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# Polymer-Based Batteries—Flexible and Thin Energy Storage Systems

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Batteries have become an integral part of everyday life—from small coin cells to batteries for mobile phones, as well as batteries for electric vehicles and an increasing number of stationary energy storage applications. There is a large variety of standardized battery sizes (e.g., the familiar AA-battery or AAA-battery). Interestingly, all these battery systems are based on a huge number of different cell chemistries depending on the application and the corresponding requirements. There is not one single battery type fulfilling all demands for all imaginable applications. One battery class that has been gaining significant interest in recent years is polymer-based batteries. These batteries utilize organic materials as the active parts within the electrodes without utilizing metals (and their compounds) as the redox-active materials. Such polymer-based batteries feature a number of interesting properties, like high power densities and flexible batteries fabrication, among many more.

## 1. Introduction

Energy is the central element of our modern society and is directly connected to the emission of greenhouse gases (i.e., carbon dioxide). Energy fuels our daily life in the truest sense of the word, and the discussion of sustainable energy has reached everybody's life (e.g., Fridays for Future).

Within this context, the utilization of renewable energy is gaining increasing interest. One important aspect is the storage of electrical energy. The different applications to store electrical energy range from stationary energy storage (i.e., storage of the electrical energy produced from intrinsically fluctuating sources, e.g., wind parks and photovoltaics) over batteries for electric vehicles and mobile devices (e.g., laptops as well as mobile phones or other smart mobile devices such as smart watches), down to miniature devices for biochips, sensors, as well as "smart packaging" or miniaturized medical devices.

Despite being essential in modern life, (some) batteries can look back on a long history—for instance, the lead-acid battery was discovered 150 years ago. Yet, the lead acid battery is still the system of choice for starter batteries in cars until today. Even the beginnings of modern lithium batteries date back to the 1970s. Recently, John B. Goodenough (The University of Texas at Austin, USA), M. Stanley Whittingham (Binghamton University, State University of New

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York, USA), and Akira Yoshino (Asahi Kasei Corporation, Tokyo, Japan) have been awarded with the Nobel Prize in chemistry "for the development of lithium-ion batteries."[1] Remarkably, their research was also already motivated by the desire to create a society, which does not depend on fossil fuels.

Despite the successive story of lithium-ion batteries (LIBs), there is still a growing need for new additional battery technologies. Current drivers for the research on batteries and the development of novel battery technologies are multifarious. One important aspect is safety. Within this context, solid electrolytes (e.g., polymer electrolytes for LIBs) or self-detecting separators are considered.[2,3] The next important aspect is the required/desired energy density of the batteries. Particularly mobile applications, first and foremost electric cars, require (very) high energy densities. In this context, lithium–sulfur and lithium–air batteries are currently studied intensively.[4] If their specific challenges are mastered, both technologies could potentially provide an increase in energy density by at least a factor of two if not more. However, flexible mobile devices require very different battery design principles. Hence, new technologies are also leading to a growing need for novel battery technologies. Different requirements arise and result in new innovative properties of energy storage devices, for example, flexible batteries[5] or even stretchable devices.[6] Additionally, flexible wearable devices are another potential area of application for such systems.[7] Increasingly important is the sustainability of the different battery technologies that are considered. Currently, the established battery systems are mainly based on materials employing less abundant elements, which might in the future lead to a shortage of the required raw materials.[8,9] For instance, cobalt, which is still a key resource for lithium-ion metal oxide batteries, is listed in the European report as a critical raw material.[10] In addition, cobalt was in the media due to intensive child labor in the mining process.[11] Consequently, cobalt oxide is substituted more and more by other metal oxides. The sustainability of a battery system is also connected to the energy required for the production of the battery and its possibility to be recycled. Due to the required high thermal energy processes in the production of LIBs, one kWh of battery requires 300 to 400 kWh of energy in its production process.[9] Needless to say that this high energy demand also leads to a significant $CO_2$-footprint. As a consequence, other production processes (e.g., hydrothermal processes) are con-

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sidered for lithium-ion batteries, which could result in much lower manufacturing temperatures, hence reducing the $CO_2$-footprint. Of no less importance is the utilization of batteries after their usage, namely, their recycling process. This issue still seems to be a challenge for many classical batteries. This challenge has led to the development of a future "dream" battery life cycle by Poizot.[12] Organic/polymer materials, based on biomass, would for the first time enable a closed life cycle of a (polymer-based) battery. However, this cycle is only closed for bio-based materials, in contrast to the utilization of polymers based on fossil resources. These oil-based materials can potentially be recycled. However, one has to take into account that there are already difficulties in the recycling of classic plastics—leaving "thermal recovery" as the ultima ratio.[13]

In the future, also power-to-X/power to chemicals[14] processes can be potentially be utilized for the synthesis of redox-active polymers, which would allow also a closed life cycle. Syngas obtained from $CO_2$ as well as hydrogen (derived from the electrolysis utilizing renewable energy) is the basis for further synthesis of different building blocks like olefins or commodity chemicals.[15]
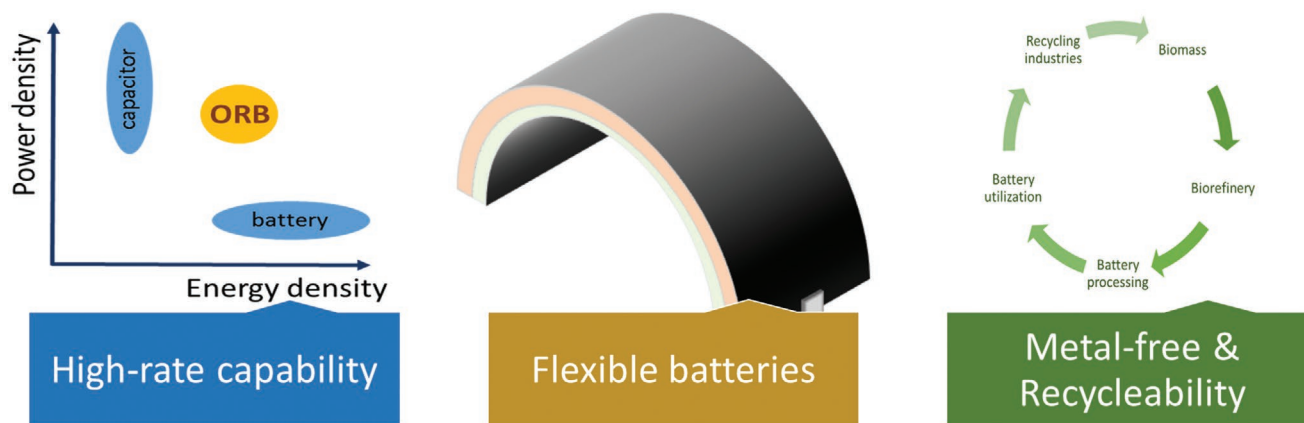


**Figure 1.** Advantages of polymer-based batteries.[1,5,93]

Overall polymer-based batteries[16–21] offer several advantages (see **Figure 1**). If the right active materials are utilized, high power densities can be achieved. These systems feature a performance that lays in-between classical batteries and supercapacitors as typical high-power systems. As mentioned above, the utilization of polymeric materials enables to employ unique processing techniques, such as printing, and allows for the fabrication of mechanically large-area, flexible batteries. Due to the utilization of widely available elements (C, H, N, O, and sometimes S), polymeric active materials do not contain scarce and unbenign (heavy) metals. Furthermore, a closed life-cycle can be imagined.

## 2. Historical Perspective

The research on polymer-based batteries has made several scientific borrowings. One important milestone was the discovery of conductive polymers in the late 1970s, leading to the award of the Nobel Prize to the laureates Heeger, Shirakawa, and MacDiarmid, which constituted the ever-growing field of conductive $\pi$-conjugated polymers.[22] This was a breakthrough for many new applications of polymeric materials. Polymers have not any longer been used only for their insulating properties, but they can also feature the (opto-)electronic properties of semiconductors or even metals. Consequently, these materials found their way into a wide range of different applications: Polymer-light-emitting diodes (PLEDS),[23] organic solar cells,[24] electrochromic devices,[25] or as electroactive polymers in artificial muscles.[26] Not surprisingly, $\pi$-conjugated polymers were also used in the first polymer-based batteries.[27,28] However, the $\pi$-conjugated system of the polymers also causes the major disadvantage of batteries based on these materials. The $\pi$-conjugation leads to a sloping cell voltage profile due to the change in redox potential during charging/discharging (i.e., doping/de-doping of the polymer). Voltage differences of $\approx$1 V are not uncommon, hampering the utilization of such batteries in potential applications. The solution to this problem is obviously the utilization of polymers with well-defined and non-conjugated redox moieties, which provide a redox potential that is nearly independent from the charge state. However, these materials will also lose the good electric conductivity of their conjugated counter parts. Consequently, the usage of conductive additives like carbon materials is required. Interestingly, the first redox-active polymers, which are structurally related to the today utilized polymers, were already described by Cassidy in 1949—over 50 years before the first polymer batteries based on the stable TEMPO-radical [(2,2,6,6-tetramethylpiperidin-1-yl)oxyl)] were reported. The early research on these materials was inspired by ion-exchange/proton-exchange resins.[29,30] Comparably, the redox-exchange resin was intended to provide electrons (or vice versa) similar to the protons provided by a proton-exchange resin. Later the research on redox polymers was continued by Manecke in Berlin (Germany). The first major breakthrough, which can be considered as the starting point of the current research thrust, was reported in 2002. Polymers featuring stable TEMPO radicals as the side groups were introduced as cathode materials.[31] These distinct redox-active, radical-based moieties led to the term organic radical battery (ORB). During the following years the research on ORBs was almost exclusively performed in Japan, in particular by

the research group of Nishide.[32] It should be mentioned that Nishide was a postdoc with Manecke—a circle closes.

## 3. What is a Polymer-Based Battery?

Polymer-based batteries can be defined as batteries, in which (organic) redox-active polymers are used as active materials for either of the respective electrode, cathode, or anode. The combination of two electrodes based on polymeric active materials can lead to full-polymeric batteries[17,33] (see **Figure 2**, top)—one of the polymers can be oxidized and one can be reduced during the charge process. Nevertheless, polymer-based electrodes can also be combined with other electrodes. Metal anodes such as lithium, zinc, and others are often used as counter electrodes (Figure 2, bottom), particularly, for the detailed characterization of the battery materials. The electrodes include the redox-active polymers, and, where appropriate or necessary, conductive additives (i.e., different carbon materials), well as a polymeric binder. Cathode and anode materials are separated by a separator to prevent electrical short circuits and by an electrolyte allowing for the transport of ionic charge carriers. Besides polymeric materials also different small organic molecules (e.g., different benzoquinones) have been utilized as active materials in battery electrodes.[20] However, for many of these materials the solubility of one of the redox states represents a challenge, which can lead to severe capacity loss. Due to the redox reactions of the active materials, that is, the overall charge of the molecule is changing, the solubility of the active molecule can change dramatically. A polymer, particularly crosslinked polymers, can circumvent this issue. Furthermore, the processability of polymeric materials is often also better compared to powders of small organic molecules.

Important parameters for the materials, the electrodes as well as the whole cells are the redox potential of the respective material which, in turn, determines the cell voltage. For all-polymer based batteries voltages between 1 to 2 V can be obtained. The capacity of the electrode materials (100 to several 100 mAh g$^{-1}$) will determine the overall capacity of the cell. The C-rate is a measure for the power density, which can be applied (charging with 1C means the cell is charged within an hour, 60C within a minute). The cycle life is another important parameter as well as the self-discharge.

## 4. Polymer-Based Batteries: Materials and Components

Polymer-based batteries typically consist of the electrodes and the electrolyte/separator (see Section 4.4). The electrodes themselves typically consist of three components in different ratios: The active polymer (see Section 4.1), a conductive additive (see Section 4.2) as well as a polymeric binder (see Section 4.3). Typically, the compositions of the composite electrodes are based on $\approx$40 to 60 wt% of the redox polymer, 35 to 55 wt% conductive additive as well as 2 to 10 wt% binder. Most of the reported examples in Section 4.1 have been tested versus lithium anodes. This setup represents an excellent test system; however, it has the same limitations (e.g., lithium dendrite formation, safety issues) like all other systems with solid lithium metal anodes (e.g., lithium–sulfur batteries). An alternative could be here the usage of graphite anodes
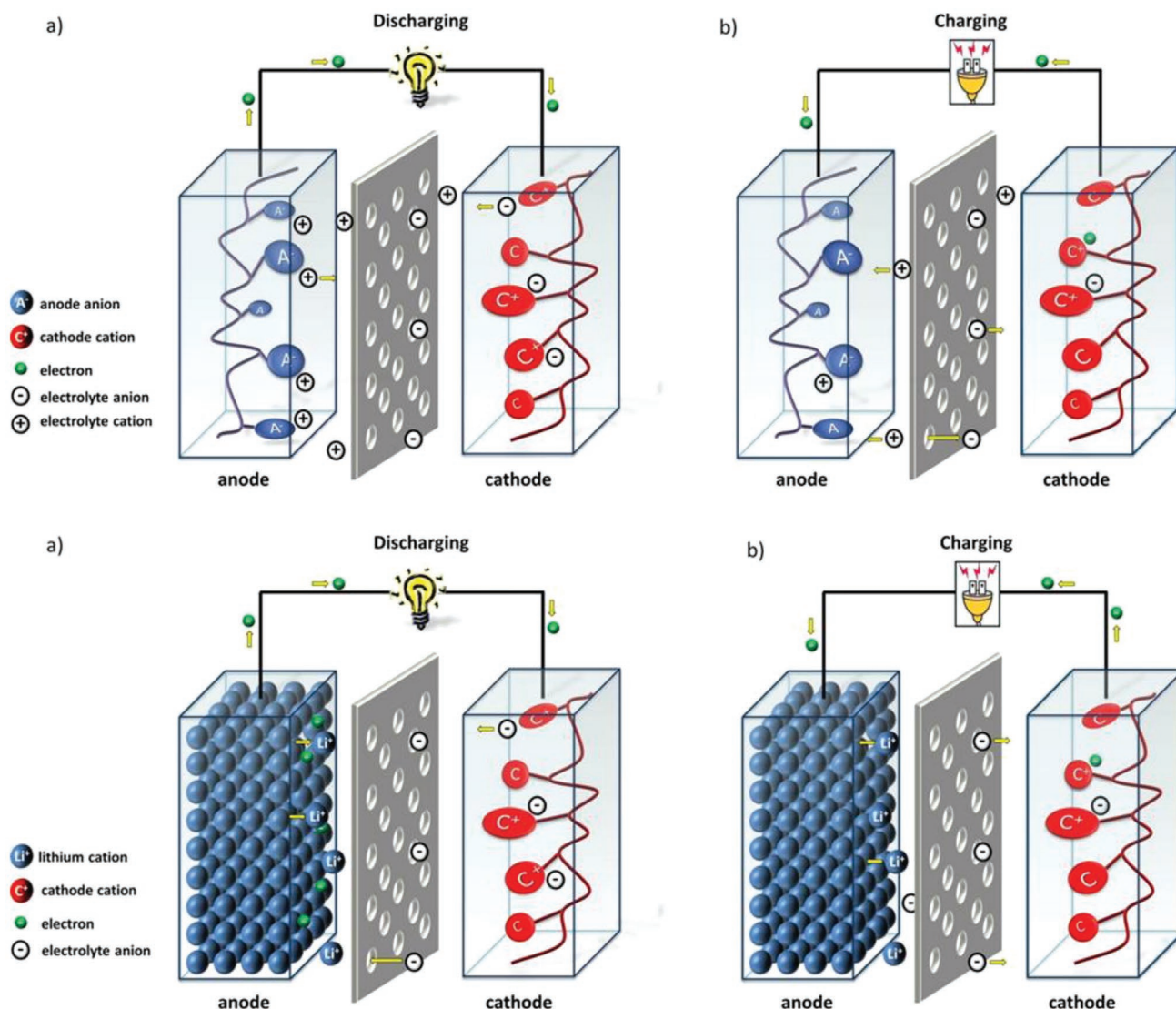
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**Figure 2.** Top: Schematic representation of a polymer-based battery in dual-ion configuration with two polymer-based electrodes: a) discharging and b) charging (top). Bottom: A polymer-based battery with a polymer-based cathode and metal anode: a) discharging and b) charging (bottom). Reproduced with permission.[18] Copyright 2016, American Chemical Society.

resulting in a special type of a lithium-ion battery (or dual-ion battery depending on the used active material). However, there are huge efforts for the design of all-polymer-based batteries. However, often the anode materials are still limiting the performance.

**4.1. Redox-Active Polymers**

Two different polymer classes of redox-active polymers can be distinguished: $\pi$-conjugated polymers as well as redox polymers with well-defined isolated redox centers. The first polymers feature the required redox properties as well as a good electric conductivity, in particular when these materials are doped. A wide range of different conjugated polymers has been investigated as electrode materials (for a detailed overview see

refs. [18,19,21,26,27]). Polyacetylene—the "mother of all" conductive polymer—was amongst the first materials tested.[34] Moreover, polypyrroles (PPY) have been intensively evaluated as electrode materials. Typically, PPY is utilized as a cathode material (i.e., oxidized during charging). However, PPY can also be reduced, allowing for its use as an anode material. Polymer-based batteries with two PPY electrodes have been fabricated. These batteries are pol-less, meaning the electrodes can be utilized as both anode and cathode.[35] Last, polythiophene (PT), poly(ethylenedioxythiophene) (PEDOT), and other alkoxy-substituted polythiophenes have been evaluated. These materials are also interesting for application in polymeric anodes (e.g., in combination with PPY), resulting in a maximum cell voltage of 1.4 V.[36] Often the performance of polymer-based batteries with conjugated active materials is characterized by a sloping cell potential. In addition, the capacities of the materials itself are
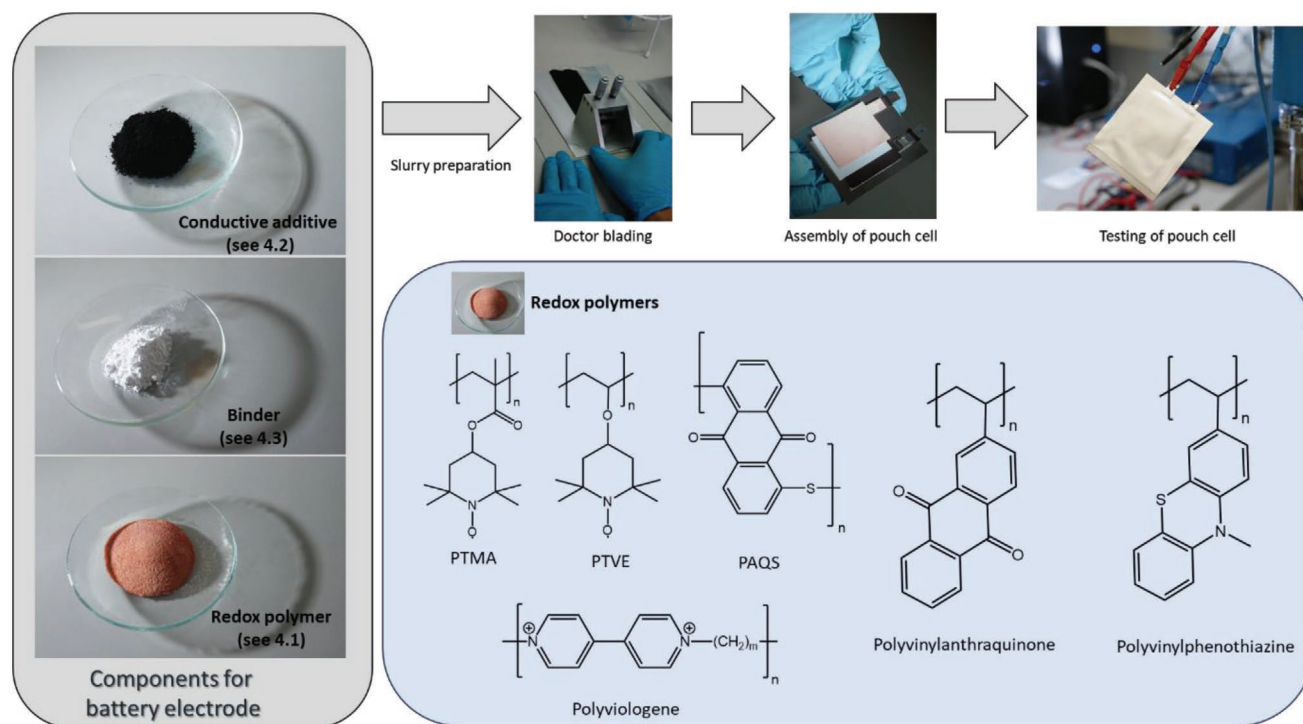
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**Figure 3.** Photographs of the components of the composite electrodes (left), the workflow of electrode preparation and the final pouch cells (top right) and selected structures of redox polymers (bottom left).

comparably low (mostly <100 mAh g$^{-1}$). However, the usage of an additional conductive additive is not required. Furthermore, the applicable current density is limited. Many systems described lay well below 100 reported cycles, that is, they show limited lifetime compared to the other materials described below. Nevertheless, conjugated polymers have also been utilized in hybrid systems, that is, where a conjugated polymer backbone is combined with well-defined redox moieties.[37]

The second important class of polymeric active materials are redox polymers, that is, non-conjugated polymers with defined redox moieties (which are typically attached as side groups). The most studied redox moieties are based on stable radicals (e.g., TEMPO),[38] quinones as well as other redox-active organic moieties. At present, TEMPO-based polymers are probably the most investigated polymers as active materials for polymer-based batteries. The TEMPO moiety can be oxidized yielding an oxoammonium ion. The PTMA (poly(2,2,6,6-tetramethyl-piperidinyloxy-4-ylmethacrylate)) was the first and is still until today the most studied polymer of this kind in polymer-based batteries (**Figure 3**).[23] PTMA already clarifies one challenge, which is connected with these redox polymers. In contrast to conjugated polymers, which are mostly synthesized in a straight-forward manner by cross-coupling reactions and oxidative couplings as well as electropolymerization, redox polymers are mainly prepared by classical chain-growth reactions, that is, radical polymerization and ionic polymerization processes. However, the redox moieties often interfere with the polymerization method, for example, the stable radical TEMPO will prevent any radical polymerization, while quinoid monomers might also act as inhibitors. As a consequence, PTMA has to be

synthesized in a two-step process. First, the amine-containing monomer is polymerized followed by an oxidation to yield the active nitroxide radical. Alternatively, also the anionic polymerization as well as the group transfer polymerization of 4-meth-acryloyloxy-TEMPO have been explored—both methods allow the direct polymerization of the radical.[39,40] Furthermore, different polymer backbones have been investigated enabling the use of other polymerization techniques, for example, the cationic polymerization of vinylethers (PTVE—poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl-vinylether)) (Figure 3),[41] the ring-opening metathesis polymerization (ROMP) of norbornenes,[42] and the anionic ring-opening polymerization of glycidyl ethers,[43] as they all allow for a polymerization in the presence of a radical centers. Besides the synthetic accessibility of the corresponding polymers, the polymer backbone also has an influence on the theoretical specific capacities of these materials (e.g., 131 mAh g$^{-1}$ for the poly(vinyl ether) and 110 mAh g$^{-1}$ for PTMA). A lighter backbone is preferable because this non-conjugated part of the polymer is redox-innocent, that is, electrochemically dead freight. For comparison, cathode materials for lithium-ion batteries have theoretical specific capacities of 170 mAh g$^{-1}$ for LiFePO$_4$ and up to 280 mAh g$^{-1}$ for mixed oxides (LiNi$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$).[44] However, one also has to consider the often low ratios of active polymeric materials in electrode composites. One remarkable feature of a TEMPO-based organic radical battery is the high current density, which can be applied for charging/discharging. These cells are often charged with high C-rates ranging from several C up to even 100C,[45] the latter example being obtained with polymer-carbon nanotube composites. This unique feature renders ORBs as

highly interesting charge-storage systems, which close the gap between supercapacitors and classical battery systems in terms of power density. Although the self-discharge of the battery system reprents a relevant parameter for practical applications, the reported values are scarce throughout the literature. First studies on PTMA electrodes with vapor-grown carbon fibers revealed a rather high self-discharge rate of ≈40% within a week.[46] This process is attributed to the presence of soluble polymer chains, therefore crosslinking of the polymer is anticipated to improve this behavior (without giving clear proof by numbers).[47] Evidence for the importance of the solubility was provided in a recent study.[48] The self-discharge of PTMA electrodes was evaluated in different electrolytes (carbonates and ionic liquids). The solvent had a large influence on the self-discharge: ranging from complete discharge within 3 days to ≈10% in 3 days. Latter value is the lowest value reported so far; however, for many practical applications it might be too high.

Another important subclass of materials are carbonyl compounds, in particular quinones and imides.[49] The former materials are mainly based on quinones/hydroquinones as well as anthraquinones and their corresponding derivatives. The redox chemistry is characterized by the reversible reduction of the carbonyl groups yielding, in most cases, the corresponding anions. These materials—for instance the poly(anthraquinone sulfide) PAQS (Figure 3)—feature high capacities due to the two-electron redox process.[50] Capacities of ≈170 mAh g$^{-1}$ have been achieved in a Li-organic battery. PAQS was structurally modified by the introduction of oligosulfide chains yielding PAQxS,[51] by which very high capacities (>200 mAh g$^{-1}$) after 100 cycles could be obtained. Poly(1,4-anthraquinone) (P14AQ) can be considered as one of the best anthraquinone-based polymers (and is also amongst the best of all polymers) as it features high capacities (260 mAh g$^{-1}$) and excellent stabilities.[52] Besides the above described main-chain systems, anthraquinone was also utilized in side-chain systems. Vinylanthraquinone was polymerized yielding the corresponding polymer (Figure 3).[53] Moreover, also the ROMP of norbornenes containing anthraquinones was successfully utilized.[54] Noteworthy, these materials were applied in polymer/air batteries (cathode with manganese oxide as catalyst). Such a polymer/air battery featured high capacities (≈200 mAh g$^{-1}$) and an excellent cyclability as well as rate performance. Overall, the anthraquinone systems can be considered as the most stable ones.

Polyimides represent another interesting material subclass, however, due to the irreversible second reduction step only the first reversible redox reaction can be utilized in a battery. Yet, as non-conjugated polymers, these materials feature a comparably high conductivity due to the conjugation within the oligomer units (e.g., perylene, naphthalene), and hence require only a minimal amount of conductive additive.[55,56]

Additional redox-active moieties worth mentioning are viologens, which represent redox centers that are amongst the few good anode materials. Hereby, polyviologen (Figure 3) was utilized as the anode material in combination with poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl acrylamide)[57] or polyvinylcarbazole.[58] In principle two redox steps can be used in viologens, however, only the first highly reversible step is applied in batteries (reduction to a radical cation). In contrast to many other anode materials, polyviologens can also be used with aqueous electrolytes.

The last materials subclass, which will be discussed in this brief overview, are organosulfur polymers.[59] Noteworthy, the boundaries between organic radical batteries/polymer-based batteries on the one hand and lithium–sulfur[60] as well as sodium–sulfur batteries[61] on the other hand are blurry. The electrochemistry of organosulfur compounds is very rich, and different redox reactions are of interest for battery systems, for example, that of thioethers, disulfides, and polysulfides. The former compounds are for instance based on dithiolanes.[62] These materials typically feature modest capacities and low voltages (versus lithium). Further, aromatic thioethers such as thianthrene are also interesting materials,[63] as they allow for very high cell potentials of 4.1 V (versus lithium). However, the capacity was fading rather fast. In particular, aromatic active moieties allow often higher cell potentials. Additionally, a thianthrene-containing polymer was utilized for an all-organic battery with poly(extended-tetrathiafulvalene (poly(exTTF)).[64] Recently, also phenothiazine polymers[65,66] (Figure 3) and a polymer of the related phenoxazine[67] were applied as cathode materials and due to strong $\pi-\pi$-interactions between the phenothiazine groups in the poly(vinylphenothiazine) PVMPT in their oxidized states, a high cycling stability, and rate capability was obtained.[68,69] Batteries based on these materials feature a self-discharge of ≈10% within 3 days, which is comparable to other systems.[66]

Important aspects for the selection of the corresponding active moieties are the synthetic accessibility of the materials. First, the redox moieties itself has to be synthesized. Subsequently, the functional monomers have to be polymerized. Hereby, some materials (e.g., anthrachinone-based monomers) feature limitations due to a low solubility of the monomers as well as the resulting polymers. For the usage of aqueous electrolytes there is currently only a limited number of usable systems (e.g., PTMA/polyviologen). In particular, the TEMPO-based polymers allow high power densities. Quinone-type systems often feature higher stabilities. However, recent studied in the field of organic flow batteries have shown that the stability of organic species is limited in the case of RFBs and that some test methods/cycling tests could not reveal these instabilities.[70] Therefore some of the stabilities of the reported polymer-based batteries have to be reconsidered.

## 4.2. Conductive Additive

Polymers with defined redox moieties, that is, non-conjugated polymers, often possess rather low electric conductivities. For thin films (e.g., in PTMA) it has been demonstrated that electrons can be transferred via a hopping process within the film.[71] However, composite electrodes with a thickness in the µm-range the utilization of additional conductive additives is required. For this purpose, different carbon materials have been applied. Unfortunately, in most cases structure-property relationships are still completely unknown, that is, several conductive additives have to be screened in almost a trial-and-error approach when a new redox-active polymer is utilized. Currently, there is not "a" best carbon material, which can be used for all applications and polymers. The elucidation of structure-property relationships is an important topic.

The "simplest" materials applied are carbon particles. In this context, the commercially available graphite and SuperP have been used. However, the achievable performance is limited due to their comparably low surface area resulting in composites with low conductivity. Consequently, only rather low loadings of active material realized, limiting the specific capacity of the electrode.[27] The second generation of additives represent mesoporous carbons, such as the commercial Ketjenblack. These materials often lead to a better performance compared to carbon particles.[72]

Typically, the active-polymer (also crosslinked polymers can be used, the polymer has not to be soluble), the carbon material and the binder are mixed to a slurry (see also Figure 3). Depending on the used solvent (water or *N*-((methylpyrollidone)) the binder can be changed ranging from poly(vinylidene difluoride) (PVDF) to carboxymethylcellulose. The resulting slurry is used for the doctor blading resulting in the corresponding electrodes with thicknesses in the 100–200 µm-range. Consequently, capacities of ≈4–5 mAh cm$^{-2}$ can be obtained by such electrodes. Moreover, also other approaches for the preparation of the "polymer carbon composites" have been investigated. For instance, the melt polymerization in the presence of carbon was studied.[73] Composites of PTMA and 30% carbon featured already good conductivities.

One of the most promising conductive additives are vapor-grown carbon fibers. The application of these carbon fibers also leads to a better mechanical performance of the electrodes.[74] Due to the optimal morphology of the composite electrode, high loadings of active polymer (80 wt%) are achievable also enabling a high power capability (50C).[75] This performance can be further improved if nanostructured conductive additives such as graphene or carbon nanotubes are utilized. For example, very high material loadings of PTMA (96 wt%) could be achieved with CNTs.[76]

Overall, the conductive additive has to provide a sufficient conductivity at a minimal mass loading, in order to achieve high loadings of active material can be. Noteworthy, the resulting morphology has to enable a full charging/discharging of the active material, that is, percolation pathways for charges as well as ions of the electrolyte have to be present. Considering commercial applications loadings of the active material of ≈60% are desired and the costs of the carbon material will become crucial (limiting the usage of expensive carbon materials).

### 4.3. Polymeric Binder

The composite electrodes comprising the active material often include polymeric binders. These materials should increase the mechanical stability of the corresponding electrode as well as providing a good contact between the current collector and the composite electrode. Typically binders also used in lithium-ion batteries are fluorinated polymers such as PVDF and poly(tetrafluoroethylene). Due to the need to use organic solvents for the processing of these binders, polymer binders for aqueous processing have also been established—namely carboxymethylcellulose.[74] It has to be noted that up to now, there is no systematic investigation of new binder materials, specially dedicated to polymer-based batteries. The utilization of ionic binder materials as well as conductive binders would be of great interest.[77] For instance, poly(ionic liquids) have already

been successfully utilized for lithium-ion batteries.[78–80] Due to their ionic structure, the ion conductivity within the composite is increased in comparison to the standard binder PVDF. Therefore, such ionic binders often lead to increased specific capacities as well as increased stabilities over many cycles.

### 4.4. Electrolyte

One key component for the use of polymeric electrodes is the electrolyte (i.e., solvent and salt), which is, however, often overlooked. Due to the extensive testing of half-cells against lithium anodes, many applied electrolytes are simply "borrowed" from LIBs, that is, organic carbonates with lithium salts (e.g., tetrafluoroborate, perchlorate, hexafluorophosphates). Thereby, the potential of developing tailor-made electrolytes for polymer batteries has not been addressed yet in detail.

Noteworthy, a polymer-based battery—in particular batteries with two polymeric electrodes—does not have a specific necessity for certain ions such as the lithium-ion battery, which requires the use of lithium ions. Hence, other ions can be used that enable for instance the fabrication of metal-free batteries, for example, by employing tetrabutylammonium salts.[81] Moreover, different cell configurations have to be considered.[25,26] LIBs are based on the cation rocking chair principle, which can also be the case for some polymeric materials.[26] Interestingly, also an anion-rocking chair principle can be present in polymer-based batteries—for instance for PTMA and polyviologen as active materials.[48] In contrast to the former system, here only the anion conductivity is of importance and, hence, a typical electrolyte for LIBs might not be the best choice. Whereas the two rocking-chair cell configurations are based on electrolytes with constant ion concentration, the third system—the dual-ion principle[82]—leads to changing ion concentrations, where and the electrolyte serves the reservoir for ions. For instance a battery based on PTMA and lithium such as reported works according to dual-ion principle.

Lower cell voltages in polymer-based batteries also allow for the utilization of organic solvents other than carbonates (e.g., acetonitrile[71]) or even water.[83,84] In general, ionic liquids (ILs) are often considered as alternative electrolytes for battery applications,[85] and indeed ILs have also been utilized for TEMPO-based polymer batteries.[86,87] Moreover, polymerized ILs were applied as solid electrolytes.[88,89] Despite only few examples, solid-state electrolytes/polymer electrolytes have only been scarcely reported for polymer-based batteries. However, solid state electrolytes are of particular interest considering the potential roll-to-roll fabrication of polymer-based batteries. Within this context further developments are required in order to pave the way for applications. Recently, crown ethers have been studied as additives in electrolytes, which lead to an increase in the cell voltage of ORBs based on PTMA and lithium.[90]

## 5. Are Polymer-Based Batteries Already Used in Commercial Applications?

Despite the still existing need for further scientific research, polymer-based batteries have been utilized in commercial applications. Astonishingly, the first attempts date back over 30 years. In the late 1980s two company consortia developed

polymer-based batteries. Bridgestone/Seiko used polyaniline (with lithium anode) and BASF/VARTA used later polypyrrole.[91] Despite having lower energy densities than at the utilized NiCd-batteries at that time, these batteries can be considered as more environmentally friendly. However, after a few years, this cell chemistry was discontinued, and the next years have been very quiet in regards to commercialization of polymer-based batteries. Only in the early 2000s the Japanese company NEC started to develop new polymer-based batteries utilizing PTMA. In the following years different potential applications have been presented: from a computer back-up system to a battery integrated into a flash card. Latter application was one of the first applications utilizing the special properties of these batteries—the high power density (i.e., charging/discharging within a few seconds). Nevertheless, these systems have not found a commercial application. Today, Evonik Industries provides materials for printable, polymer-based batteries, which can be used for thin and flexible devices.[92]

## 6. Conclusions and Outlook

The recent years have shown an increasing interest in polymer-based batteries. The large structural variety of organic materials offers a multitude of different possible structures of redox-active polymers, which can be utilized as active materials. However, despite the large number of available materials, the number of full-organic batteries is still rather small. Furthermore, the extension of linear polymers to the second dimension is an interesting approach yielding layered covalent organic frameworks (2D COFs) featuring redox active moieties. Overall, polymer-based batteries offer some unique properties. High power densities can be achieved, and flexible or even bendable electrodes and, subsequently, devices can be fabricated. The materials utilized do not contain (heavy) metals and open up the possibility for a sustainable battery fabrication. Yet, with more and more battery types evolving, the borders between the different battery systems are becoming increasingly blurred—for instance a polymer-based battery can also be considered as special type of lithium-ion battery (i.e., lithium anode plus polymer cathode) or as a special dual-ion battery. Future research will take advantage of the large structural varieties available within organic polymers. Further, block copolymers offer a good opportunity to tune the morphology of the resulting electrodes.[93] In particular, characterization techniques developed for lithium-ion batteries offer exciting opportunities for in situ and operando investigations of polymer-based batteries. Similar to other applications of polymers in organic electronics, for example, in solar cells or PLEDs, the stability of the organic compounds is extremely important. Consequently, the limits of the currently known materials for polymer-based batteries have to be further explored and more stable systems to be developed and investigated. All in all, polymer-based batteries represent a highly interesting new battery type, which will enable new fascinating applications.

## Conflict of Interest

The authors declare no conflict of interest.

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