Toward radical polymer batteries: strategies, mechanism and perspectives

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This chapter gives a comprehensive overview of the recent advancement in the emerging field of radical polymer batteries, also named as organic radical batteries. The rationale behind the use of a polymer with stable radicals as an electrode-active material of a secondary battery lies in the fact that this type of radical polymer has powerful capability of rapid oxidation to a cation and reverse reduction to an anion during the charge/discharge process. Radical polymer batteries promise as the replacement for lithium-ion battery, due to its intriguing features of extremely rapid charge/discharge rate, low toxicity, long lifecycle, cost-effectiveness, and high performance. Thus far, through molecular design, a couple of strategies have been applied to afford radical polymers with high discharge capacity. Because of their high flexibility and lightweight, the dream of paper-like transparent battery would become true if both cathode and anode employ radical polymers. This chapter focuses on elaborating on the strategies toward this new type of battery, its underlying mechanism, composite electrodes, cell device fabrication, and future opportunities and challenges.

Keywords: radical polymers; secondary battery; redox reaction; electrode-active materials; charge/discharge

1. Introduction

The quest for portable or ubiquitous electronic devices in recent years has led to develop flexible and small rechargeable batteries with high energy and power densities. Nowadays, lithium-ion batteries represent the canonical rechargeable power sources compatible with portable electronics, and can provide energy densities above 190 Wh/kg [1]. Thus, it is not surprising that they find a broad spectrum of applications into various fields and become indispensable in our everyday lives. However, the use of metal- or metal oxide-based materials such as LiCoO$_2$, LiMnO$_2$, and V$_2$O$_5$ as a cathode-active material brings inescapable problems into lithium-ion batteries such as short service life, thermal safety, high cost and toxicity, capacity restraint, and low tolerance [2, 3].

Alternatively, polymeric electrode-active materials stand out as excellent candidates for rechargeable batteries, primarily due to their easy processing, light weight, environmental benignity and extreme flexibility. The discovery of conducting polymers [4-7] has spurred the exploitation of them as potential alternatives to inorganic-based electrode-active materials [5, 6]. Unfortunately, the intrinsic limitations of these materials such as the low degree of doping, slow electrochemical processes, and fluctuating voltage present a formidable obstacle to their practical applications. On the other hand, redox polymers containing ferrocene [8], tetrathiafulvalene [9], or carbazole [10], butylviologen dibromide [11] were also investigated for electrode-active materials. The redox centers pendant to the main chain backbone give rise to electrochemical behaviors as well as the conductivities through exchange electrons by the way of hopping between redox sites in the polymer. Nevertheless, these redox polymers encounter problematic practical issues including the concurrent decomposition during repeated redox reactions and the lack of long-term stability arising from the dissolution of polymer layers into electrolyte solutions, which impeded further studies to employ them as active materials for batteries.

Very recently, the pioneering report by Nakahara et al. [12, 13] has shown that radical polymers can be employed to perform as a cathode-active material for a secondary battery, which has incited researchers to initiate activities on the so-called “radical polymer batteries” (or “organic radical batteries”). This new type of rechargeable battery utilizes reversible redox reactions of stable radical functional groups in the polymer as its cathode and/or anode reactions [14, 15], and is characterized by a short charging time, a long life cycle, high power and energy densities, environmental friendliness, and capability of fabricating purely organic, flexible, paper-like, and transparent rechargeable energy-storage devices [16, 17]. Through tuning the molecular structure, radical polymers for anode-active materials are also achievable, and so the dream of full-polymer flexible battery can be realized [17].

This review aims to bring witness of the state-of-the-art development of radical polymer battery, emphasizing the underlying mechanism of this new type of battery, molecular design and synthetic approaches of radical polymers, fabrication of composite electrodes and battery cells, as well as the imperativeness and future challenges in this ever-growing field.

2. Electrochemical feature of radical redox reaction

In general, an organic radical molecule bearing one unpaired electron is unstable and intractable species. Fortunately, stable organic radicals can be obtained by chemical modification through a combination of the resonance effect of
electrons and the sterically hindered effect of substituent groups around the radical center [18, 19]. A stable radical compound was first synthesized in 1961 [20]. Since then, a series of stable radical structures, such as nitroxyl, phenoxyl, galvinoxyl, hydrazyl, and verdazyl, have been discovered one after another [15]. To date, many derivatives of these stable radical structures have been successfully synthesized. Because stable radical compounds have an electron spin in spite of being organic materials, they have been considered to have a promise as ferromagnets, which has led to the evolution of organic ferromagnets with higher spin numbers [21-23]. Chemical groups such as nitroxyl, phenoxyl, and hydrazyl are robust structures with less reactive unpaired electrons in the uncharged state. The well-known examples of stable radicals are referred to as nitroxide radicals including 2,2,6,6-tetramethylpiperidinyl-N-oxyl (TEMPO) and 2,2,5,5-tetramethylpyrrolidin-1-oxyl (PROXY), which are stable under the ambient condition as a result of delocalization of an odd electron in oxygen centered radical onto a nitrogen atom [24]. They have found applications into a variety of fields, to name a few, spin labels for investigating conformation and structural mobility of biological systems [25, 26], scavengers of unstable radical species [27], and oxidizing agents [28, 29]. Most intriguingly, polymers carrying TEMPO or PROXY robust radicals can be applied to cathode- or anode-active materials in radical polymer batteries. Because of the smooth and fast electrochemical reaction of nitroxide radical, this type of battery is chargeable and dischargeable with high current density and high efficiency.

The nitroxide radical displays two redox couples, namely, oxidation to a cation and reduction to an anion: it can be oxidized to form the corresponding oxoammonium cation, the oxidation process of the radical is reversible and leads to p-type doping of the radical material, and it can also be reduced to the aminooxy anion, thus resulting in n-type doping of the material. Fig. 1 shows the charging and discharging mechanisms of a prototype nitroxide radical-based radical polymer battery [17]. During the charging process, the p-type radical polymer in the cathode is oxidized to the oxoammonium form. During the discharging process, the nitroxide radical is regenerated by the reduction of the oxoammonium. The most important electrochemical feature of nitroxide radical redox reactions is the extremely rapid electron transfer with a transfer-rate constant of \(~10^{-7}\) cm/s, about six orders faster than that of other organic redox couples like disulfides [12].

3. Unique characteristics of radical polymer batteries

Similar to the commercialized lithium-ion battery, a radical polymer battery usually consists of cathode and anode active electrodes separated by a porous film immersed in an electrolytic solution. The cathode of radical polymer battery uses p-type radical polymer for replacing lithionated metal or metal oxide materials used in a lithium ion battery. Furthermore, if the anode of a radical polymer battery also employs n-type radical polymer to replace the graphite anode in a lithium ion battery, a new type of fully polymeric battery will be achieved.

There are many unique features of radical polymer batteries as compared to other secondary batteries (e.g. lithium ion batteries). The most outstanding performance of radical polymer batteries is the rapid charging capability, for example, it is enabled to charge up to 80% within 1 min (60 C), which facilitates it to being charged whenever and wherever necessary [30]. The rapid electron-transfer processes of the nitroxide radical in the polymer generate high charging and discharging rates. A short charging time would lead to significant advantages in the use of portable electric devices equipped with a secondary battery. Conventional lithium ion batteries cannot be rapidly charged because the charging process involves the slow de-intercalation of lithium ions from the metal oxide cathode, often taking more than 30 minutes for the full charging [31].

The other striking characteristic of radical polymer batteries is the high power capability, which originates from the large heterogeneous electron-transfer rate of redox centers and the efficient mass-transfer process within polymer layers, allowing the facile accommodation of electrolyte ions to compensate charges generated from neutral radicals [14]. Also, the fast-reaction kinetics of the active material during charge-discharge operations leads to a high power-rate capability for the battery. Another unique feature of radical polymer battery is its extraordinary cycle life. No significant capacity fade is observed during a cycling regime lasting more than 1000 cycles. The long cyclability of the cathode has been attributed to the chemical stability of the nitroxide radical as well as to the absence of structural changes in the organic polymer during the charge–discharge processes [14, 24].

Furthermore, conventional batteries generally use heavy metals such as mercury, lead, or cadmium—all toxic substances that would cause serious environmental damage if not properly disposed of at recycling centers [1]. In contrast, the fact that the nitroxide radical polymer is completely combustible to yield only carbon dioxide, water and a small amount of nitrogen oxide is another attractive nontoxic feature of this material. This type of battery is also neither flammable nor explosive. Other advantages of radical polymer battery encompass tunable redox property via molecular design, mechanical flexibility, processing compatibility (e.g. film casting from solution), and lightweight. These allow it to promise as high power density and environmental benign secondary battery for the next-generation energy-storage device.
4. Synthetic strategies toward radical polymer batteries

Molecular design and synthesis represent powerful strategies for making radical polymers. To date, radical polymers fall into one of two categories: p-type and n-type, which have been used for cathode and anode of a radical polymer battery, respectively. The two main components of most radical polymers are the macromolecular backbone and the robust radical center. A few key requirements of molecular design of radical polymers for the use in rechargeable batteries are given as follows: (a) a radical polymer must be robust over a long period of time; (b) it possesses insolubility in but affinity to electrolyte to support the ionic conductivity; (c) the unpaired electrons in the polymer must be sufficiently unreactive in the electrolyte; (d) it can support high energy density. Over the past decade, a variety of synthetic strategies have been advanced for meeting these design requirements, and the major backbone polymers include polymethacrylate, polystyrene, polyether, polysiloxane, poly(vinyl ether), polynorbornene, polyacetylene, cellulose, and DNA complexes. Since it is impossible for radical-bearing monomers to perform radical polymerization, most of radical polymers were synthesized by an indirect method, that is, polymerization of monomers containing amino group followed by the oxidation to afford radical polymers [12, 13, 15]. However, the obvious drawback of this method is incomplete oxidation of amino group along the macromolecular chain, which in turn leads to relatively low power density of this kind of battery [12, 13]. Therefore, a direct method of polymerizing radical monomers is much more appreciated for these systems where the radical is tolerant of catalysts [32].

4.1  p-Type radical polymers

4.1.1  Poly(methacrylate)-based radical polymers

Poly(2,2,6,6-tetramethylpiperidinyloxy methacrylate) (PTMA, P1) was the first polymer to be examined for radical polymer batteries, which was synthesized by radical polymerization of a methacrylate monomer bearing an amino group and the subsequent radical formation of the polymer by the successive oxidation [12, 13]. The good solubility of this polymer in common solvents made it amenable to processing using wet, printing and roll-tape techniques. The theoretical charge capacity of PTMA as the cathode-active material was predicted to be 111 mAh/g, which was about two-thirds of the charge capacity of metal oxide-based cathode materials (150-170 mAh/g) in conventional lithium-ion batteries [2]. But experimental results demonstrated that the first fabricated batteries had a discharge capacity of 77 mAh/g with an average discharge voltage of 3.5 V. The performance was largely improved in their subsequent studies to achieve 100% active material utilization using a solution-based process [33] and a water based slurry method [34] for the cathode fabrication. It is worth mentioning that the capacity remains unchanged for over 500 cycles of charging and discharging at a high current density of 1.0 mA/cm².

One of the biggest challenges in utilizing PTMA as the cathode material of a battery is its solubility in organic electrolytes. Till now, several approaches (e.g. crosslinking and grafting) have been developed to address this challenge. Hauffman et al. synthesized poly(styrene)-block-poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate) (P2) diblock copolymers, which were self-assembled into nanostructured thin films of radical polymer cathodes [35]. UV curing was used to crosslink the PS block for preventing the dissolution of PTMA block into the battery electrolyte and thus maintaining structural integrity of the cathode. The perpendicular orientation of PTMA cylinders allowed the continuity between electrochemical active moieties and the current collector. Hung et al. [36] synthesized nitroxide polymer brushes (P3) for thin-film electrodes via surface-initiated atom transfer radical polymerization and the patterned nitroxide polymer brush thin-film electrodes were fabricated by microcontact printing. Another strategy to immobilize radical polymers was to graft PTMA brushes onto silica nanoparticles (P4) [37]. The grafting density of PTMA brushes grafted on silica nanoparticles was 0.74-1.01 chains nm².

Because phenoxy radicals had a lower molar mass than comparable anode materials like galvinoxyls and feature a reverse redox reaction at a lower potential, they were used to fabricate electrodes for radical polymer batteries with higher capacities and cell potentials. Jahnert et al. [38] synthesized radical polymers (P5) bearing a methacrylate backbone and stable phenoxy radicals by free radical polymerization, followed by oxidation with PbO₂. Reversible redox reactions at relatively low potentials of -0.6 V (vs. Ag/AgCl) were observed.
4.1.2 Polystyrene-based radical polymers

Because it was ready to introduce radical moiety onto the phenyl ring of styrene, poly[4-(N-tert-butyl-N-oxylamino)styrene] (P6) and poly[3,5-di(N-tert-butyl-N-oxylamino)styrene] (P7) with respective radical densities of 2.97 x 10^11 and 4.27 x 10^11 unpaired electrons/g were synthesized via free radical polymerization of protected precursor styrenic derivatives and subsequent chemical oxidation. These polystyrene-based radical polymers were used as p-type cathode-active nitroxide radical materials, and they possessed a compact molecular structure and a relatively low molecular weight per active nitroxide site, giving rise to a high charge capacity [17]. Furthermore, they exhibited selective solubility in common organic solvents such as tetrahydrofuran and chloroform and remained insoluble in typical electrolytes containing propylene carbonate. Noticeably, the theoretical capacities of P6 and P7 were 141 and 194 mA h/g, respectively, which corresponded to a 26 % and 74 % enhancement over that of PTMA (111 mA h/g). The two nitroxide groups per repeated unit in P7 endowed the polymer with the highest capacity among structures thus far reported [12, 13, 15].

4.1.3 Polynorbornene-based radical polymers

Since stable radicals are compatible with transition-metal catalysts, it is quite possible to directly polymerize norbornene monomers bearing radical moieties. Interestingly, the discharge capacity of poly(norbornene-2,3-endo,exo-(COO-4-TEMPO)n) (P8) polymerized with a ruthenium catalyst practically reached its theoretical value (109 mA h/g) [32]. It should be noted that a series of polynorbornenes containing PROXY moieties were also investigated, and some of these polymers displayed high capacity (up to 117 mA h/g, practically coincided with the theoretical capacity values (119 mA h/g)) as well as quick discharge properties [39]. In order to facilitate the lithium ion transport, oxygen atom was introduced into the backbone of polynorbornenes to become polyoxanorbornenes, which were polymerized via ring-opening metathesis of the corresponding monomers containing TEMPO using a ruthenium carbene catalyst [40]. The capacity of the polyoxanorbornenes (P9 and P10)-based cells reached 107 and 92.8 mA h/g, respectively, corresponding to 98.3 and 85 % of their theoretical capacity values. The cells fabricated with P9 and P10 as cathodes demonstrated a promising cycle life, for instance, their capacity hardly deteriorated even after 100 cycles. Furthermore, another nernstian adsorbate-like bulk layer with a thickness of tens to hundreds nanometer of cross-linkable polynorbornene functionalized with TEMPO groups was developed for high-density charge storage purposes as well [41]. Such capability was pursued also with a view to maximize a storage capacity of radical polymer batteries using organic polymers as electrode-active materials. Similarly, a radical polymer P11 with a polynorbornene backbone and bis-phenoxyl radicals possess high capacities and efficiency with no loss thereof after 100 cycles [38].

4.1.4 Polyacetylene-based radical polymers

Polyacetylenes (P12-P14) were polymerized directly from acetylene monomers bearing radical moieties by using rhodium catalysts, and the capacities of cells fabricated with P12-P14 were 67, 82, and 23 mA h/g based on the weight, respectively [32]. Nesvadba et al. [42] developed a straightforward synthesis of a novel spirobisnitroxide (P15) by Rhodium-catalyzed polymerization. Cyclovoltammetry revealed two distinct reversible oxidation/reduction steps separated by ca. 740 mV indicating the formation of the corresponding oxoammonium cations. Furthermore, 3 mol% of N, N'-dipro-2-ynyl-oxalamide was used to prepare crosslinking network. If the oxidation of both nitroxide groups was considered, this polymer possessed an unprecedented high theoretical charge capacity of 174 mA h/g. Evaluation of the cross-linked polymer as a cathode material for a radical polymer battery showed very good cycling stability when the potential was kept below the oxidation potential of the five-membered nitroxide subunit. A presumable irreversible degradation of the polymeric backbone occurred at higher potentials, limiting the experimentally obtained charge capacity to 73 mA h/g.
4.1.5 Polythiophene-based radical polymers

A conjugated polymer backbone like polythiophene is expected to exhibit semiconductivity and thus facilitate electron transfer in the electrode. The first polythiophene derivative (P16) bearing TEMPO radical was synthesized by Aydin, et al. through the oxidative chemical polymerization of its monomer [43]. The first radical polymer battery utilizing a TEMPO bearing polythiophene based cathode material demonstrated an initial specific discharge capacity of 79 mA h/g (87% of the theoretical capacity) and an average output voltage of 3.6 V. The specific energy capacity initially discharge was 268 W h/kg. Later, Aydin, et al. synthesized another polythiophene (P17) bearing two (2,2,6,6-tetramethylpiperidin-1-yl)oxidanly (TEMPO) radicals per repeat unit and showed a completely reversible electrochemical oxidation [44]. This radical polymer was used as a cathode-active material for a rechargeable lithium ion battery, exhibiting an initial specific discharge capacity of 88.8 mA h/g (about 82% of its theoretical capacity of 108.8 mA h/g) and a specific energy density of 321 mW h/g. Lin et al. [45] synthesized PTMA-grafted polythiophene (P18) by first synthesizing the polythiophene-based macroinitiator PEBBT from 3-[1-ethyl-2-(2-bromoisobutyrate)]thiophene and then grafting with poly(2,2,6,6-tetramethylpiperidin-4-yl methacrylate) (PTMPM) to yield PEBBT-g-PTMPM via atom transfer radical polymerization (ATRP). PEBBT-g-PTMPM was oxidized by m-chloroperbenzoic acid to yield P18 with a relatively high molecular weight (Mn = 483,300) that prevented the dissolution of the polymer into electrolytes. The cell performance showed that this radical polymer battery has good electrochemical stability and good cyclability.

4.1.6 Polypyrrole-based radical polymers

Xu et al. [46] reported the synthesis of two 2,2,6,6-tetramethylpiperidinyl-N-oxy (TEMPO) contained polypyrrole derivatives (P19) with different side-chain lengths by esterification of 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl free radical with pyrrole butyric acid and pyrrole caproic acid. The polymers were prepared by chemical oxidative polymerization. One polypyrrole polymer with short side-chain exhibited an initial discharge capacity of up to 86.5 mA h/g with two well-defined plateaus, while the other with long side-chain displayed a discharge capacity of 115 mA h/g. These superior electrochemical performances were ascribed to the flexible linking side-chain and the introduction of stable conductive polypyrrole main chain, which benefited the improvement of charge carrier transportation in the aggregated polymer bulk.

Three-dimensionally ordered macroporous nitroxide polymer brush electrodes (P20) for radical polymer batteries were synthesized via polystyrene colloidal crystal templating with electropolymerization of polypyrrole, modification of surface initiator, and surface-initiated atom transfer radical polymerization [47]. The discharge capacity of the resultant electrodes was proportional to the thickness of the inverse opal, and it is 40 times higher than that of the planar electrode at a discharge rate of 5C. Its cycle-life performance exhibited 96.1% retention after 250 cycles.
4.1.7 Polyethers/poly(vinyl ether)-based radical polymers

Due to the extreme chain flexibility and high affinity to electrolyte solution, polyethers P21 and P22 bearing stable TEMPO or PROXY radicals were also in pursuit for candidates as electrode-active materials [24]. These polymers were prepared by anionic polymerization of their corresponding epoxide derivatives and characterized by the high-density charge storage capability, resulting from the fact that the flexible ionophoric polymer with a low glass transition temperature allowed propagation of charges deep into the polymer layer from the polymer/electrode interface. The use of radical polymers as electroactive materials led to the fabrication of organic-based rechargeable devices with an excellent charging-discharging property. Test cells fabricated with the polymer/carbon composite as the cathode and a Li anode, sandwiching an electrolyte layer, performed as a secondary battery at output voltages near 3.6 V without substantial degradation even after 100 charging-discharging cycles.

Poly(vinyl ether) (PTVE, P23) was successfully achieved by direct cationic polymerization of a vinyl ether monomer bearing a TEMPO radical moiety [48]. Such radical polymer had a spin concentration of approximately $2.75 \times 10^{21}$ unpaired electron/g (100% spin per repeating unit), and in turn compact molecular design of PTVE produced a much higher capacity (theoretical capacity: 135 mAh h/g) than that of polymethacrylate (theoretical capacity of PTMA: 111 mA h/g) [13] or polynorbornene (theoretical capacity: 109 mA h/g) [32]. A Li/PTVE coin-type cell consisted of a PTVE/vapor grown carbon composite electrode possessed discharge capacity of PTVE is 114 mA h/g (84% of the theoretical value). An aqueous electrolyte-based radical polymer battery based on PTVE demonstrated very fast charging characteristics of 3 mC/cm² in as short as 3 seconds, because PTVE is electrode-active and hydrophilic, which allowed it to show a reversible one-electron oxidation capability even in aqueous electrolytes [31]. On the other hand, poly(allene ether) P24 containing TEMPO was synthesized by free radical polymerization of 4-allenylloxyl-2,2,6,6-tetramethyl piperidine at 100 °C to obtain the homopolymer and then quantitatively oxidized by $\text{H}_2\text{O}_2/\text{Na}_2\text{WO}_4/2\text{H}_2\text{O}/\text{EDTA}$ at room temperature [49]. The unsaturated structure of P24 due to the attached double bonds enhances the electron transport. Such a radical polymer exhibited excellent charging/discharging reversibility and stability with a high columbic efficiency of 98%.

4.1.8 Polysiloxane-based radical polymers

A silicone-based radical polymer (P25) was synthesized by hydrosilylation of poly(methylhydrosiloxane) with 4-allyl-2,2,6,6-tetramethylpiperidine-N-oxyl ether in the presence of a platinum- or rhodium-catalyst. A reversible redox peak at 3.56 V (vs. Li/Li⁺) was observed by cyclovoltammetry measurements [50]. A coin-shaped cell showed a discharge capacity of 46 mAh/g, which was 47% of the theoretical capacity of (98 mA h/g). A directly TEMPO-substituted silicone, poly[methyl(2,2,6,6-tetramethylpiperidine-N-oxyl-4-oxyl)silicone] was also obtained by rhodium-catalyzed dehydrogenative alcoholysis of poly(methylhydrosiloxane) with TEMPO-OH. The coin-shaped cell showed a discharge capacity of 80 mAh/g, which was 69% of the theoretical capacity of 116 mAh/g.

4.1.9 Biomaterial-based radical polymers

In contrast to synthetic polymers discussed above, biomaterials are very intriguing from the viewpoint of increasing interests of biocompatibility and environmental concerns. Recently, a series of ethyl cellulose derivatives and cellulose acetate derivatives P26 carrying TEMPO or PROXY radicals were synthesized with moderate number average molecular weights of 62,400–126,000 in 84-88% yield by the reaction of 4-carboxy-TEMPO or 3-carboxy-PROXY with residual hydroxyl group of ethyl cellulose or cellulose acetate. These cellulose derivatives demonstrated the discharge capacities ranging from 42.8 to 61.1 mA h/g, and in particular, the total capacity of a cellulose acetate carrying TEMPO-based cell reached 61.1 mA h/g, which corresponded to 153% of the theoretical value for one electron redox reaction. More recently, Qu et al. [51] disclosed the first example of radical polymer battery with DNA. As we know, DNA is an anionic polyelectrolyte, which can be quantitatively reacted with cationic surfactants in water to form DNA/cationic-lipid complexes. All the TEMPO-containing DNA–lipid complexes displayed reversible two stage charge/discharge processes, the discharge capacities of which were 40.5–60.0 mA h/g. The total capacity (60.0 mA h/g) of one TEMPO-containing DNA–cationic lipid complex P27 reached 192% of the theoretical value for one electron redox reaction, suggesting two-electron redox reactions between the cation and the anion.
4.2 n-Type radical polymers

Till now, most of work focused on exploiting p-type radical polymers for cathode-active materials. Therefore, the challenge for all polymeric batteries is to develop an n-type redox polymer as an anode-active material. The first n-type nitroxide radical polymer, poly[4-(N-tert-butyl-N-oxyamino)-3-trifluoromethylstyrene] (P28) was synthesized by ortho-substitution of polymer P6 with an electron-withdrawing trifluoromethyl group [17]. This polymer possessed radical densities of $1.82 \times 10^{21}$ unpaired electrons/g and showed a reversible redox at -0.76 V vs Ag/AgCl, which was attributable to the n-type redox pair between nitroxide radical and aminoxy anion. During the charging process, the p-type nitroxide radical polymer in the cathode was oxidized to the oxoammonium cation form, whereas the n-type polymer in the anode was reduced to the aminoxy anion form. In the case of discharging process, the nitroxide radicals were regenerated through the reduction of the oxoammonium cation and via oxidation of the aminoxy anion in the cathode and anode, respectively. The tunability of nitroxide radical polymers from p-type to n-type behavior using substituent electronic effects paves a novel way to stable n-type radical polymer for prospective all-polymeric batteries.

Jahner et al. [52] reported the synthesis of electroactive functionalized polymers (P29-P31) with n-type nitroxides. Electron-poor phenyl nitroxide radicals with substituents like trifluoromethyl-, flurine- or nitro-groups constituted the basic structural motif. Monomers were synthesized employing thio-click chemistry and polymerized by free radical polymerization or cationic polymerization techniques. All these polymers showed stable redox behavior over several cycles at potentials of -1.3 V (vs. Fe/Fe³⁺) and lower. These nitroxides, substituted with electron-withdrawing groups, possessed redox-potentials lower than many of the commonly used nitroxide-radicals and represented interesting candidates for redox-active polymers for radical polymer batteries.

N-type radical polymer, poly(nitronylnitroxylstyrene) (P32) was proven to be a new class of bipolar redox polymer and enabled a totally organic-based rechargeable battery with simple, symmetric configuration (poleless battery) and rocking-chair configuration in conjugation with n-type poly(galvinoxylstyrene) (P33) [53]. A charge capacity of 29 mAh/g (91% of the available capacity for the total loaded amount of cathode and anode), 90% of the original capacity maintained at 150 C rate, and good cycle stability exceeding 250 cycles were
obtained. Beside the shape flexibility and reduced environmental impact of such plastic-based batteries, bipolar redox-active radical polymers will promise potential applications such as actuators, organic complementary circuits, and organic transistors.

Jahnert et al. [54] explored the use of galvinoxyls with poly(acetylene) backbones (P34) as redox-active materials for radical polymer batteries with aqueous electrolytes and examined the charge and discharge behaviors. Monomers were synthesized employing C–C coupling reactions, polymerized with Rh(nbd)BPh₄ as a catalyst, and subsequently oxidized. These galvinoxyl-containing polymers represented interesting anode materials for radical polymer batteries and employed stable organic radicals, which were bound to polymers; hereby, metals and metal oxide, as active compounds, could be replaced. With the use of ethynylphenyl-galvinoxyles (P35) as an anode-active material and poly(2,2,6,6-tetramethylpiperidine-N-oxyl)methacrylate (PTMA) as a cathode-active material, metal-free batteries with an aqueous and environmental-friendly electrolyte are built. The synthesized radical polymers showed reversible redox reactions over dozens of cycles and are stable under ambient conditions for months. The use of an aqueous electrolyte gave the possibility of using these cells in biological environments. The fabricated all-polymeric radical battery represented a first step to the use of synthetic polymers in future devices, also using inkjet printing as a processing technique.

5. Design and applications of radical polymer batteries

5.1 Fabrication of radical polymer electrodes

Despite many unique features of radical polymers, they have some intrinsic limitations like electrical insulation that restrict their applications as an electrode material for batteries. Much effort has been devoted to enhancing the electrical conductivity and charge collection of radical polymer electrodes by using conductive materials, among which carbon materials such as carbon black, carbon fibers, carbon nanotubes and graphenes are most widely used. The working mechanism of the radical polymer electrode involves five electron transfer steps [55]: (a) interfacial electron transfer from the current collector to the conductive carbon; (b) electron transfer within the carbon network; (c) heterogeneous electron transfer at the carbon/polymer interface; (d) electron hopping between radical sites within the radical polymer, and (e) diffusion of electrolyte counter anions throughout the composite. However, the performance of these batteries heavily depends on the quality of radical polymer cell and on the degree of polymer dispersion. Isolated and large polymer aggregates suppressed the penetration of counter ions and greatly reduced the total capacity. Therefore, homogeneous dispersion and strong interaction between carbon materials and radical polymers were crucial to achieving significantly improved cycle performance and capacity. A suitable radical polymer for batteries should be insoluble in the electrolyte and contain minimal amount of conductive carbon to balance between specific capacity and power capabilities. A few strategies have been made to attain this goal, as illustrated below:

5.1.1 Direct mixing of radical polymers with carbon materials

The first approach is to mix radical polymers with carbon materials to form composite electrodes for rechargeable radical polymer batteries. Carbon materials play a dual role in such composite electrodes: they not only enhance the charge collection efficiency but also absorb the soluble species and thus retard the slow dissolution of the active material. The charge/discharge performance of the radical battery was dominated by the interfacial electron transfer process at the current collector/carbon interface and the rate performance would be much improved by suitably design the interfacial structure [56]. The highest possible active material content in the electrode is of utmost significance for achieving a high specific energy for the electrode and hence for the cell. Being an electrical insulator, PTMA is required to blend with a conductive material like carbon black for fabricating a cathode. Thus, it is essential to control the active material content in the cathode as well as the cathode thickness, ensuring that that a continuous conductive network of carbon is present, which can support the transfer of charge during the redox reactions. Only a low active material content of ~10 wt% was present in the early studies of PTMA radical battery [12, 13, 57], which was elevated to a higher content of 30–50 wt% in their recent studies [33, 34, 58]. It was found out that a thin cathode of ~17 μm performed the best for delivering full discharge capacities at moderate C-rates [59].

5.1.2 Crosslinking of radical polymers

Incorporation of conductive agents was performed afterwards, either by physical blending with crosslinked PTMA or by mixing solubilized polymer with conductive carbon. The drawback of these approaches is that soluble PTMA is gradually dissolved ant that physical blending of carbons with cross-linked polymer hinders the formation of a
nanoscale-homogeneous composite material. The melt polymerization of TEMPO-based methacrylates (PTMA) afforded a crosslinked, insoluble PTMA radical polymer-carbon composite, in which carbon was dispersed homogeneously on the nanoscale [60]. These characteristics endowed better electrodes constructed using melt-polymerized PTMA with superior electrochemical performances while maintaining a low carbon content. Sukegawa et al. synthesized a crosslinking poly(4-glycidyloxy TEMPO) via anionic ring-opening copolymerization of 4-glycidyloxy TEMPO and a diglycidyl ether using a pentaerythritol/phosphazene base initiator [61]. A fast and reversible charge storage capability was established for the polyethyler/single wall carbon nanotubes (SWCNT) composite layer with a layer thickness of several tens of micrometers. This composite electrode exhibited a quantitative charging/discharging at high current densities with a long cycle life, due to the low resistance supported by the conductive network of SWCNT.

5.1.3 Wrapping radical polymers onto carbon surfaces

Current collection is an important issue in radical polymer battery research, which may be solved by the addition of metallic carbon nanotubes to the poly-redox material. The efficient wrapping of the polymer around the nanotubes represents an effective method for enhancing current collection. Polyacetylene backbone containing TEMPO radicals (P36) were used to wrap with carbon nanotubes, and scanning tunnelling microscopy of semiconducting carbon nanotubes treated with radical polymers showed helical wrapping morphology [62]. Polyacetylene containing TEMPO radicals (P36) had a higher theoretical capacity of 127 mAh/g. Lin et al. [63] reported the use of nitroxide radical polymer/carbon nanotube array electrodes for improving C-rate performance in radical polymer batteries, which was attributed to the continuous conduction paths for electrons provided by the array.

5.1.4 Grafting radical polymers onto carbon surfaces

Aquil et al. [53] designed composite electrodes by electrografting of PTMA on entangled and robust carbon nanotube networks. The key step of this approach involved the chemisorption of an alkoxyamine-bearing acrylate by electrografting onto carbon nanotube buckypaper, followed by the quantitative generation of the polynitroxide via thermal activation of the alkoxyamine pendant groups. This composite electrode showed a charge capacity of 104 mA h/g, which was attributed to the synergistic combination of the highly conductive carbon nanotube buckypaper of large 3-dimensional surface area with the grafted polynitroxide of high radical content. Du et al. [64] reported organic radical functionalized graphene via a simple esterification of carboxylic groups on graphene oxide with the hydroxyl group on 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl. The functional graphenes exhibited a high reversible capacity with excellent cycling stability for lithium storage in terms of 1080 mA h/g at a current density of 100 mA/g after 400 cycles.

5.1.5 Reactive inkjet printing of electrodes

Janoschka et al. [65] developed a reactive inkjet printing strategy for the manufacturing of printed electrodes used in radical polymer batteries. The low molar mass, electroactive radical polymer, PTMA, which was used for inkjet printing, was prepared by reversible addition-fragmentation chain transfer (RAFT)-polymerization and a subsequent partial oxidation. The incomplete oxidation was an easy way of obtaining a reactive copolymer, which not only bore electroactive sites but also chemically reactive amine groups. Electrodes of good stability, as proven by repeated charging/discharging experiments, were prepared by initiator-free, thermal crosslinking of the free amine-bearing PTMA and the epoxy-based crosslinker. By employing epoxidized carbon nanopowder as chemically reactive conductive additive a further improvement could be observed. The printed electrodes were stable for over one hundred cycles. This technique might be of interest for the manufacturing of patterned, flexible radical polymer batteries used in sensor devices, smart packaging, DNA chips, or battery-powered smart cards.

5.2 Cell performance

Practically, most of radical polymer batteries reported employed liquid electrolytes as a means for effectively transporting ions between the electrodes. A few typical examples are LiClO$_4$ in propylene carbonate [57], LiPF$_6$ in mixed carbonate solvents [13, 15, 33, 34, 58], tetraethylammonium tetrafluoroborate in dichloromethane or acetonitrile [12]. More recently, Kim et al. [66] have developed high-rate-capable, polymer electrolyte based on electrosyn poly(vinylidene fluoride-co-hexafluoropropylene) membrane activated with 1 M LiPF$_6$ in ethylene carbonate/dimethyl carbonate (1:1 by vol). The presence of fully interconnected pores and fibers with high surface area in the electrosyn membrane has resulted in high electrolyte uptake and imparts high ionic conductivity at room temperature for the polymer electrolyte. By employing a thin cathode of 17 µm thickness, a specific capacity of 111 mA h/g (100% of theoretical capacity) at 1 C (0.1 mA/cm$^2$) and about 88% of theoretical capacity at higher current densities up to 50 C has been accomplished. The replacement of liquid electrolytes by their polymer counterparts makes the radical polymer battery much lighter and safer.

The totally radical polymer battery can be constructed by using a p-type radical polymer as the cathode-active material and an n-type radical polymer as the anode-active material. A representative example is illustrated in Fig.2, where
PTMA (P1) was used as the cathode while poly(galvinoxylstyrene) (P33) was used as the anode [67]. This totally radical polymer battery exhibited a charge capacity of 32 mA h/g, which corresponded to 92% of the theoretical capacity (34.8 mA h/g). The fabricated cell also showed extremely high current capability, allowing rapid charging within 10 s and large discharge currents (360 C rate). It should be emphasized that the solubility of these radical polymers in solvents enabled them to easily fabricate flexible, thin-film, see-through, paperlike energy-storage devices by wet or solution-based processing techniques (e.g. roll-to-roll and inkjet printing).

5.3 Applications of radical polymer batteries

In view of its prominent performances, radical polymer battery has prospect to apply in a variety of fields ranging from power sources for laptop computers and mobile phones to ubiquitous appliances such as intelligent papers, smart cards, sensors, and radio frequency identification tags [15]. The excellent rapid charge–discharge and little self-discharge characteristics of this new class of battery make it attractive for electric vehicle applications and the new generation of energy devices, especially as a ubiquitous power source.

Inspired by the structure of radical polymer battery, a nonvolatile and rewritable memory architecture was constructed by employing PTMA (P1) as cathode and a radical polymer bearing galvinolate anion as anode, sandwiched by an electrolyte layer [68]. This memory device was based on the principle of nernstian electrochemical behaviors found in robust radicals, such as the 1e\(^-\) oxidation of TEMPO to the oxoammonium cation and the 1e\(^-\) reduction of galvinoxyl radicals to galvinolate anion[69]. Later on, another nonvolatile, bistable, and rewritable memory device was successfully fabricated using PTMA as a p-dopable material and poly(methyl methacrylate) containing silver salt as an n-dopable material [70]. Furthermore, a totally organic polymer-based electrochromic cell was developed using a polyion complex consisted of poly(decyl viologen) and poly(styrene sulfonate) (PV10-PS S) as an electrochromic material and a TEMPO-substituted polynorbornene P8 as a counter electroactive material [71]. The use of the organic redox polymers, not only for the low energy-driven electrochromic switching but also for the charge-storage purposes, allowed a universal design of a battery-like display device, with possible application to a flexible and totally organic electrochromic cell.

6. Concluding remarks and perspectives

Since the discovery of radical polymer batteries, dramatic improvements in fundamental understanding, device construction, and processing of electroactive materials have led to high efficiency and power density of such a unique secondary battery. The major accomplishment has been the development of a much deeper understanding of how molecular structures of radical polymers ultimately affect the device performance. The lessons learnt from the present generation of radical polymer battery will definitely assist in the design of the next generation of optimized full-polymer battery for replacing lithium-ion batteries.

Radical polymer batteries can be used not only as an alternative to lithium transition-metal oxide but also the electrode active material for various types of rechargeable devices. A totally radical polymer-based rechargeable battery has been reported. These batteries are attractive as flexible, printable, and green batteries. Furthermore, radical polymers have been used not only for rechargeable batteries but also for diodes, non-volatile memories, and electrochromic devices. The use of radical polymers is thus spreading as they become used as electro-active polymers for new functional devices.

Although a radical polymer battery exhibits a plethora of unique properties like satisfactory charge/discharge rate and excellent cycling performance, thus far, its charge storage capacity is still lower than that of a conventional battery like lithium-ion battery and its practical applications are still in the early stage. Therefore, the greatest challenge in
achieving a radical polymer battery with high power and high capacity is to design and synthesize new radical polymer with high radical concentrations as well as to optimize the fabrication process in the future. However, from the point of view of specific power per active material weight, radical polymer battery is superior to lithium-ion battery, and then it is very encouraging to serve as a high specific power energy source in electronic devices, which require high-power capability rather than high-energy density. For the purpose of fabricating full-polymer radical battery, it is imperative to develop high-performance n-type radical polymers and efficient polymer electrolytes.

Another challenge of further improvement of the high rate property or power-density of radical polymer battery is to overcome the poor electrical conductivity of radical polymers, which requires a much deeper level of mechanistic understanding of the process as well as develop and optimize new materials to capitalize on such new knowledge. For this purpose, it might be possible to introduce specific structures into radical polymers for achieving electrical conductivity along the main-chain backbone of the polymer, which would render high electron transport of these polymer electrodes. The future of the organic radical cathode appears to depend on the progress in organic synthesis technologies. Empirically, the pursuit of maximizing the redox capacity of the composite electrode is to increase the loaded amount of radical polymers while retaining their redox activity. Much room still exists for further improvement in radical polymer batteries, which deserves persistently and ultimately intensive endeavor.

References


