material for organic batteries, *ACS. Sustain. Chem. Eng* 8 (2020) 238–247.
- [224] S. Phadke, M. Cao, M. Anouti, Approaches to electrolyte solvent selection for poly-anthraquinone sulfide organic electrode material, *ChemSusChem* 11 (2018) 965–974.
- [225] M. Ruby Raj, R.V. Mangalaraja, D. Contreras, K. Varaprasad, M.V. Reddy, S. Adams, Perylenedianhydride-based polyimides as organic cathodes for rechargeable Lithium and Sodium batteries, *ACS. Appl. Energy. Mater.* 3 (2020) 240–252.
- [226] K. Sakaushi, G. Nickerl, F.M. Wieser, D. Nishio-Hamane, E. Hosono, H. Zhou, et al., An energy storage principle using bipolar porous polymeric frameworks, *Angew. Chem. Int. Ed.* 51 (2012) 7850–7854.
- [227] D. Schmidt, B. Häupler, C. Stolz, M.D. Hager, U.S. Schubert, Poly[N-(10-oxo-2-vinylanthracen-9(10H)-ylidene)cyanamide] as a novel cathode material for li-organic batteries, *J. Polym. Sci. Part. A. Polym. Chem.* 53 (2015) 2517–2523.
- [228] T.B. Schon, A.J. Tilley, C.R. Bridges, M.B. Miltenburg, D.S. Seferos, Bio-derived polymers for sustainable Lithium-Ion batteries, *Adv. Funct. Mater* 26 (2016) 6896–6903.
- [229] Z. Song, Y. Qian, T. Zhang, M. Otani, H. Zhou, Poly(benzoquinonyl sulfide) as a high-energy organic cathode for rechargeable Li and Na batteries, *Adv. Sci* 2 (2015), 1500124.
- [230] Z. Song, Y. Qian, M.L. Gordin, D. Tang, T. Xu, M. Otani, et al., Polyanthraquinone as a reliable organic electrode for stable and fast lithium storage, *Angew. Chem. Int. Ed.* 54 (2015) 13947–13951.
- [231] Z. Song, Y. Qian, M. Otani, H. Zhou, Stable Li-organic batteries with nafion-based sandwich-type separators, *Adv. Energy. Mater* 6 (2016), 1501780.
- [232] G.S. Vadehra, R.P. Maloney, M.A. Garcia-Garibay, B. Dunn, Naphthalene diimide based materials with adjustable redox potentials: evaluation for organic Lithium-Ion Batteries, *Chem. Mater.* 26 (2014) 7151–7157.
- [233] W. Walker, S. Grugeon, O. Mentre, S. Laruelle, J.M. Tarascon, F. Wudl, Ethoxycarbonyl-based organic electrode for Li-Batteries, *J. Am. Chem. Soc* 132 (2010) 6517–6523.
- [234] Z. Wang, C. Xu, P. Tammela, P. Zhang, K. Edström, T. Gustafsson, et al., Conducting polymer paper-based cathodes for high-areal-capacity Lithium-organic batteries, *Energy. Technology* 3 (2015) 563–569.

- [235] J. Wang, C.S. Chen, Y. Zhang, Hexaazatrinaphthylene-based porous organic polymers as organic cathode materials for Lithium-Ion batteries, *ACS. Sustain. Chem. Eng* 6 (2018) 1772–1779.
- [236] X. Wang, C. Zhang, Y. Xu, Q. He, P. Mu, Y. Chen, et al., Conjugated microporous polytetra(2-Thienyl)ethylene as high performance anode material for lithium- and sodium-ion batteries, *Macromol. Chem. Phys* 219 (2018), 1700524.
- [237] T. Xu, J. Xiong, X. Du, Y. Zhang, S. Song, C. Xiong, et al., Polytriphenylamine derivative and carbon nanotubes as cathode materials for high-performance polymer-based batteries, *J. Phys. Chem. C* 122 (2018) 20057–20063.
- [238] C.J.X. Yao, W. Wu, J. Xu, Zhenzhen, J. Zhichuan, Shanjing Zhang, Qichun Zhang, Novel conjugated copolymer as promising cathode for rechargeable Lithium-Ion Battery, *Chem. Asian. J.* (2019) 14.
- [239] C. Yuan, Q. Wu, Q. Li, Q. Duan, Y. Li, H-g. Wang, Nanoengineered ultralight organic cathode based on aromatic carbonyl compound/graphene aerogel for green lithium and sodium ion batteries, *ACS. Sustain. Chem. Eng* 6 (2018) 8392–8399.
- [240] H. Zhang, W. Sun, X. Chen, Y. Wang, Few-layered fluorinated triazine-based covalent organic nanosheets for high-performance alkali organic batteries, *ACS. Nano* 13 (2019) 14252–14261.
- [241] Y. Zhang, Y. Huang, G. Yang, F. Bu, K. Li, I. Shaker, et al., Dispersion–assembly approach to synthesize three-dimensional graphene/polymer composite aerogel as a powerful organic cathode for rechargeable Li and Na batteries, *ACS. Appl. Mater. Interfaces* 9 (2017) 15549–15556.
- [242] C. Zhang, Y. He, P. Mu, X. Wang, Q. He, Y. Chen, et al., Toward high performance thiophene-containing conjugated microporous polymer anodes for lithium-ion batteries through structure design, *Adv. Funct. Mater* 28 (2018), 1705432.
- [243] T. Xia, Y. Wang, B. Wang, Z. Yang, G. Pan, L. Zhang, et al., Natural compounds gallic acid derivatives for long-life Li/Na organic batteries, *ChemElectroChem* 6 (2019) 4765–4772.
- [244] Z. Lei, X. Chen, W. Sun, Y. Zhang, Y. Wang, Exfoliated triazine-based covalent organic nanosheets with multielectron redox for high-performance lithium organic batteries, *Adv. Energy. Mater* 9 (2019), 1801010.
- [245] M. Zhang, R. Lu, H. Yuan, K. Amin, L. Mao, W. Yan, et al., Nanowire array-coated flexible substrate to accommodate lithium plating for stable lithium-metal anodes and flexible lithium–organic batteries, *ACS. Appl. Mater. Interfaces* 11 (2019) 20873–20880.
- [246] A. Wild, M. Strumpf, B. Häupler, M.D. Hager, U.S. Schubert, All-organic battery composed of Thianthrene- and TCAQ-based polymers, *Adv. Energy. Mater* 7 (2017), 1601415.
- [247] Y. Hu, W. Tang, Q. Yu, C. Yang, C. Fan, In Situ electrochemical synthesis of novel lithium-rich organic cathodes for all-organic Li-Ion full batteries, *ACS. Appl. Mater. Interfaces* 11 (2019) 32987–32993.
- [248] N. Casado, D. Mantione, D. Shanmukaraj, D. Mecerreyes, Symmetric all-organic battery containing a dual redox-active polymer as cathode and anode material, *ChemSusChem* 13 (2020) 2464–2470.
- [249] H. Chen, Y. Zhou, Y.C. Lu, Lithium–Organic Nanocomposite Suspension for High-Energy-Density Redox Flow Batteries, *ACS. Energy. Lett* 3 (2018) 1991–1997.
- [250] B. Ernould, L. Sieuw, G. Barozzino-Consiglio, J.F. Gohy, A. Vlad, Negative Redox Potential Shift in Fire-Retardant Electrolytes and Consequences for High-Energy Hybrid Batteries, *ACS. Appl. Energy. Mater.* 2 (2019) 7879–7885.
- [251] P. Leung, J. Bu, P. Quijano Velasco, M.R. Roberts, N. Grobert, P.S. Grant, Single-step spray printing of symmetric all-organic solid-state batteries based on porous textile dye electrodes, *Adv. Energy. Mater* 9 (2019), 1901418.
- [252] G. Li, B. Zhang, J. Wang, H. Zhao, W. Ma, L. Xu, et al., Electrochromic Poly (chalcogenoviologen)s as anode materials for high-performance organic radical lithium-ion batteries, *Angew. Chem. Int. Ed.* 58 (2019) 8468–8473.
- [253] C. Luo, X. Ji, J. Chen, K.J. Gaskell, X. He, Y. Liang, et al., Solid-state electrolyte anchored with a carboxylated azo compound for all-solid-state lithium batteries, *Angew. Chem. Int. Ed.* 57 (2018) 8567–8571.
- [254] F. Otteny, G. Studer, M. Kolek, P. Bieker, M. Winter, B. Esser, Phenothiazine-Functionalized Poly(norbornene)s as high-rate cathode materials for organic batteries, *ChemSusChem* 13 (9) (2020) 2232–2238.
- [255] F. Otteny, M. Kolek, J. Becking, M. Winter, P. Bieker, B. Esser, Unlocking full discharge capacities of poly(vinylphenothiazine) as battery cathode material by decreasing polymer mobility through cross-linking, *Adv. Energy. Mater* 8 (2018), 1802151.
- [256] J.Y. Shin, T. Yamada, H. Yoshikawa, K. Awaga, H. Shinokubo, An antiaromatic electrode-active material enabling high capacity and stable performance of rechargeable batteries, *Angew. Chem. Int. Ed.* 53 (2014) 3096–3101.
- [257] H. Shin, D. Kim, H.J. Kim, J. Kim, K. Char, C.T. Yavuz, et al., Fluorinated covalent organic polymers for high performance sulfur cathodes in lithium–sulfur batteries, *Chem. Mater.* 31 (2019) 7910–7921.
- [258] M. Stolar, C. Reus, T. Baumgartner, Xylene-bridged phosphaviologen oligomers and polymers as high-performance electrode-modifiers for Li-Ion batteries, *Adv. Energy. Mater* 6 (2016), 1600944.
- [259] C. Stolze, T. Janoschka, S. Flauder, F.A. Müller, M.D. Hager, U.S. Schubert, Investigation of ice-templated porous electrodes for application in organic batteries, *ACS. Appl. Mater. Interfaces* 8 (2016) 23614–23623.
- [260] H. Kim, J.E. Kwon, B. Lee, J. Hong, M. Lee, S.Y. Park, et al., High energy organic cathode for sodium rechargeable batteries, *Chem. Mater.* 27 (2015) 7258–7264.
- [261] H-g Wang, S. Yuan, D-l Ma, X-l Huang, F-l Meng, X-b. Zhang, Tailored aromatic carbonyl derivative polyimides for high-power and long-cycle sodium-organic batteries, *Adv. Energy. Mater* 4 (2014), 1301651.
- [262] K.S. Weeraratne, A.A. Alzharani, H.M. El-Kaderi, Redox-active porous organic polymers as novel electrode materials for green rechargeable sodium-ion batteries, *ACS. Appl. Mater. Interfaces* 11 (2019) 23520–23526.
- [263] L. Fan, R. Ma, J. Wang, H. Yang, B. Lu, An ultrafast and highly stable potassium–organic battery, *Adv. Mater* 30 (2018), 1805486.
- [264] J. Bitenc, K. Pirnat, T. Bančić, M. Gaberšček, B. Genorio, A. Randon-Vitanova, et al., Anthraquinone-based polymer as cathode in rechargeable magnesium batteries, *ChemSusChem* 8 (2015) 4128–4132.
- [265] J. Tian, D. Cao, X. Zhou, J. Hu, M. Huang, C. Li, High-capacity Mg–organic batteries based on nanostructured Rhodizonate salts activated by Mg–Li dual-salt electrolyte, *ACS. Nano* 12 (2018) 3424–3435.
- [266] C. Clausen, E. Dražević, A.S. Andersen, M.L. Henriksen, M. Hinge, A. Bentien, Anthraquinone oligomers as anode-active material in rechargeable nickel/polymer batteries with Aqueous Electrolyte, *ACS. Appl. Energy. Mater.* 1 (2018) 243–248.
- [267] G. Dai, Y. He, Z. Niu, P. He, C. Zhang, Y. Zhao, et al., A dual-ion organic symmetric battery constructed from phenazine-based artificial bipolar molecules, *Angew. Chem. Int. Ed.* 58 (2019) 9902–9906.
- [268] M. Joshi, T.K. Ghanty, Hybrid organic–inorganic functionalized dodecaboranes and their potential role in lithium and magnesium ion batteries, *J. Phys. Chem. C* 122 (2018) 27947–27954.
- [269] H-g Wang, H. Wang, Z. Si, Q. Li, Q. Wu, Q. Shao, et al., A bipolar and self-polymerized phthalocyanine complex for fast and tunable energy storage in dual-ion batteries, *Angew. Chem. Int. Ed.* 58 (2019) 10204–10208.
- [270] J. Xie, Z. Wang, Z.J. Xu, Q. Zhang, Toward a high-performance all-plastic full battery with a single organic polymer as both cathode and anode, *Adv. Energy. Mater* 8 (2018), 1703509.
- [271] C. DeBruler, B. Hu, J. Moss, J. Luo, T.L. Liu, A sulfonate-functionalized viologen enabling neutral cation exchange, aqueous organic redox flow batteries toward renewable energy storage, *ACS. Energy. Lett* 3 (2018) 663–668.
- [272] Y. Imada, H. Nakano, K. Furukawa, R. Kishi, M. Nakano, H. Maruyama, et al., Isolation of Hypervalent Group-16 radicals and their application in organic-radical batteries, *J. Am. Chem. Soc* 138 (2016) 479–482.
- [273] M.A. Goulet, L. Tong, D.A. Pollack, D.P. Tabor, S.A. Odom, A. Aspur-Guzik, et al., Extending the lifetime of organic flow batteries via redox state management, *J. Am. Chem. Soc* 141 (2019) 8014–8019.
- [274] K. Hatakeyama-Sato, T. Nagano, S. Noguchi, Y. Sugai, J. Du, H. Nishide, et al., Hydrophilic organic redox-active polymer nanoparticles for higher energy density flow batteries, *ACS. Appl. Polym. Mater.* 1 (2019) 188–196.
- [275] X. Judez, L. Qiao, M. Armand, H. Zhang, Energy density assessment of organic batteries, *ACS. Appl. Energy. Mater.* 2 (2019) 4008–4015.
- [276] T. Liu, X. Wei, Z. Nie, V. Sprenkle, W. Wang, A total organic aqueous redox flow battery employing a low cost and sustainable methyl viologen anolyte and 4-HO-TEMPO Catholyte, *Adv. Energy. Mater* 6 (2016), 1501449.
- [277] K. Oka, R. Kato, K. Oyaizu, H. Nishide, Poly(vinylidenebenzothienophenesulfone): its redox capability at very negative potential toward an all-organic rechargeable device with high-energy density, *Adv. Funct. Mater* 28 (2018), 1805858.
- [278] H. Rath, S. Tokui, N. Aratani, K. Furukawa, J.M. Lim, D. Kim, et al., A stable organic radical delocalized on a highly twisted π -system formed upon palladium metalation of a Möbius Aromatic Hexaphyrin, *Angew. Chem. Int. Ed.* 49 (2010) 1489–1491.
- [279] K. Sato, T. Sukegawa, K. Oyaizu, H. Nishide, Synthesis of Poly(TEMPO-Substituted Glycidyl Ether) by Utilizing t-BuOK/18-Crown-6 for an Organic Cathode-Active Material, *Macromol. Symp* 351 (2015) 90–96.
- [280] D. Schmidt, B. Häupler, M.D. Hager, U.S. Schubert, Poly(DCAQI): synthesis and characterization of a new redox-active polymer, *J. Polym. Sci. Part. A. Polym. Chem.* 54 (2016) 1998–2003.
- [281] Z. Zhao-Karger, P. Gao, T. Ebert, S. Klyatskaya, Z. Chen, M. Ruben, et al., New organic electrode materials for ultrafast electrochemical energy storage, *Adv. Mater* 31 (2019), 1806599.