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The Emergence of "Redox Polymers" in the Field of Energy-Storage Applications*

Study Goals

- Knowledge of the history and development of energy-storage devices
- Knowledge of important redox polymers from the different eras

1.1 An Introduction to Battery Systems

In recent years, the market for stationary energy-storage systems has experienced a tremendous growth – a trend that is expected to continue almost undamped in the future (Figure 1.1) [1]. Moreover, the society calls for efficient, durable batteries to satisfy their specific wishes: electric vehicles, laptops, cell phones, wearable/portable gadgets, Internet of things (IoT), etc. [2]. To fulfill these as well as projected needs, worldwide research is focused on the improvement and development of tailor-made, energy-storage systems. In this respect, the implementation of new redox-active materials represents one approach, and *inter-alia* redox polymers have gained significant attention in recent years [3–7]. Before introducing these materials, the long history of energy-storage devices will be briefly summarized.

In 1936, numerous items – a ceramic pot, a tube of copper, and a rod of iron – were found in Khujut Rabu, Iraq. These artifacts have been assigned to the Parthian (150 BC–223 AD) or Sasanian era (224–650 AD). Though their actual meaning still remains unclear, it has been speculated that they were used as an "energy-storage device" (a potential of c. 0.8 V was calculated) [8]. Far later, the term "battery" was coined by Benjamin Franklin, who in 1748 compared multiple, simultaneously acting "Leyden jars" to an artillery battery [9]. The first electrochemical cell, the so-called "voltaic pile," was constructed by Alessandro Volta in 1800 [10]. In subsequent years, various alternatives of this original device have been created. From these, the Daniell cell (initially reported in 1836) represents the first practical

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An Introduction to Redox Polymers for Energy-Storage Applications, First Edition.
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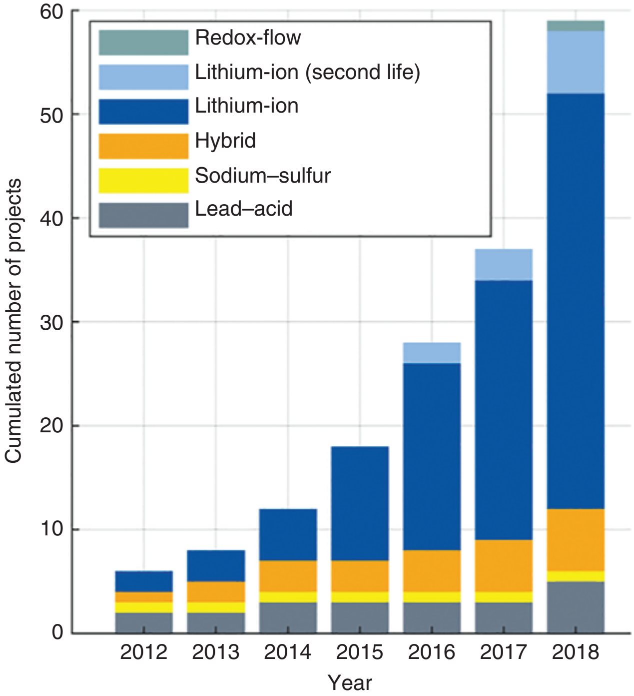

Figure 1.1 Development of the number of large-scale energy-storage projects in Germany according to battery technology [1]. Source: Figure reproduced with kind permission; © 2020 Elsevier B.V.

and durable power source, which even became an industry standard and was employed by the early British electrical telegraph networks [11]. All these batteries were "wet cells," which were constructed from glassware and contained liquid electrolytes; however, in many cases, their fragile and dangerous nature prevented any portable applications, and they were superseded by the portable, hence more convenient dry-cell batteries. In this respect, the Leclanché cell and Gassner's zinc–carbon cell – the first real "dry cell" batteries – have to be explicitly named; these dry cells offered potentials of 1.4 and 1.5 V, respectively [12]. The latter, patented in Germany in 1886, comprised a MnO_2 cathode, which was dipped into the NH_4Cl/$ZnCl_2$ electrolyte paste; the surrounding Zn shell acted as the anode [13].

Along these primary batteries, the secondary batteries, *i.e.* rechargeable batteries, were also disclosed in the second half of the nineteenth century. Credit must be given to Gaston Planté, who in 1859 invented the lead–acid battery, which could be recharged by applying an appropriate reverse current. This device can certainly be considered, so far, the most successful secondary battery [14]. Similarly, the first alkaline battery, the Ni–Cd cell, was invented in 1899 [15]. This cell, which then entered the market in 1910, offered a much higher energy density to that of the lead–acid battery but was by far more expensive. Research in the last century culminated in the development of the secondary lithium-ion batteries (LIBs) [16, 17]. Though initially studied by Lewis in 1912, LIBs were brought to market in the 1970s, and, today, LIBs represent the leading technology in the field of secondary batteries. The outstanding contributions in LIB research by J.B. Goodenough, M.S. Whittingham, and A. Yoshino were honored with the Chemistry Nobel Prize in 2019 [18]. Though LIBs feature distinguished benefits (*e.g.* low costs, high voltages, increased power densities), some serious downside aspects have to be noted. Firstly, LIBs are nonelastic and mechanically treated, leading to possible leakage and thus serious hazards [19]. Secondly, cobalt raw materials are required for the LIB fabrication. These materials are often mined under unsustainable mining conditions, which involve slavery and/or children labor work [20, 21]. Policies against these unacceptable mining conditions led to a significant increase in the world market prices for cobalt, which has recently led to overproduction stagnation [22]. Finally, large battery packs need reliable temperature-control systems to guarantee safe conditions and to prevent serious hazards, *e.g.* fires or explosions [23, 24]. These aspects limit the applicability of LIBs, in particular with respect to small and flexible devices (*e.g.* smart clothing, and packaging) or other demanding applications, such as grid stabilization and on-site storage [4].

Regarding their applications, redox polymers that are derived from organic raw materials represent one promising alternative approach [3–7]. For example, organic polymers allow the fabrication of flexible devices, and their use is almost independent from the fluctuating commodity prices of rare metals. Moreover, polymers can be synthesized in a wide range of structures and topologies, thus facilitating the preparation of tailor-made materials. Today, the field of redox-active polymers is a result of eight decades of research, which will be briefly summed up next.

1.2 Redox Polymers: A Short View on Their Long History

In 1920, Herman Staudinger published his famous article, in which polymers were defined as “long chains of high molecular weight, which are comprised of covalently linked repeating subunits, the self-styled monomers” [25]. Though his proposal met heavy opposition at the time, this perception represents the initial spark that ignited modern polymer science. His fundamental research on macromolecules and persistence was honored in 1953, when he received the Nobel Prize in Chemistry [26, 27]. Carothers, a pioneer in the field of synthetic polyesters and polyamides, suggested the first classification scheme for synthetic macromolecules, taking into account the monomer subunit as well as the applied polymerization technique [28]. This about 90-year-old material classification remains contemporary and is still commonly used to rationalize the differences between macromolecules synthesized *via* different polymerization methods (*e.g.* step-growth *vs.* chain-growth polymerization). The field of polymer chemistry has experienced a tremendous evolution, and a range of reliable controlled/living polymerization techniques (*i.e.* metathesis, ionic, and radical) has become available, thus enabling

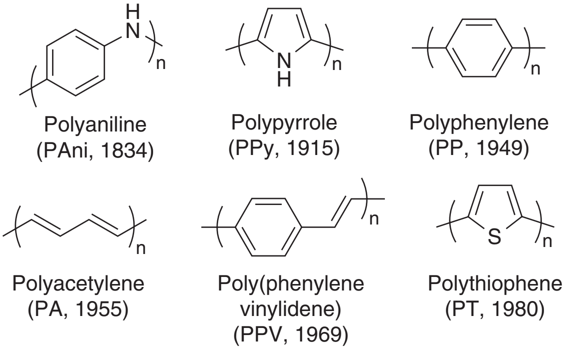

Figure 1.2 Schematic representation of the most relevant parent conjugated polymers along with their years of discovery. Source: [55], figure 1 (p.1413)/John Wiley & Sons.

the controlled and precise synthesis of polymers of various topologies (*i.e.* linear, star-shaped, and branched). However, Carothers' fundamental systematics are generally obeyed in all of these cases.

Concurrent with the fast development in synthesis and characterization, the focus of polymer research has moved away from the traditional areas of interest (*e.g.* tire technology or packaging materials) toward targets, which address the special needs of today's society [29]. Hence, tailor-made polymers with sophisticated properties can be offered for a broad range of applications, which have relevance for today's daily life style. The long list of potential applications includes photovoltaics [30–32], light-emitting devices [33, 34], electrochromic devices [35], smart coatings [36, 37], self-healing materials [38, 39], shape-memory materials [40, 41], bioimaging [42], carriers in drug/gene delivery [43–48], biodegradable packages [49, 50], and, last but not least, energy storage [3, 4, 51–53].

In 2000, the Nobel Prize in Chemistry was awarded to H. Shirakawa, A.G. MacDiarmid, and A.J. Heeger "for the discovery and development of electrically conductive polymers" [18]. Though it is commonly believed that these authors' collaborative research on polyacetylene (PA) represents the origin of conductive polymers, their history can actually be traced back to the middle of the nineteenth century [54]. The first, fully synthetic polymer, polyaniline (PAni), was already reported by F.F. Runge in 1834 [54–56]. Although pyrrole was discovered in 1834 [56], its oxidative polymerization to afford polypyrrole (PPy), as another type of conjugated polymer, was noticed by Angeli in 1915 [57]. The parent structures of the most relevant conductive polymers, along with their years of discovery, are shown in Figure 1.2. In general, their conductivity results from the (reversible) oxidation or reduction of the parent π-conjugated polymer.

1.2.1 The First Era of Redox Polymers

Due to the tremendous interest in these previously mentioned materials, nonconjugated, redox-active polymers have been overlooked for some time. The interest in such polymers with respect to energy-storage applications can be traced back to the early days of ion-exchange polymers, thus defining the first era of redox-active polymers (Figure 1.3). Cassidy proposed that polymers – in analogy to the proton-exchange capacity of acidic polymers – should also be able to exchange electrons, as another “fundamental particle” [58]. Due to the chaos of the World War II era, this conception was realized independently by H. Lauth and H.G. Cassidy. Thus, in 1944, Lauth filed a patent for poly(resorcin-trihydroxybenzene-formaldehyde) redox polymers, as water deoxygenation agents [59], whereas Cassidy studied the applicability of poly(vinyl quinone) (PVQ), as electron-exchange polymers [60]. In subsequent work, Cassidy *et al.* prepared a wide range of PVQ-type polymers and studied their properties as well as applicability [61–64]. The following years faced a scientific dualism between the Cassidy and Manecke groups [65], the latter first published a study in 1953 on “electron-exchange polymers” [66]. These authors mainly focused on polymers, which were equipped with 1,4-/1,2-benzoquinone [67–83] or 9,10-anthraquinone moieties [84]. These early contributions were summarized by Cassidy in his seminal textbook on “oxidation–reduction polymers” [58] as well as in numerous review articles [85]. Noteworthy, a range of other redox-active polymers was also investigated in this timeframe; these species however remained virtually marginal. During the first era of redox-active polymers, some prominent redox-active materials, which are commonly used nowadays, were initially published: polymers containing methylene blue [86], thiol [87], ferrocene [88, 89], indigo [90], and pyridinium or quinolinium moieties [91]. Moreover, Harwood and Cassidy reported polypeptides, which incorporated 2,5-dihydroxyphenylalanine or 3,4-dihydroxyphenylalanine (DOPA), as redox-active sites [92]. One further notable milestone is the synthesis of the first stable, polymer-bound free *N*-radicals. Henglein and Boysen prepared such a polymer by γ-irradiation of a precursor polymer [93]; more conveniently, Braun *et al.* obtained similar polymers by oxidizing the precursor polymer with PbO_2 or Ag_2O_2 in solution [94]. In the same context, the first report of poly(TEMPO methacrylate) (PTMA), as a nitroxide-containing polymer, is worth mentioning (TEMPO: 2,2,6,6-tetramethyl-piperidinyloxy-4-yl) [95]. Today, this polymer represents one of most used active materials in organic radical batteries (ORBs) [3, 53, 96].

In summary, the time was not ready for a significant technological breakthrough during the first era of redox-active polymers. These materials attracted only interest from a scientific point of view and their use was devoted mainly in water deoxygenation and H_2O_2 production [59, 97–101]. The first battery, which contained a redox-active polymer as an electrolyte, was invented in 1958 [102]; a few years later, the first secondary LIB using a redox polymer, as cathode, was demonstrated [103]. However, these inventions did not promote the technological breakthrough of redox polymers and were only on the scientific fringes for many years.

1.2.2 The Second Era of Redox Polymers

The second age of redox polymers, which appeared in the groundbreaking research of Heeger, MacDiarmid, and Shirakawa, was dominated by the class of π-conjugated polymers and notably polymers from the first era almost fell into oblivion. These

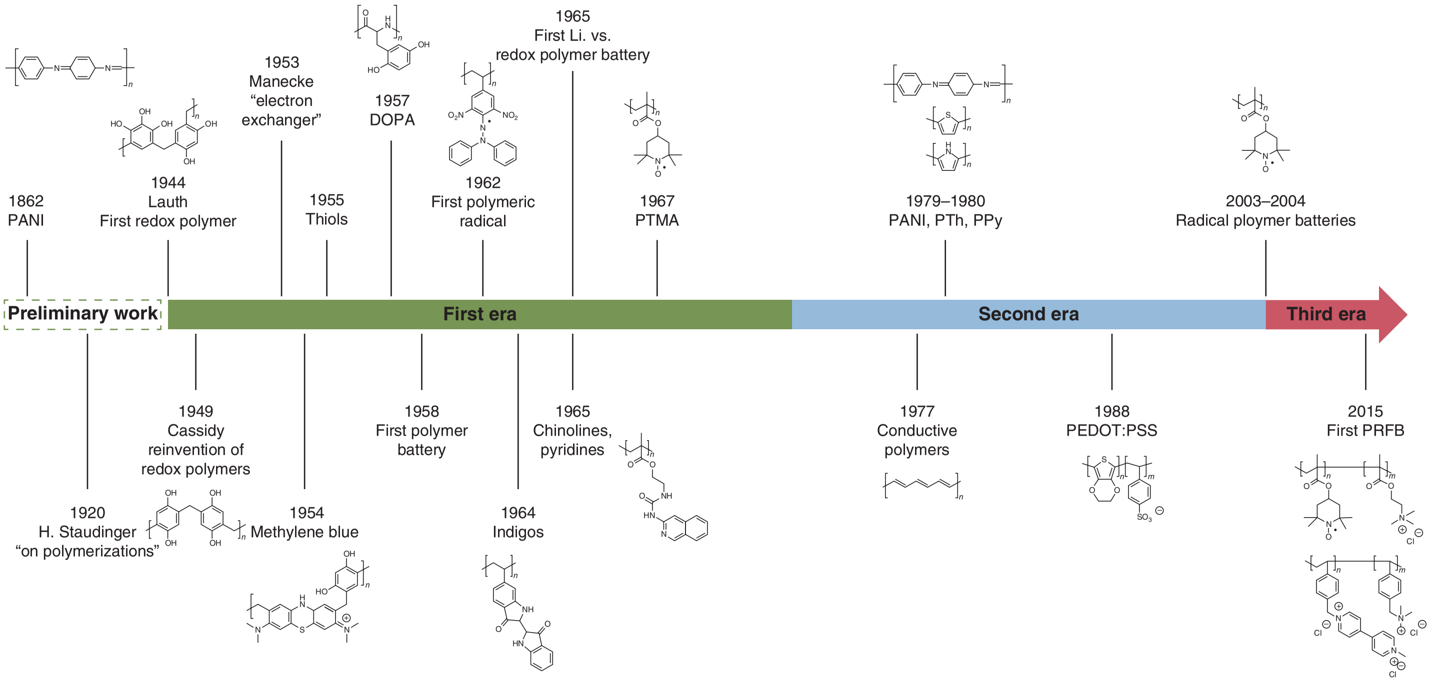

Figure 1.3 Timeline with the most noteworthy inventions and scientific milestones in the field of redox-active polymers [4]. Source: Figure reproduced with kind permission; © 2021 Elsevier B.V.

authors showed that (partially) oxidized PA exhibited a significantly increase in the electric conductivity when compared to the parent all-*trans*-PA [104]. However, the initial goal – replacement of Cu by organic polymers in electric wires – had to be abandoned, and the focus of interest shifted toward an improvement of the polymer's properties. Recently, Rasmussen summarized the fascinating history of PA; the reader is referred to this article for a detailed view on this topic [55]. At about the same time, new redox-active polymers were synthesized, and the long-known materials were rediscovered. For example, Yamamoto *et al.* [105] as well as Koßmehl and Chatzitheodorou [106] pioneered the research on polythiophene (PT, Figure 1.2). Poly(phenylene vinylidene) (PPV) represents one further material, which – similar to PA – can be doped to achieve electric conductivity; thus, the physical and electric properties can be tuned *via* functional groups on the aromatic rings. Noteworthy, the first polymer-based, light-emitting diode (LED), which used PPV as the emissive layer, was reported in 1989 [107]. This discovery boosted the research in light-emitting π-conjugated polymers for applications in electroluminescent devices. Since then, a plethora of polymers have been prepared and utilized accordingly [108, 109]; however, a survey of these will not be given within this book. Special credit goes to Diaz, who not only revisited PPy and PAni but also established electropolymerization, as a fast and reliable technique to fabricate conjugated polymer films on conductive surfaces [110]. Finally, the studies by Diaz *et al.* on PPy [111–113] and PAni [114, 115] enabled one to better understand the physical background, which, in turn, is responsible for the observed phenomena [116–118].

Electropolymerization is a highly versatile method to prepare polymer films directly on substrates, *i.e.* processing steps from solution become obsolete; however, the latter represented a significant restriction, when aiming for post-synthetic processing. At that time, the common redox polymers were barely soluble (particularly in water) and, thus far, from being easy to process. In 1991, Epstein and coworkers showed that sulfonated PAni was readily soluble, even in water, thus facilitating its processability; moreover, the self-doping effect, due to intramolecular acid–base reactions, induced electric conductivity [119]. The improved post-synthetic processability finally enabled the commercialization of redox polymers. The first generation of commercial products incorporating redox polymers was summarized by Miller in 1993 [120, 121]. In particular, two rechargeable LIBs must be highlighted in this context. In 1987, Bridgestone/Seiko began selling 3V coin cells, which contained PAni and $LiBF_4$, as cathode material and electrolyte, respectively (Figure 1.4a) [122, 123]. The Varta/BASK coin cell contained partially oxidized (*i.e.* p-doped) PPy, as the active material [124]. Miller pointed out that these batteries had lower energies than the conventional batteries available at that time, *e.g.* NiCd batteries, but could be kept longer in the charged state, hold their charge longer, and were environmentally more compatible [121]. However, these batteries could not compete with *e.g.* the ones developed by Valence Technologies, which instead utilized a Li^+-conductive polymer (interestingly, in 1992, Motorola ordered \$$10^8$ worth of this battery [125]). At least in the case of Bridgestone/Seiko battery, their sale was discontinued after only five years.

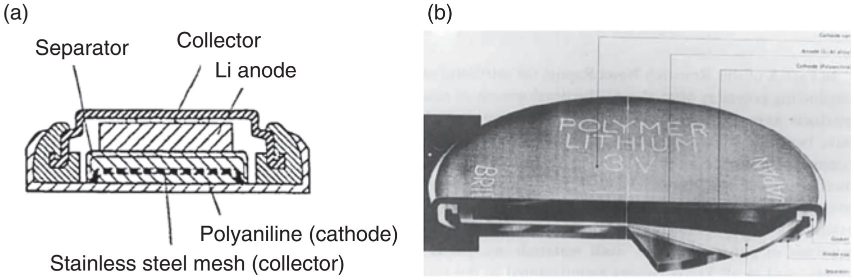

Figure 1.4 (a) Schematic section through a Bridgestone/Seiko coin-cell battery. (b) Photograph of a Varta/BASF coin-cell battery. Source: (b) [121] Reproduced with permission/ John Wiley & Sons, Inc.

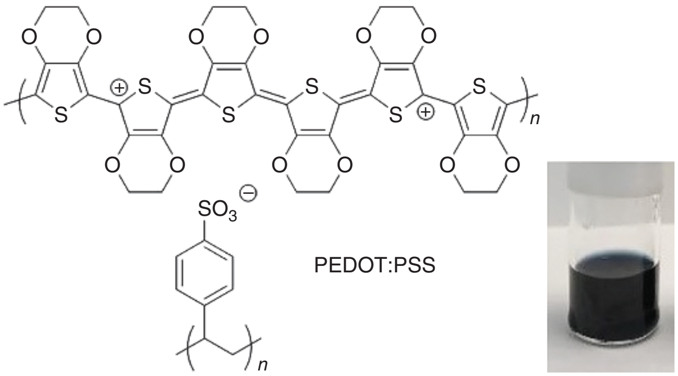

Figure 1.5 Schematic representation of the chemical structure of PEDOT:PSS. The picture shows a beaker filled with an aqueous solution of PEDOT:PSS. Source: B. Jewłoszewicz, K. A. Bogdanowicz, W. Przybył, A. Iwan, I. Plebankiewicz, POlymers 2000, 12, article ID 565.

The synthesis of PEDOT [poly(3,4-ethylendioxythiophene)] represents the next mentionable milestone in the context of redox polymers. This particular polymer featured a higher conductivity, stability, and biocompatibility when compared to the parent PT; however, PEDOT and PT have a common downside, which is a restricted processability from solution due to their low solubilities [126]. The solubility problem could be solved by using poly(styrene sulfonic acid) (PSS), as a water-soluble polyelectrolyte for the charge-balancing of partially oxidized PEDOT (Figure 1.5) [127]. The resulting PEDOT: PSS, which was commercialized by Bayer under the trade name Baytron-P®, which featured reasonable solubility in water and, thus, enabled its processing from solution. These homogeneous, flexible films were highly conductive (up to c. $10\,\mathrm{S\,cm^{-1}}$), transmissive for visible light, and thermally stable [128]; however, the initial target, *i.e.* the replacement of indium tin oxide (ITO)-coated glass substrates in polymer LEDs, could, due to the insufficient currents, not be reached. Nonetheless, it was demonstrated that both the performance and stability of such devices could be vastly improved by depositing a thin PEDOT–PSS film onto the ITO-coated substrate [129].

Two further prominent inventions of redox-active polymers appeared: bulk heterojunction (BHJ) solar cells and organic field-effect transistors (OFETs). Research on the former was pioneered by Wudl and coworkers [130] as well as by Holmes and coworkers [131]. In BHJ devices, a conductive polymer, as the electron-donor material, is blended with an acceptor compound, typically a fullerene derivative; however, this application represents a topic of its own and its evaluation is far beyond the scope of this book – the reader is referred to three excellent reviews [132–134]. The same holds true for OFETs, where initially PA- and PT-type polymers were used [135–138].

To conclude, it may be mentioned that substantial progress was made in the second era of redox polymers regarding energy-storage applications [139, 140]. However, this period was dominated by the class of π-conjugated polymers and the emergence of cutting-edge applications, which are commonly referred to as "organic electronics" (*e.g.* polymer LEDs, BHJ solar cells, and OFETs).

1.2.3 The Third Era of Redox Polymers

The beginning of the third, ongoing era of redox polymers can be marked by the research of Nakahara *et al.* [141] as well as Nishide *et al.* [142], who developed the concept of ORBs in the beginning of the twenty-first century. These authors utilized PTMA, as the nitroxide-containing, redox-active polymer in their initial studies (Figure 1.6a). As depicted in Figure 1.6b,c, the TEMPO moiety exhibits a fast and highly reversible one-electron oxidation to afford a *N*-oxoammonium species (the latter is formed in batteries during the discharging process).

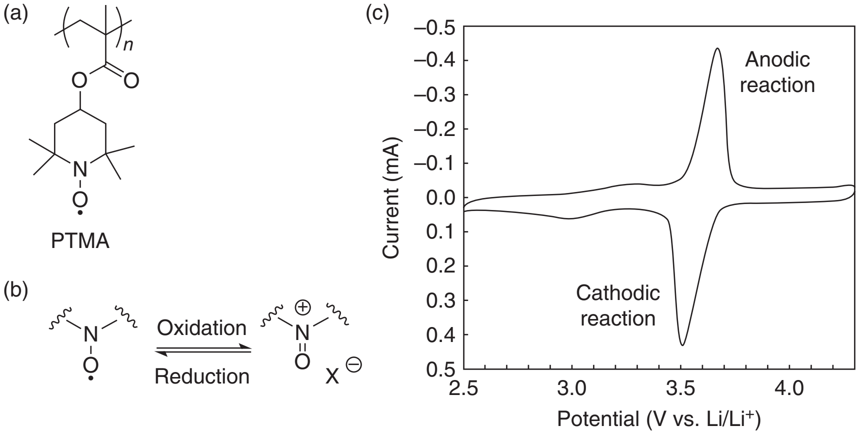

Figure 1.6 (a) Schematic representation of PTMA; (b) schematic representation of the reversible one-electron oxidation of nitroxide radicals; (c) representative cyclic voltammogram (CV) of a composite electrode comprising of PTMA, graphite, and a binder (1 : 8 : 1 ratio) at a scanning rate of 10 mV s^{-1} (counter electrode: Pt wire; reference electrode: Li/Li$^+$; electrolyte: carbonate mixture containing 1 M $LiPF_6$) [141]. Source: Figure reproduced with kind permission; © 2002 Elsevier B.V.

Starting from these groundbreaking studies, the field of polymer-based organic batteries literally exploded with diverse research groups joining this field [53]. We have come full circle – the redox-active polymers, which are commonly used, as active materials, in today's energy-storage application, are mostly nonconjugated polymers equipped with redox-active moieties (along with conjugated polymers bearing localized charges) [3]. Accordingly, these materials, which have already been described during the first era of redox polymers (*vide supra*), have been revisited and, if necessary, modified to use them in state-of-the-art battery applications. Diverse active scaffolds have recently been reported and intense research has been devoted not only to the discovery of new redox polymers but also to the optimization of battery setups (*i.e.* choice of battery type, active materials, electrolyte, and counter electrodes) [143]. Notably, redox polymers have been implemented in different types of rechargeable energy-storage devices, such as the various metal-ion-based batteries. Besides the most prominent example, LIBs [3, 144], also sodium [145, 146], potassium [147], magnesium [148, 149], calcium [149], zinc [149], and aluminum [149] have been used in the same context. Moreover, metal-free, all-organic batteries have been fabricated by Nishide and coworkers [150, 151], and in 2015, Schubert and coworkers reported the first redox-flow battery (RFB), which used redox polymers as both catholyte and anolyte [152].

Substantial progress has also been made in other fields of research where redox-active polymers of the latest generation are involved: electrochromic devices [153], sensors [154], drug delivery [155], etc. Notably, these applications will not be evaluated within this book, since the following focus will only be on redox-active polymers for battery applications. In this context, various types of polymeric architectures, relevant polymerization methods, and a range of energy-storage devices will be discussed.

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