

Electroactive Materials Based on TEMPO

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The redox-active TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl-4-yl) fragment is a popular component of organic energy storage and catalytic systems as its benefits include remarkable electrochemical performance and decent physical properties. TEMPO is a versatile compound that finds its use in various chemical and biological systems, and is also known to be an efficient catalyst for alcohol oxidation, oxygen reduction, and various complex organic reactions. It can be attached to various aliphatic and conductive polymers to form energy storage compounds for organic batteries or high-loading catalysis systems. The performance and efficiency of TEMPO-containing materials strongly depend on the molecular structure, and thus rational design of such compounds is vital for successful implementation.

TEMPO

nitroxyl

stable radicals

redox polymers

conductive polymers

organic radical polymers

charge transfer mechanisms

1. Introduction

At present, inorganic compounds dominate the market of electrode materials for various electrochemical energy storage systems. This raises some issues, especially in lithium-ion batteries that employ nickel- and cobalt-based compounds, which poses problems of price, safety, toxicity, and ethics [1][2]. Hence, the replacement of such materials by environmentally friendly organic compounds is vital for the development of sustainable energy systems. These devices range from supercapacitors and batteries that utilize internal redox transformations of organic materials to fuel cells where the catalytic activity of organic compounds helps produce electrical energy from various fuel species [3]. As a result, fast development of the emerging research topics focused on the creation of novel organic and metal-organic materials with designed functionality produces hundreds of publications both on theoretical and empirical aspects in this area. Attractive candidates for both storage and catalytic applications exist among polymers bearing organic radical substituents as high capacitance groups [4]. One of the most prominent is the group of organic polymers bearing stable nitroxyl radicals, such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) [5][6]. The attractiveness of use of such organic radical polymers in batteries and supercapacitors is due to the high cell voltage and theoretical specific capacitance. At the same time, unpaired electrons of nitroxyl radicals ensure high catalytic activity of such compounds, which is promising for fuel cells and catalytic synthesis. The stability of polymeric materials in target solvents during electrochemical transformations is the most important challenge addressed by the molecular design of nitroxyl radical-containing polymers. To reach the best stability, two separate problems should be solved: chemical stability of the target molecule and solubility of the material in the adjacent electrolyte. Additional requirements may be applied to the materials made for specific applications,

such as particular size of the polymer molecules or polymer solution viscosity, crucial for redox-flow cells with porous membranes. Molecules matching these requirements should retain basic features of the materials based on nitroxyl radicals, such as charge–discharge reversibility, energy storage capacity and catalytic activity. Moreover, low electronic conductivity of materials based on nitroxyl radicals limits the rate of charge transfer inside the polymer layer. It hampers broad application of such polymers as an electroactive material both in energy storage and electrocatalysis. Therefore, the design and synthesis of novel materials based on nitroxyl radicals that possess high conductivity while retaining high power density or catalytic activity represents another relevant problem in the development of new polymers. Abovementioned technological challenges inspire numerous publications focused on molecular design, synthetic approaches, and material chemistry of nitroxyl radical-containing polymers. Topical reviews, focused on energy storage [\[4\]\[5\]\[7\]\[8\]\[9\]\[10\]\[11\]\[12\]](#) or electrocatalytic materials [\[7\]\[9\]\[13\]\[14\]](#), usually pay little attention to systematic study of the features of such polymers.

2. Electroactive Materials Based on TEMPO

2.1. Synthetic Approaches

Due to continuously growing production, the cost of TEMPO derivatives, and especially 4-hydroxy-TEMPO (TEMPOL) is drastically decreasing. For example, according to the Sigma-Aldrich catalogues, the price of the TEMPOL in 2010 was EUR 295.5 per 25 g of 97% purity substance, while in 2022 the same package costs only EUR 49.9, and the price of the technical grade substance on industrial marketplaces lies below EUR 10/kg. The synthetic route for TEMPO consists of three simple stages, namely condensation of acetone with ammonia, reduction of the carbonyl group and oxidation of the N-H fragment, which makes the TEMPOL an inexpensive building block for industrial production of the functional materials for energy storage and other applications.

TEMPOL itself is an ecological-friendly and non-toxic (LD50 1 g/kg, oral, rat) substance, considered as an antioxidant and drug precursor [\[15\]\[16\]](#). Unlike many inorganic high-energy materials, TEMPO-based polymers have no tendency of thermal runaway, are non-toxic and non-corrosive and, like most of the polymeric materials, can be disposed of by incineration. Due to these factors, TEMPO provides environmental and operational safety.

2.1.1. Non-Conductive Backbones

Proper selection of the compatible polymeric backbones to bear TEMPO groups is the main step in obtaining the material with the best properties for the desired purpose. Such factors as dissolution of the material, which directly causes device self-discharge [\[10\]](#), and its electrochemical stability, define the choice of backbone polymers [\[7\]](#). At the same time, due to the complex chemical behavior of nitroxyl compounds, synthetic availability also plays a significant role. Due to this reason, low-cost 4-hydroxy-TEMPO, or TEMPOL, is the most popular precursor for the synthesis of TEMPO-containing monomers by attachment via the hydroxyl group. Alternatively, significantly more expensive 4-carboxy- or 4-amino-derivatives of TEMPO may be used. Although most of the reported syntheses of these polymers use TEMPO-containing monomers, another option is to introduce TEMPO by the polymer-analogous transformations.

Without any doubt, poly(2,2,6,6-tetramethylpiperidine-N-oxyl-4-oxymethacrylate) (PTMA) is the most popular TEMPO-containing polymer for energy storage purposes. Despite the presence of the nitroxide moiety imposing appreciable restrictions on the polymerization techniques, PTMA can be obtained by direct polymerization of 2,2,6,6-tetramethylpiperidine-N-oxyl-4-oxymethacrylate using anionic [17] or group-transfer polymerization [18]. The same synthetic approaches are used to prepare other TEMPO-modified polyalkenes based on acrylamides [19], vinyl ethers [20] or more complicated systems [21]. Another way to introduce nitroxide functionality is by oxidation of the properly functionalized polymers using peroxide oxidants [22] or using starting materials with the reduced TEMPO protected by O-alkylation [23] (Figure 1).

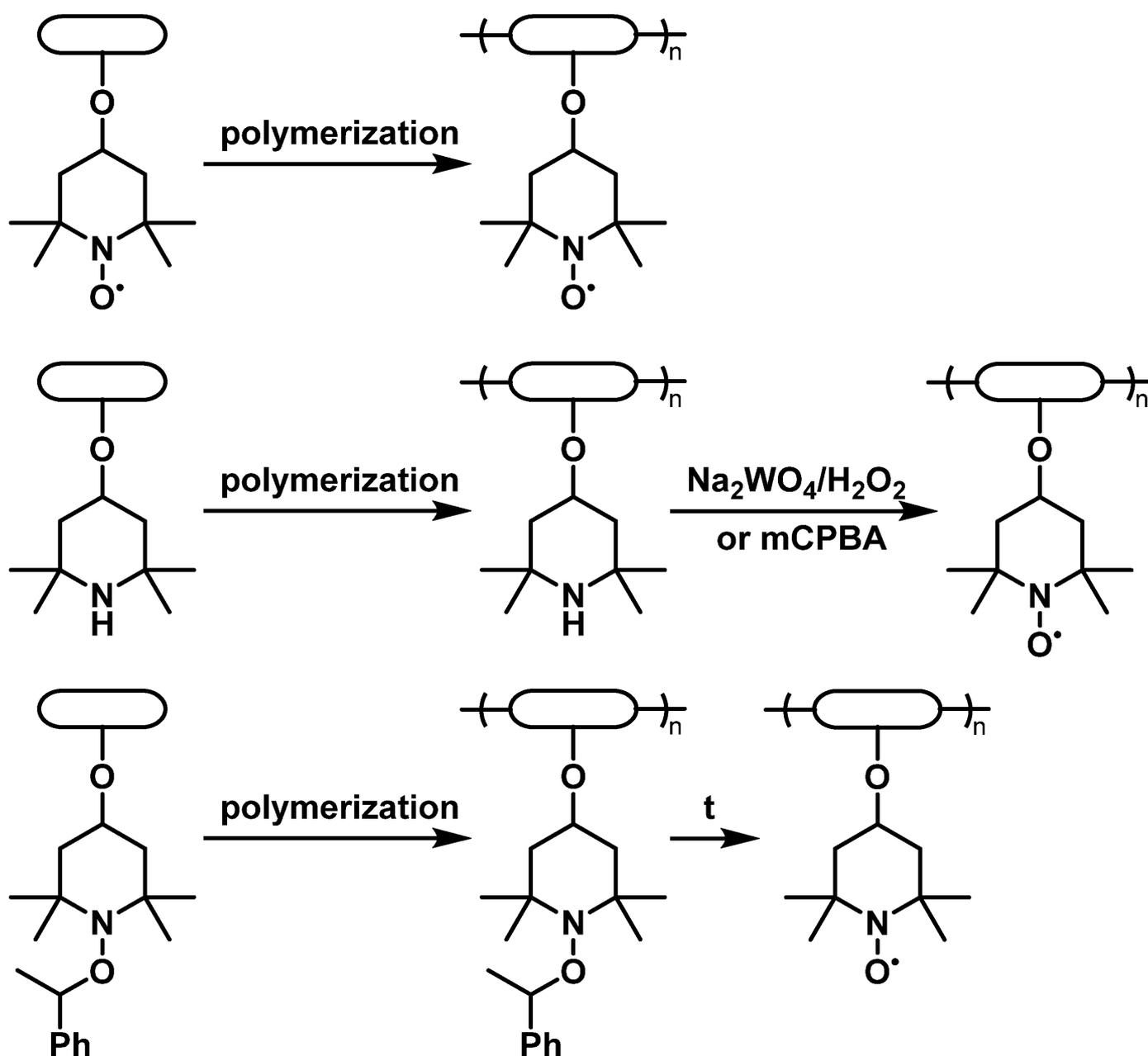


Figure 1. Polymerization of unprotected and protected TEMPO-containing monomers.

Other approaches are also useful for the preparation of TEMPO-containing polymers, including ring-opening anionic polymerization of TEMPO glycidyl ether [24], ring-opening metathesis polymerization of TEMPO-containing cyclic alkenes [25], or Michael polyaddition of TEMPOL-acetylacetates to acrylate dendrons [26]. Cross-linked [27], grafted [28], or bifunctional [29] TEMPO-containing polymers are accessible by the copolymerization using the same approaches.

Post-modification of the polymers with the TEMPO-containing blocks is rarely employed, but several examples exist, including the modification of polyimine [30] and poly(ethylene-alt-maleic anhydride) [31]. Natural polymers, such as cellulose, can also be employed as carriers of the TEMPO fragments attached by esterification [32].

2.1.2. Conductive Backbones

Most TEMPO-bearing conductive polymers are prepared by electrochemical or chemical oxidative polymerization of TEMPO-containing monomers (**Figure 2**). Electrochemical polymerization results in deposition of the polymer films directly on the electrode, which is a convenient method for the formation of thin films suitable for electrocatalytic purposes or for basic electrochemical characterization of the materials. At the same time, polymerization with chemical oxidants allows preparative scale synthesis of the conductive polymer for use in the fabrication of battery cell electrodes. Chemical oxidative polymerization is mostly conducted using FeCl_3 in the presence of CH_3NO_2 [33] with ammonium persulfate [34]. Alternatively, Kumada polycoupling of 2,5-dihalothiophene may replace electrochemical polymerization [35].

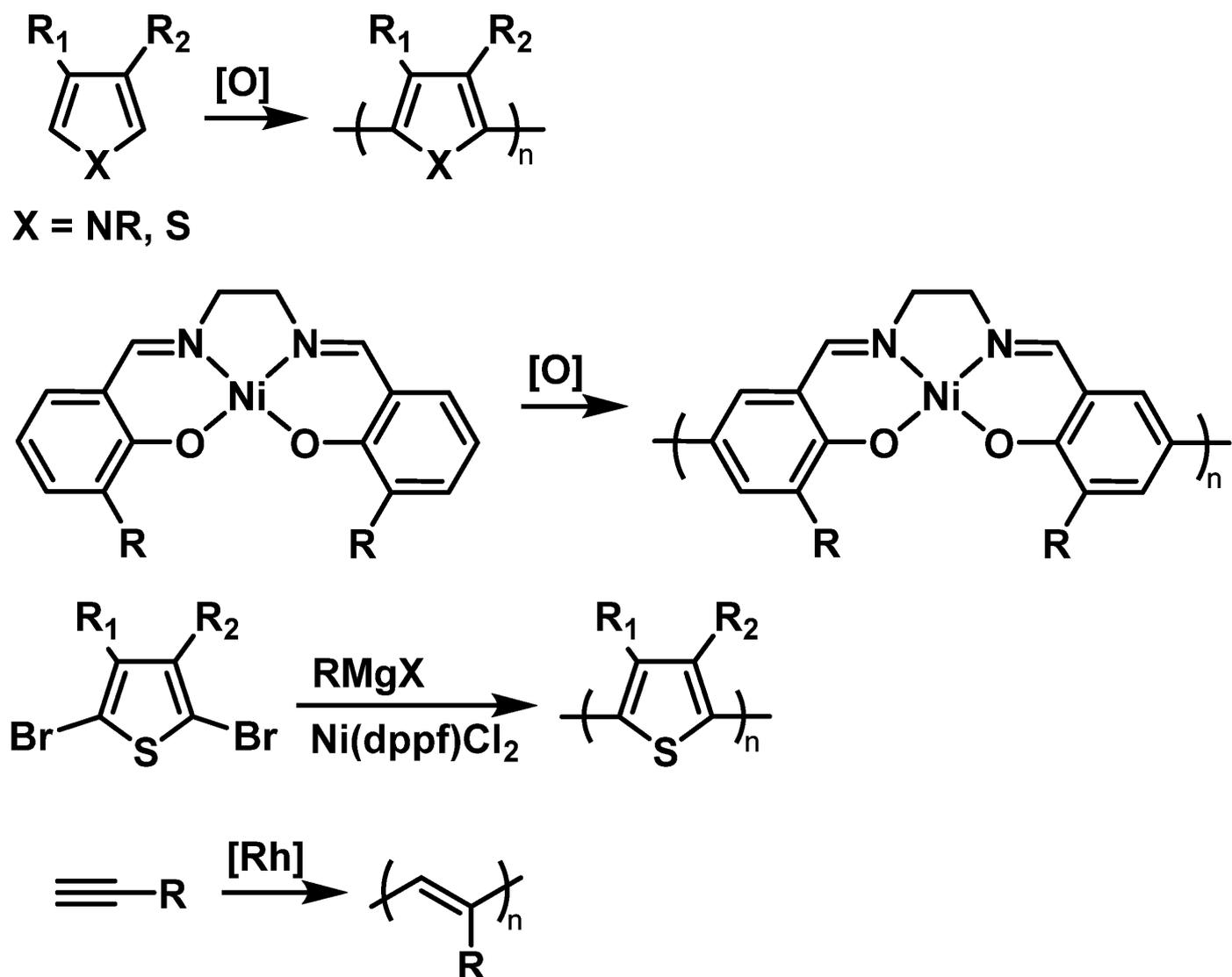


Figure 2. Typical polymerization schemes for the preparation of functional conductive polymers.

Polyacetylenes with TEMPO fragments are not available by oxidative polymerization but can be synthesized by rhodium-catalyzed polymerization of terminal acetylenes [36].

Several classes of electron-rich (hetero)aromatic molecules such as anilines, pyrroles, and thiophenes represent the monomers for the TEMPO-modified conductive polymers. Due to the complex chemical behavior of these fragments, the synthetic approaches to obtain these monomers are often more complicated than the polymerization approaches.

Polymerization of pyrrole proceeds at the 2- and 5-positions, which allows functionalization with TEMPO by N-alkylation, followed by attachment of TEMPO to the resulting linker [37][38]. High selectivity of N-alkylation makes this approach the most convenient for the synthesis of pyrrole-based monomers. Thiophenes show the same polymerization behavior, but alkylation at the 1-position is unavailable, so the TEMPO fragments are attached to the 3-position of the thiophene ring via ether [39] or ester [33] linker. 2-HydroxymethylEDOT is also used as a

precursor for the TEMPO-containing thiophene monomer [40]. Rare examples of the electrochemically polymerizable TEMPO-modified triphenylamine [41] and nickel Salen complex [42] were also reported.

2.2. Fundamental Electrochemistry of TEMPO Transformations

TEMPO is the founding piece among organic radicals for energy storage applications, as well as a touchstone for other similar materials. Its use for lithium-ion batteries can be traced back to 2002 [43], when Nakahara et al. employed a TEMPO-bearing poly(methacrylate) (PTMA) as an electrode material. Since then, a multitude of polymer backbones has been used in combination with TEMPO and other stable organic radicals [44], as such materials are quite promising. Their main advantages include high stability in standard lithium-ion electrolytes (recharging with negligible loss up to 2000 cycles [31]), and fast recharging time (available current rates of up to 100 C [45]), which results in impressive power density [11][12].

The nitroxide radical can either reversibly oxidize to form an oxoammonium cation (p-doping) or reduce to an aminoxyl anion (n-doping), which is the basis of electrochemical transformations in such materials (Figure 3). These reactions are useful in a variety of applications, allowing the use of TEMPO-based materials in metal-ion batteries, redox flow cells and oxidation catalysts [9][11]. Most reports deal with the oxidation into oxoammonium cation, as this reaction proved to be optimal in terms of its relatively high potential, which is 3.5 V vs. Li/Li⁺. TEMPO-modified poly(methacrylate) has become a de facto standard material [10] for organic cathodes in lithium-ion cells, which theoretical capacity of 111 mAh g⁻¹ can be achieved in practice. There are other options, such as poly(vinyl ether) with 131 mAh g⁻¹ [46], and numerous attempts exist to increase this value up to 224 mAh g⁻¹ [47]. However, current materials require binders and conductive agents, practically rendering this value unattainable. Utilization of intrinsically conductive polymers as a backbone might improve the situation. There are also options that allow increase in the cell density via shifting the potential of the reaction up to 3.7 V [48].

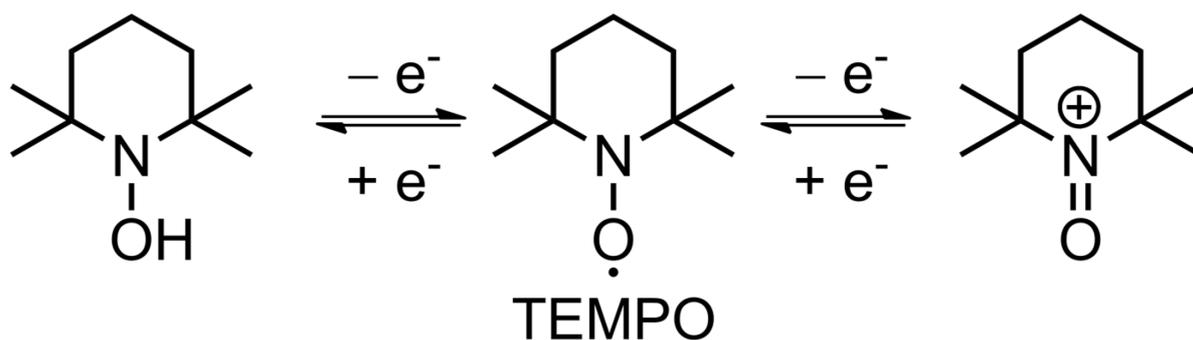


Figure 3. Schematic representation of redox couples of TEMPO radicals.

Regardless, with the average voltage vs. Li being 3.5 V, long cycle life (up to 2000 cycles [31]) and high (up to 100 C [45]) rate capability, TEMPO is an ideal candidate for use in organic radical batteries, with power density rivaling that of standard inorganic materials.

As TEMPO is overwhelmingly used as a pendant group on a polymer backbone, it is reasonable to discuss its electron transfer and doping processes in this context of the whole material, rather than individual TEMPO units. As shown in several studies [49][50], electron transfer mechanism includes two distinct steps. The first one is electron transfer between the substrate and the radical components—a heterogeneous step—and the second is self-exchange between the neighboring radicals, primarily driven by concentration gradients of the moieties (**Figure 4**). The latter is a homogeneous step and referred to as hopping.

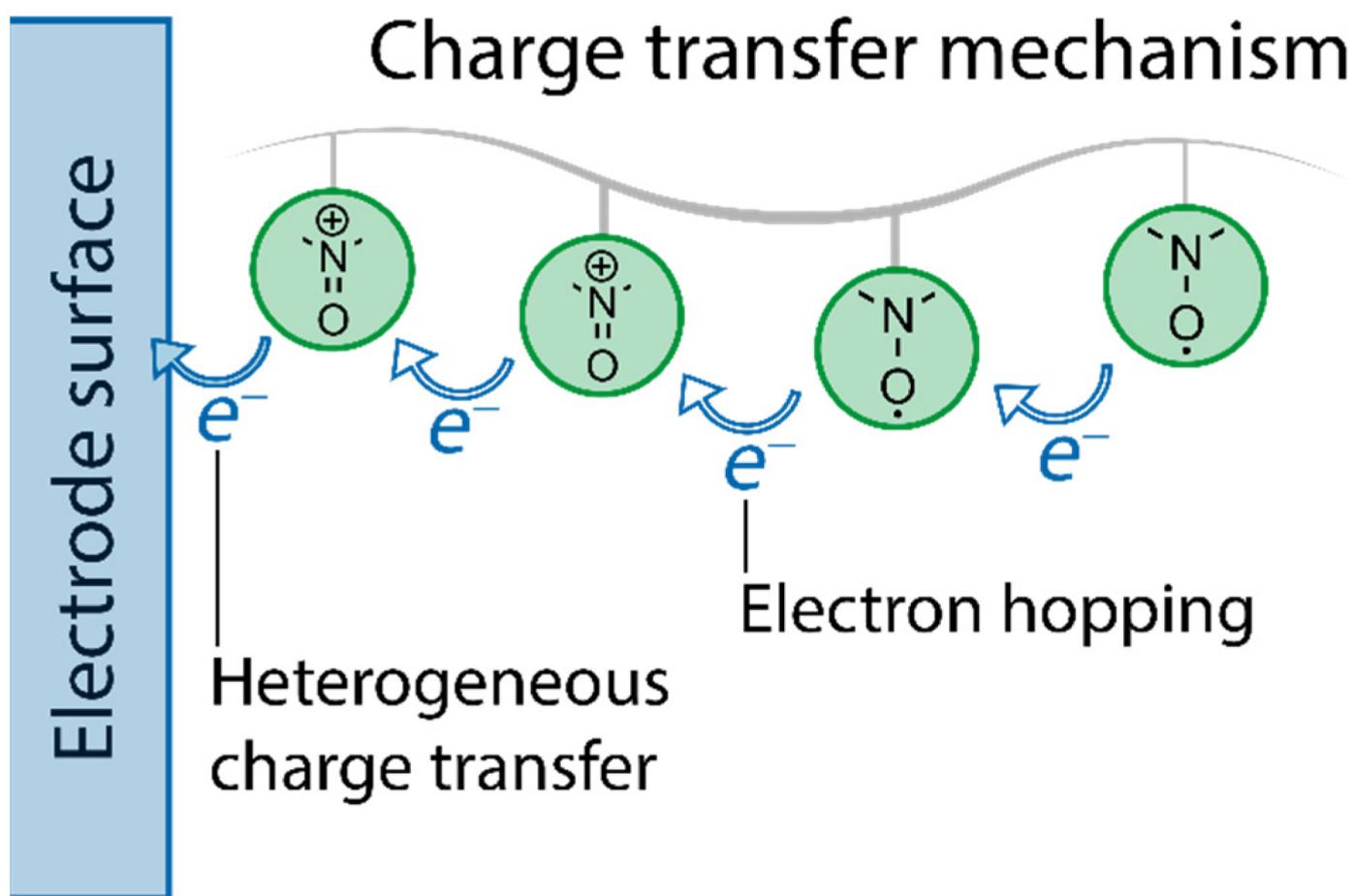


Figure 4. Schematic illustration of the redox reaction in TEMPO-containing polymer between nitroxide radical and oxoammonium cation.

The rate constant of the heterogeneous charge transport is ca. $10^{-1} \text{ cm s}^{-1}$ both for TEMPO monomers [51], and for TEMPO in PTMA deposited on Pt surface [52]. The self-exchange between neighboring radicals responsible for the homogeneous transport has a bimolecular rate constant of $1.8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ [50]. This value is up to four orders of magnitude higher for nitroxide-containing monomers [51][53][54], indicating that attachment of the molecule to the polymer chain hinders diffusion. Still, the fast kinetics cause a small gap between charge and discharge voltages, typically, ca. 100 mV, and allow extraction of almost full capacity of the material at a relatively high 1 C discharge rate: 110 mAh g^{-1} actual capacity vs. 111 mAh g^{-1} theoretical one [22].

For the polymer with 100% of monomer units modified by TEMPO (i.e., PTMA), little to no conformational changes accompany electron transfer. This enables Nernstian adsorbate-like behavior in polymer layers with thickness from 10 nm to 100 nm, which allows the use of thicker films and increase in the content of the polymer in the electrode material [50]. Conversely, the polymer with low density of TEMPO radicals becomes twice as stiff upon oxidation, compared to its reduced state [55]. While the electrochemical processes affect the conformation of the polymer, the monomer structure exerts a significant effect on the performance of the materials, such as their capacity. For example, another popular polymer backbone, poly(norbornene), can be functionalized by two TEMPO moieties per monomer unit. In the case of endo/endo configuration of the modified polymer, the capacity of the material is only 54 mAh g⁻¹, while endo/exo configuration yields full capacity of 109 mAh g⁻¹ [56]. Due to the proximity of neighboring TEMPO substituents, which in the endo/endo case are only 10 Å close, the generated positive charge on the first radical prevents oxidation of the second one (Figure 5). This presents the general issue for implementation of organic radical materials with densely packed redox-active groups.

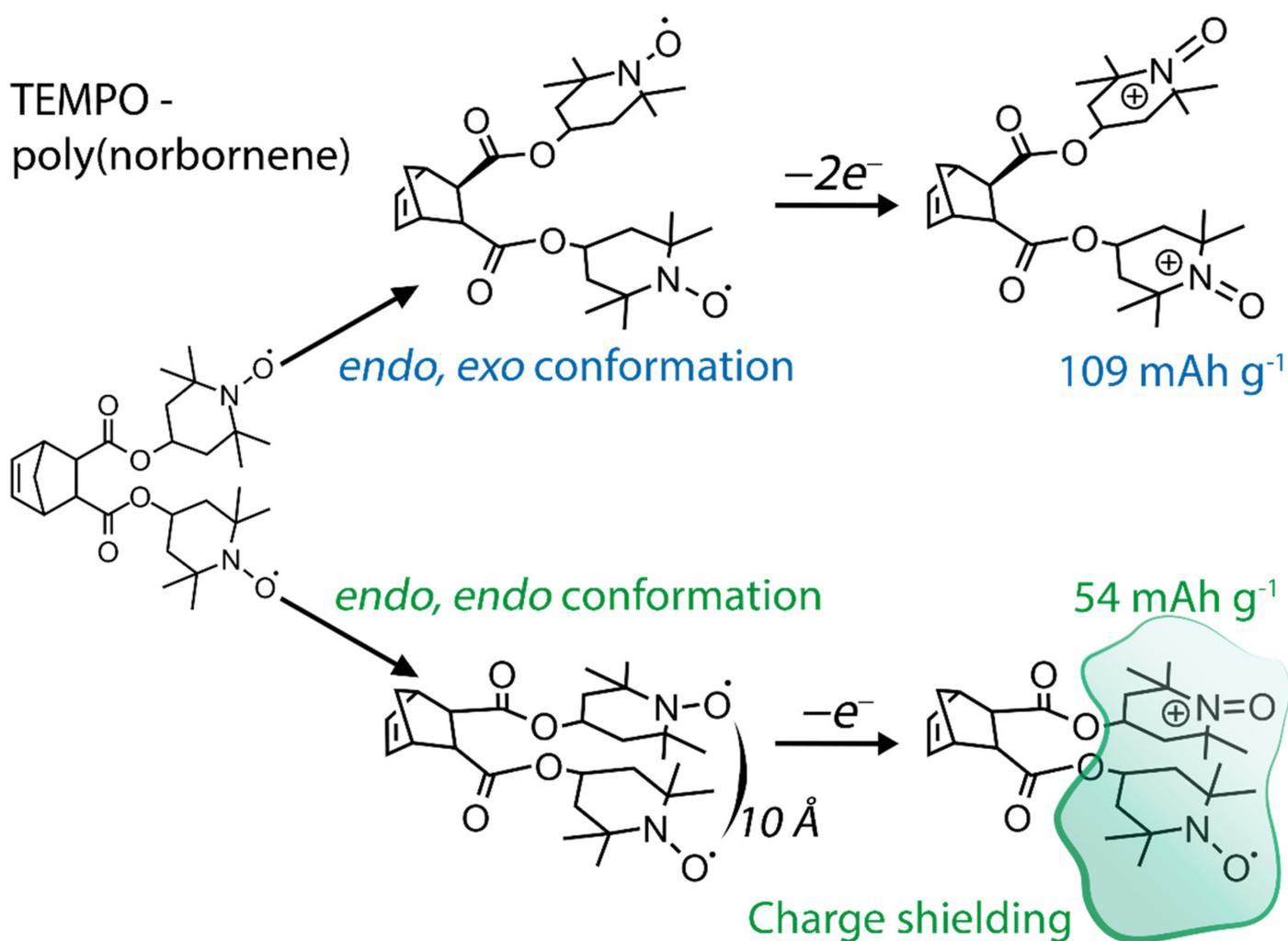


Figure 5. Schematic illustration of influence of neighboring TEMPO groups on molecule oxidation.

Another aspect worth considering is the intramolecular interactions for TEMPO substituents in long polymer chains, which require increased local concentration of charge carriers to make electron hopping more probable [57]. One

such option is annealing of a polymer with a TEMPO substituent, which results in formation of percolating networks, increasing the conductivity of the polymer to 10 S m^{-1} , compared to the $1 \times 10^{-9} \text{ S m}^{-1}$ of the initial disordered polymer with randomly oriented radical groups [58].

High electron exchange rates notwithstanding, decent electrode materials performance also involves facile ionic transport. This is directly related to the following requirements to the electrode–electrolyte interactions: the polymer should swell, yet be insoluble, to prevent self-discharging of the electrode [59], and the polymer should be either solvophilic or well-solvated to provide the mobility of the counterions.

The dissolution of the polymer may result in, e.g., 38% self-discharge in one week [22], yet this might be easily prevented by crosslinking [18] of the polymers.

Ensuring ionic conductivity requires tight control over both radical polymer and electrolyte properties. There are multiple factors at play here [4][44][59]. The effect of the porosity of the material matters most in the case of thin-film electrodes, where the increase in thickness would hinder diffusion through the material, as bulk transport becomes the limiting factor [60], which is observed already from the film thickness of $0.26 \mu\text{m}$ [61]. The pores design may be improved via porous carbon architectures [62], inclusion of porous polymers [63], or development of three-dimensional electrode structures [64].

To ensure electroneutrality, the process of electrochemical oxidation of $\text{NO}\cdot$ to $\text{N}^+=\text{O}$ must be accompanied either by anion uptake or by cation expulsion, with the opposite process on reduction. This means that proper selection of material and electrolyte compositions should provide the conditions for high diffusion rates of charged species. Even for typical lithium-ion electrolyte, LiPF₆ (in propylene carbonate, PC), the ratio between the number of TEMPO groups in PTMA and LiPF₆ molecules strongly affects the performance of the material: changing the LiPF₆-to-TEMPO ratio from 1.7 to 0.5 the self-exchange rate constant increases from $0.16 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ to $2.8 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ [65]. The decrease in the rate constant in highly concentrated electrolyte has to do with decreased mobility of ions—and predominantly with the nature of anions [66][67][68]—in swollen polymers. It is worth noting, however, that cations also affect the performance of organic radical polymers, e.g., PTMA, and even participate in charge compensation, as shown by electrochemical quartz crystal microbalance [69].

The replacement of the backbone polymer altogether may enhance ionic conductivity. For instance, (poly(2,2,6,6-tetramethylpiperidiny-N-oxyl vinyl ether)) PTVE is hydrophilic, thus providing high affinity to aqueous electrolytes, and ensuring facile ion transport [70]. Another example is (poly(2,2,6,6-tetramethylpiperidiny-N-oxyl glycidyl ether)) PTGE, which has good swelling and ionic transport in standard 1.0 M LiPF₆ in ethylene carbonate: diethyl carbonate (EC:DEC) electrolyte, providing up to 80 mAh g^{-1} capacity at 10 C [27].

Regarding the application of TEMPO-containing compounds within the battery, it should be considered that TEMPO may bear disruptive effects on other components by virtue of strong oxidizing capability of its cation. For example, cellulose-based separators are likely to decompose in its presence [71]. This presents an additional challenge when selecting optimal components.

Another way to improve the transport properties is to provide doping mechanisms via backbone polymer itself. This can be achieved by using conjugated polymers [72][73], though the competing redox processes in radical and backbone components complicate the studies of the charge transport mechanism. Still, there is some understanding of such processes. For example, in TEMPO-modified polypyrrole (with acetylene black as conductive component) [37] the charge transfer process is separated in four steps: (1) self-exchange between nitroxide radicals, (2) electron transfer from the radical to the conductive backbone, (3) electric conduction from polypyrrole to acetylene black, (4) electron transfer from acetylene black to the current collector (**Figure 6**).

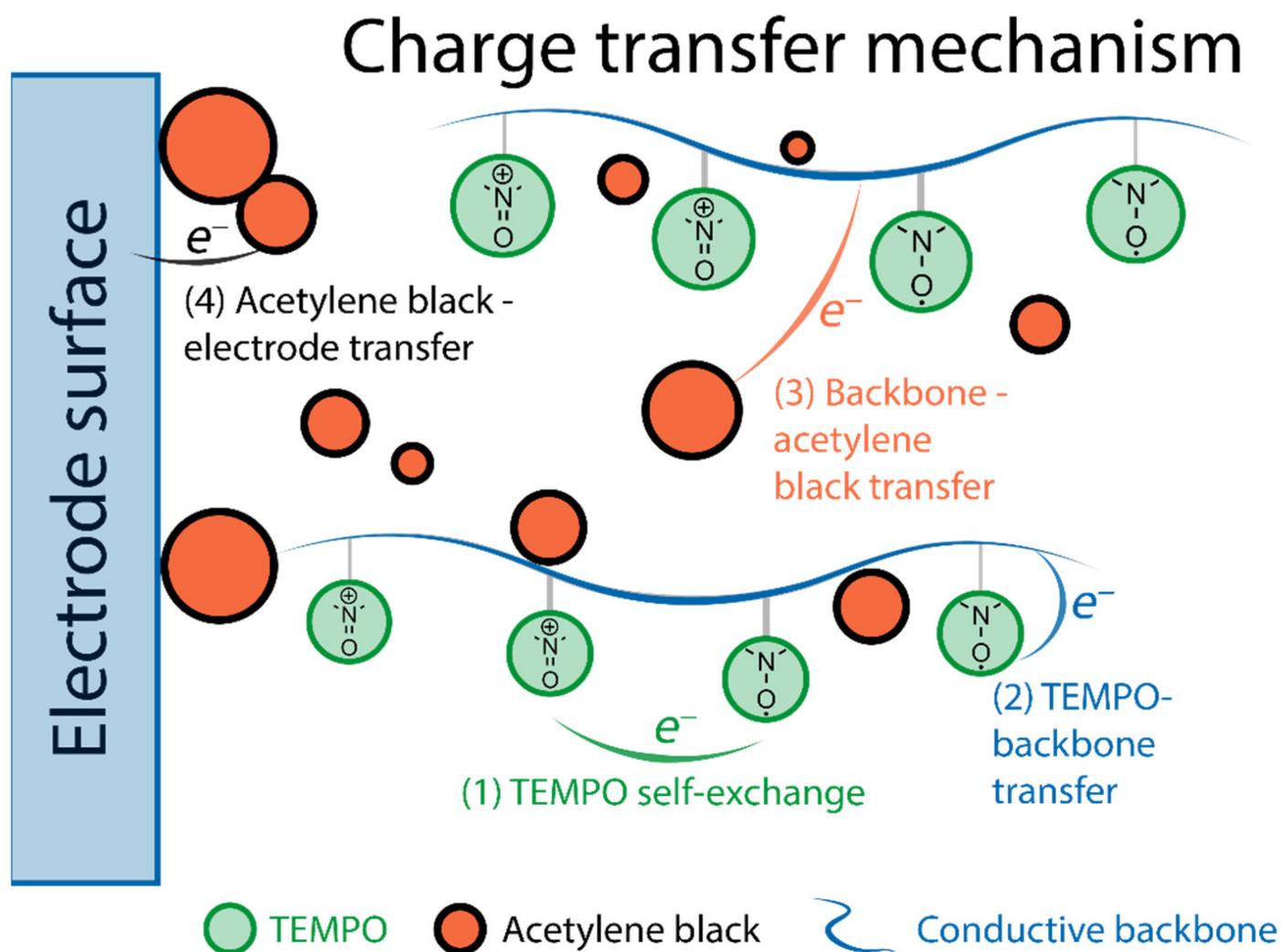


Figure 6. Schematic illustration of the charge transfer process in TEMPO-modified polypyrrole.

Polypyrrole is deemed to be an electric conduction path that assists repeatable oxidation/reduction through aggregated radical polymer bulks. The internal charge transfer between the TEMPO pendant groups and the backbone has also been observed in the case of TEMPO-modified 3,4-propylenedioxythiophene (ProDOT) [74], though the precise effect of such interaction was not firmly established.

Adverse effects of TEMPO radicals on the charge transfer within the electrode material have also been reported. In the case of TEMPO-modified poly(3-hexylthiophene) (P3HT) [35], it turns out that intrinsic conductivity of P3HT—

controlled both by intrachain and interchain hopping—is hindered by introduction of TEMPO. The impairing effect of TEMPO is due to introduced disorder in crystalline domains of the polymer, which restricts interchain hopping, thus terminating additional paths of charge transfer and decreasing conductivity. The effects of TEMPO content in P3HT on capacity were also investigated [48], and, similarly, the capacity was the highest with the minimal content of TEMPO, while 100% TEMPO-loaded conjugated polymer provided both the lowest specific capacity and the highest charge transfer resistance. Another effect was observed for polythiophenes bearing pendant TEMPO groups [39], where internal transfer of an electron from TEMPO to the polythiophene backbone caused rapid dedoping of the latter. This phenomenon led to a decrease in both capacity and conductivity and due to the thermodynamically favorable conditions: the 3.88 V oxidation potential of polythiophene is higher than that of nitroxide radical (3.60 V), thus facilitating backbone reduction. A reverse scenario, albeit with similar negative effects, was observed for poly(TEMPO–DTP) (TEMPO-modified (dithieno[3,2-b:2',3'-d]pyrrole)) [75]: the low oxidation potential of poly(DTP) (3.15 V) caused electron transfer from the backbone to the radical upon charging, thus reducing the activity of the polymer and decreasing Coulombic efficiency. This means that the balance must be found in the thermodynamic preference of the reactions, so that the potentials of both charge carriers overlap in such systems.

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