

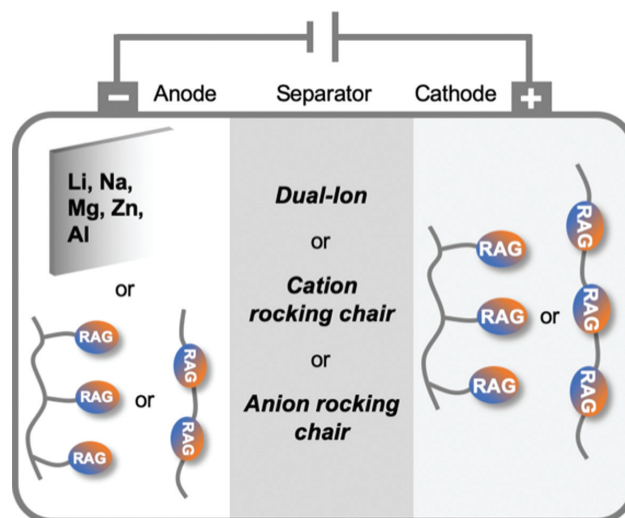
Redox Polymers as Electrode-Active Materials for Batteries

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Abstract Organic cathode materials are promising candidates for a new generation of ‘green batteries’, since they have low toxicity and can be produced from renewable resources or from petroleum. This review shows that organic redox polymers can show excellent battery performance regarding cycling stability and rate capability, and attractive specific capacities are accessible. Radical polymers and redox polymers based on heteroaromatics demonstrate superior rate capabilities and cycling stabilities at fast C-rates as well as high discharge potentials of 3–4 V versus Li/Li⁺, while quinone- or imide-based polymers deliver high specific capacities of up to 260 mAh g^{−1} with stable cycling at moderate C-rates and lower discharge potentials. This review article highlights the underlying design principles showcasing selected examples of well-performing redox polymers.

Key words organic batteries, redox polymers, cathode materials, fast charging, transition metal-free, high cycling stability

Introduction

The increasing demand for electrical energy, in particular for consumer electronics and electric vehicles, has raised the need for rechargeable batteries with high electrochemical performance and safety, and, at the same time, with small

environmental footprint. Organic electrode materials are promising for such a next generation of ‘green batteries’. The elements they are composed of (C, H, N, O, and S) are abundant, and organic materials are often nontoxic and easier to process. Furthermore, their structures can be easily tailored to adjust their redox properties. In the past decade, a large variety of organic electrode materials have been developed, as summarized in several review articles in recent years.^{1–4} They can be used as cathode-active materials in metal–organic batteries or as both anode- and cathode-active materials in all-organic batteries.⁵ Different strategies have been identified to obtain high electrochemical performance of organic electrode materials in batteries.^{6,7} The most important parameters are the charge/discharge potential, specific capacity, rate capability, and cycling stability of the materials.^{2,6} The charge/discharge potential is determined by the structure of the redox-active groups, and the specific capacity by its molecular weight and the number of electrons partaking in the redox process. The rate capability depends on the rate of the electron- and ion-transfer processes in and out of the electrode.⁸ It is influenced by the electron-transfer rate constant of the redox-active group and the morphology of the composite electrode, usually consisting of a mixture of organic material, conductive carbon and binder. The cycling stability is often limited by either dissolution of the active material into the (usually liquid) battery electrolyte or by decomposition processes. One successful strategy to improve cycling stability and – in some cases – rate capability is to incorporate the redox-active molecular units into a polymeric structure. The resulting polymers are often insoluble in battery electrolytes but should remain swellable. Such so-called redox polymers have been defined as polymers

Biographical Sketch



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focuses on organic electrode materials for batteries, small molecule semiconductors and hoop-shaped, conjugated π -systems.

containing groups that can be reversibly reduced or oxidized.⁹ Two main design types A and B exist for such redox polymers: the redox-active groups can either be attached as side groups to an aliphatic or conjugated polymer backbone (type A) or they can be incorporated into the conjugated or nonconjugated polymer backbone (type B, Figure 1a).

Redox polymers are classified according to the redox reaction they preferentially undergo: in the case of an oxidation, the polymer is defined as a p-type, while in the case of a reduction, it is defined as an n-type polymer (Figure 1b). Bipolar materials, undergoing both types of reactions, also exist. As design guidelines for a battery application, the redox-active group should have a highly reversible redox chemistry at a potential attractive for an application as an anode- or cathode-active material, but at

the same time be of low molecular mass. To obtain high specific capacities, the polymer backbone should impart the least amount of additional molecular weight. Using the molar mass of a polymer subunit M (polymer subunit), the theoretical specific capacity of a redox polymer can be calculated according to the following equation (where F is the Faraday constant and n the number of electrons transferred per subunit):

$$C_{\text{specific}} = \frac{n \times F}{M(\text{polymer subunit})} = \frac{n \times 26801}{M(\text{polymer subunit})} [\text{mAh g}^{-1}]$$

To prepare a redox-polymer-based electrode, the polymer is usually mixed with a conductive carbon additive to obtain

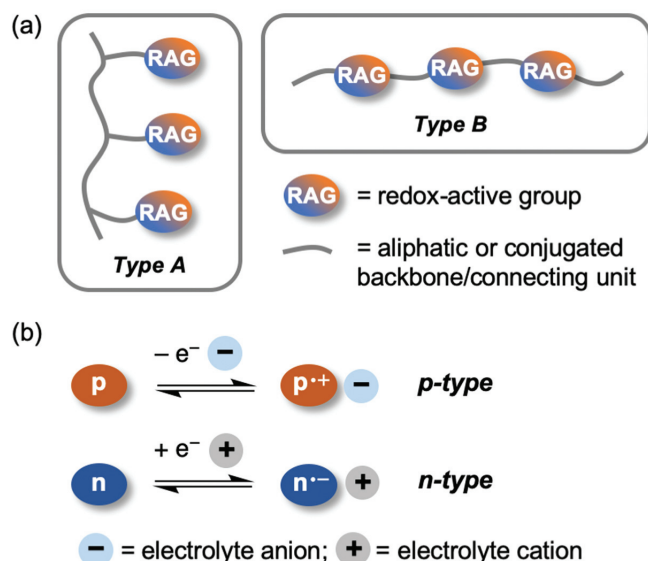


Figure 1 (a) Design types for redox-active polymers with the redox-active groups (RAGs) as pendant side units (type A) or incorporated into the main chain (type B); (b) redox reactions of p- or n-type organic compounds and charge balancing by electrolyte ions.

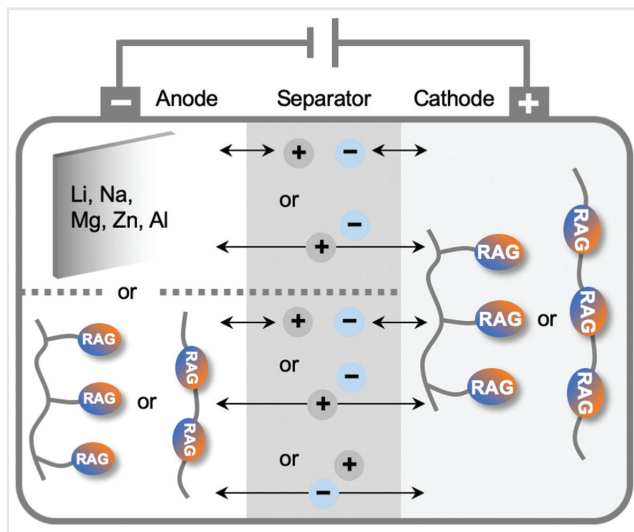


Figure 2 Schematic of a rechargeable battery with redox-active polymers as cathode-active materials combined with a metal anode or a redox-active polymer anode. Depending on whether the redox-active groups (RAGs) are p- or n-type, anions or cations from the electrolyte are required for charge balancing, respectively.

sufficient electronic conductivity.¹⁰ This adds to the inactive weight of the electrode, and the amount should therefore be held at a minimum. In most cases redox-active polymers are tested as cathode-active materials in half-cells against lithium as a counter electrode (Figure 2).^{4,10,11} Sodium^{2,7,12,13} as well as multivalent metals, such as magnesium, zinc and aluminum, have also been used.¹⁴ If the polymer is of p-type, such metal-organic cells operate in a dual-ion mode, where both electrolyte cations and anions are required for charge balancing in the anode and cathode, respectively.^{15,16} With an n-type polymer, only metal cations are needed, resulting in a cation rocking-chair battery. For all-organic batteries, redox-active polymers serve as both anode- and cathode-active materials.⁵ Three configurations are possible: combining an n-type polymer as the anode with a p-type polymer on the cathode side leads to a dual-ion configuration. Using only n-type polymers, a cation rocking-chair battery results, while with p-type polymers as the anode and active materials as the cathode, the battery operates in an anion rocking-chair mode. The progress in all-organic batteries has recently been reviewed.^{5,17}

Redox Polymers as Electrode Materials

The use of redox polymers as battery electrode materials has been reviewed on several occasions.^{10,18–22} A few selected examples will be discussed in more detail in the following including some of their most important battery

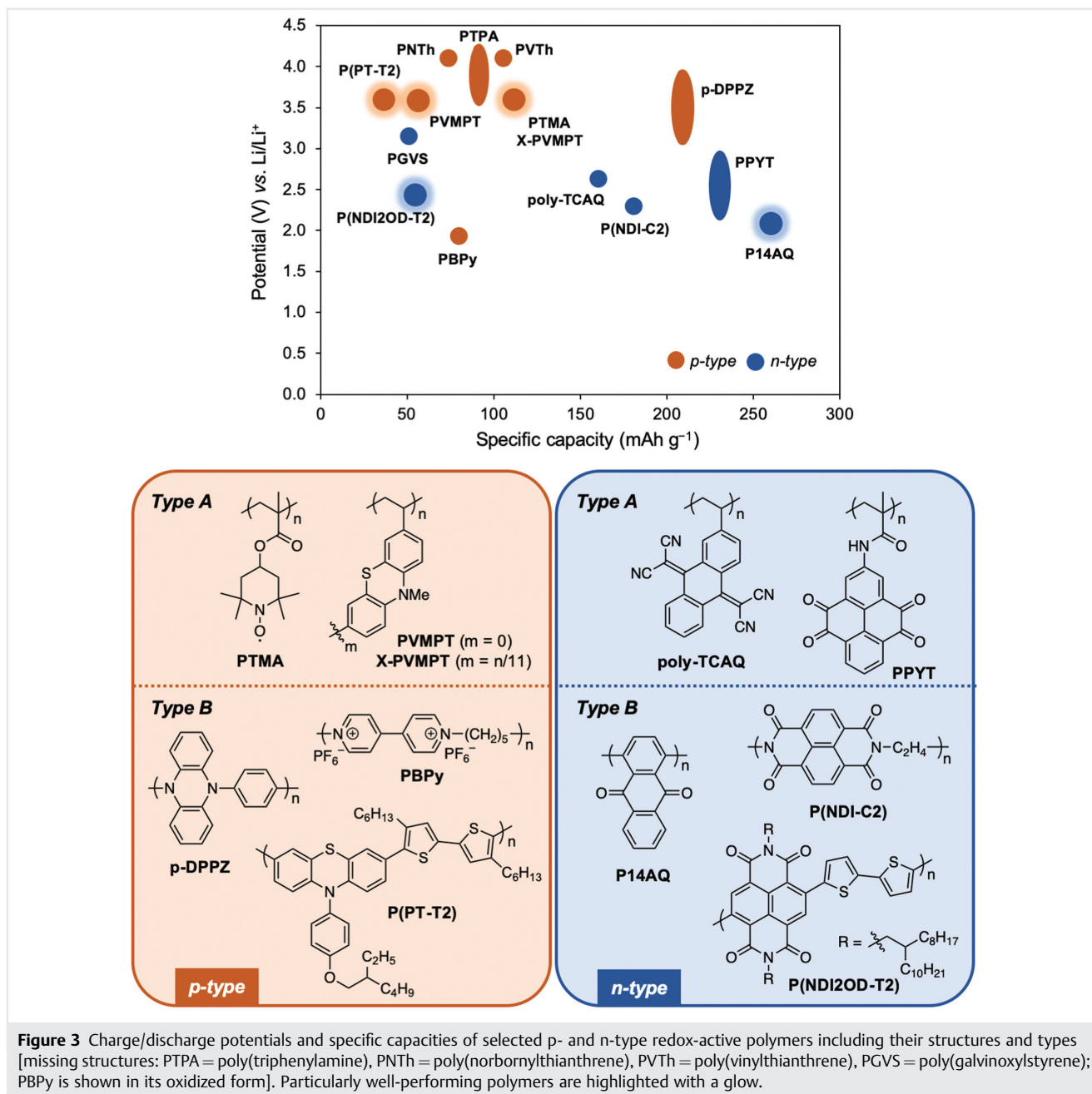
parameters, such as charge/discharge potential and specific capacity (Figure 3).

Conducting Polymers

Conducting polymers, such as poly(acetylene),²³ polythiophene, polypyrrole and polyaniline, were considered and tested as battery electrode materials already in the 1980s, shortly after their discovery, as discussed in more detail in several review articles.^{18,19,24} Most of them are p-type, but ambipolar or n-type conducting polymers also exist. Conducting polymers belong to type B, as shown in Figure 1a; however, no defined and localized redox-active groups exist. This leads to sloping charge/discharge curves due to a change in redox potential with increasing doping level. Furthermore, conducting polymers often showed low achievable doping levels.¹⁰ In more recent developments, higher performing conducting polymers have been reported as electrode materials, i.e. through nanostructuring.^{10,25–27}

Radical Polymers

In the early 2000s, the so-called radical polymers, polymers containing stable radicals as side groups, were introduced.^{28–31} These are of type A in Figure 1a, and a variety of aliphatic polymer backbones have been employed, most frequently poly(methacrylates), poly(norbornenes), poly(acetylenes), poly(styrenes) and poly(vinylethers).³⁰ In most cases nitroxide radicals, such as TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)oxyl), have been used. These are electrochemically ambipolar, but usually the oxidation to oxoammonium cations is more reversible than the reduction to aminoxyl anions (Figure 4a), and hence they were used as p-type materials. The most prominent example of a radical polymer is **PTMA**, a TEMPO-radical functionalized polymethacrylate (Figure 3).³² Its theoretical specific capacity of 111 mAh g^{−1} is nearly reached in cells, and it possesses an attractive discharge potential of 3.6 V versus Li/Li⁺. Fast C-rates are possible and high cycling stabilities have been reported due to the fast electron-transfer rate constant of the nitroxide radical. **PTMA**-based electrodes have been optimized with respect to many parameters and even tested in thin-film batteries^{29,33} as well as in pouch cells.³⁴ Other types of nitroxide radicals have also been incorporated into polymers and used as cathode-active materials.^{28,30} Attaching electron-withdrawing substituents can ease the reduction, leading to n-type radical polymers.^{29,35,36} Employing a galvinoxyl radical as a side group also renders the polymer n-type, such as in poly(galvinoxylstyrene) (**PGVS**), plotted in the graph in Figure 3.³⁷ For a more detailed overview on radical



polymers as battery electrode materials, the reader is referred to several review articles.^{28–31,38–40}

Redox Polymers Incorporating Heteroaromatics

The redox-active group can also be a closed-shell organic molecule, as long as its redox chemistry is reversible and –

ideally – associated with a high electron-transfer rate constant. To date, many such examples have been reported. A few selected redox-active p-type polymers will be discussed in the following, and their redox mechanisms are shown in Figure 4b and c. Further examples can be found in several detailed review articles.^{2–4,10,41}

Pushing the redox potential upwards increases the specific energy of the cathode, which is its product with the specific capacity. An average discharge voltage of 4.1 V

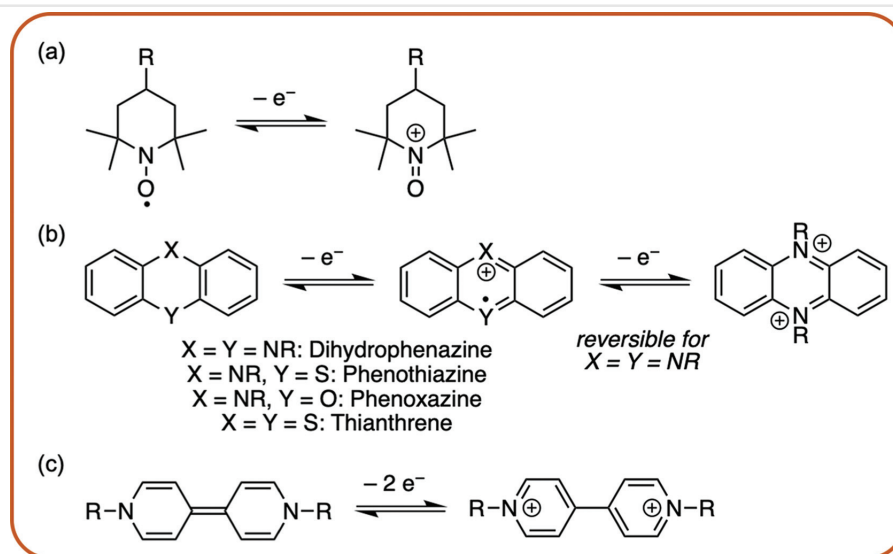


Figure 4 Redox mechanisms for selected p-type redox-active groups: (a) nitroxide radicals, (b) heteroaromatics and (c) viologens.

versus Li/Li^+ has been demonstrated using thianthrene-based polymers as cathode-active materials.^{42,43} Both examples were type A polymers with a poly(norbornene) (**PNT**)⁴² or poly(vinylene) (**PVTh**)⁴³ backbone (Figure 3). In the second case, an all-organic battery operating in the dual-ion mode was presented with **PVTh** as cathode-active material and a methacrylate derivative of **poly-TCAQ** (Figure 3) as an anode-active polymer.⁴³

A high but more sloping discharge potential between 3.6 and 4.2 V versus Li/Li^+ was obtained with a poly(triphenylamine) (**PTPA**, Figure 3).⁴⁴ This is a type B polymer with structural and electronic similarity to conducting polymers. An impressive rate capability was demonstrated with 91 mAh g^{-1} being available at 20C-rate. The rate capability could be further improved by using a hyperbranched polymer backbone.⁴⁵

A heteroaromatic with an attractively high redox potential of around 3.6 V versus Li/Li^+ is phenothiazine. Several examples of phenothiazine-based redox polymers of type A^{46–49} or type B^{50–52} as battery cathode materials have been reported. The poly(vinylene) **PVMPT** (Figure 3) showed an outstanding cycling stability due to π -interactions between neighboring oxidized (and neutral) phenothiazine units.^{47,48} After 10,000 cycles at 10C-rate (charging/discharging in 6 min), 93% of the initial specific capacity was retained.⁴⁷ This, however, came at the cost of only about half of the theoretical specific capacity being available (50 mAh g^{-1}). The dissolution and redistribution of **PVMPT** on the composite electrode upon charging and discharging facilitated the formation of π -interactions between the phenothiazine groups.⁴⁸ This was circumvented by using the cross-linked variant **X-PVMPT** (Figure 3), which furnished a specific capacity close to the

theoretical value of 112 mAh g^{-1} .⁴⁹ This demonstrates that the insolubility of redox polymers in both their charged and discharged states needs to be considered in evaluating their battery performance. The phenoxazine-based congener **PVMPO** and its cross-linked derivative **X-PVMPO** were also recently reported with high rate performance.⁵³

Conjugated phenothiazine copolymer **P(PT-T2)** of type B (Figure 3) showed an even higher cycling stability. At 100C-rate (charging/discharging in 36 s), **P(PT-T2)** provided a specific capacity of 30 mAh g^{-1} with a capacity retention of 97% after 30,000 cycles at a discharge potential of 3.6 V versus Li/Li^+ .⁵² The fast rates were facilitated by the semiconducting nature of the polymer backbone.

In none of the phenothiazine-based polymers discussed above, however, could the second oxidation of the phenothiazine groups to dications (occurring around 4.2 V vs. Li/Li^+) be accessed in a reversible fashion.

Accessing two oxidation events becomes possible when replacing the sulfur atom by nitrogen, resulting in dihydrophenazine derivatives. Two examples of type B polymers incorporating dihydrophenazines, such as **p-DPPZ**, have been reported (Figure 3).^{54,55} Using both oxidation steps at 3.1 and 3.9 V versus Li/Li^+ doubles the specific capacity of the polymers.

To build all-organic batteries that operate in the anion rocking-chair mode, p-type redox polymers with low oxidation potential are needed as anode-active materials in order to obtain a high enough cell voltage.⁵ This cell configuration has the advantage that it can be completely metal-free, since no metal ions from the electrolyte are needed for charge balancing.⁵⁶ The only example reported so far is the viologen-based polymer **PBP** with a redox

potential of 1.9 V versus Li/Li^+ (Figure 3), which has been tested in an all-organic anion rocking-chair battery against poly(*N*-vinylcarbazole) as the cathode-active material.⁵⁶ The battery operated at a potential of 1.8 V and delivered a specific capacity of 100 mAh g^{-1} at 1C-rate.

Carbonyl- and Bisimide-Based Redox Polymers

Concerning n-type redox polymers, most redox-active groups are carbonyl compounds or derivatives thereof, with few exceptions.⁵⁷ Several review articles solely focus on organic carbonyl compounds (redox polymers and small molecules) as battery electrode materials.^{58–61} The redox mechanisms of selected carbonyl-based redox-active groups are shown in Figure 5. One of the best-performing n-type redox polymers is **P14AQ** (Figure 3) as a type B polymer.⁶² At 1C-rate, a high specific capacity of 248 mAh g^{-1} was accessed with 98% capacity retention after 1,000 cycles, demonstrating high cycling stability. The charge/discharge potential lies at 2.1 V versus Li/Li^+ and the charge/discharge curves possess flat plateau areas, which shows that both electrons per anthraquinone unit are transferred at the same potential.⁶² It should be mentioned, however, that stoichiometric amounts of nickel are required for the synthesis of **P14AQ** through a Yamamoto coupling reaction,⁶² significantly increasing its environmental footprint.

For poly(bisimides), such as **P(NDI-C2)** with redox-active, n-type naphthalene bisimide (NDI) units (Figure 3),⁶³ many examples have been reported. These are also type B polymers, and their synthesis through polycondensation of the respective dianhydrides with diamines is extremely simple. Although theoretically a four-electron reduction (two on each imide group) should be possible, only two electrons can be transferred reversibly, providing a specific capacity of 180 mAh g^{-1} for **P(NDI-C2)**.⁶³ This happens at almost the same potential for both electrons, resulting in fairly flat charge/discharge curves with an average potential of 2.3 V versus Li/Li^+ .⁶³

High rate capability and excellent cycling stability were demonstrated using the well-known semiconducting NDI-containing conjugated copolymer **P(NDI2OD-T2)** (Figure 3).⁶⁴ Similar to poly(imides), **P(NDI2OD-T2)** can be reduced by two electrons at a potential of 2.5 V versus Li/Li^+ . After 3,000 cycles at 10C-rate, 96% of the initial specific capacity of 54 mAh g^{-1} was retained, demonstrating excellent cycling stability.⁶⁴ Recently **P(NDI2OD-T2)** was also employed in a Mg-organic battery showing stable cycling with MgCl insertion for charge balancing.⁶⁵

As a quinone derivative, the tetracyano-9,10-anthraquinonedimethane-containing type A polymer **poly(TCAQ)** (Figure 3) showed a – compared to anthraquinone – slightly

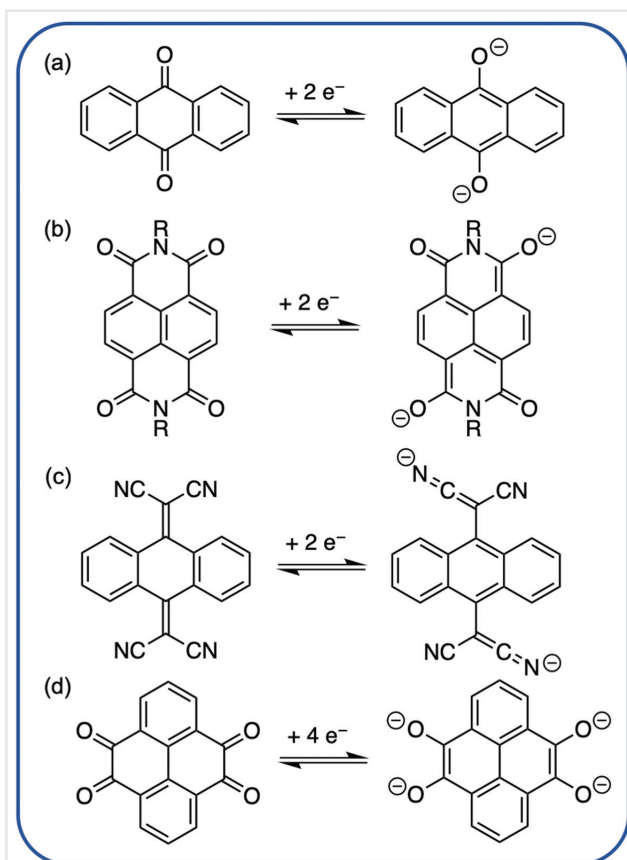


Figure 5 Redox mechanisms for selected n-type redox-active groups: (a) anthraquinone (AQ), (b) naphthalene bisimide (NDI), (c) tetracyano-9,10-anthraquinonedimethane (TCAQ) and (d) pyrenetetraone (PYT).

increased charge/discharge potential of 2.7 V versus Li/Li^+ .⁶⁶ A specific capacity of 156 mAh g^{-1} could be accessed with good cycling stability (88% capacity retention after 500 cycles at 1C-rate). However, with 10 wt% the material loading in the composite electrode was low. A poly(methacrylate) derivative with the same redox-active group was used as an anode-active material in an all-organic battery against **PVTh**, as mentioned above.⁴³

As a final example, the pyrenetetraone-containing poly(methacrylate) **PPYT** (Figure 3) delivered a specific capacity of 231 mAh g^{-1} in a two-step redox process with discharge potentials of 2.8 and 2.2 V versus Li/Li^+ , indicating that four electrons were transferred per redox-active group.⁶⁷ The cycling stability was good, the polymer retained 83% of the specific capacity after 500 cycles at 1C-rate.

Conclusions and Outlook

In summary, the examples presented above show that organic redox polymers can show high battery performance.

Quinone- or imide-based n-type polymers can possess high specific capacities of 160–260 mAh g⁻¹ with stable cycling at moderate C-rates and discharge potentials between 2 and 2.9 V versus Li/Li⁺. This makes them attractive in comparison to established transition metal-based cathodes. p-Type polymers, in comparison, provide higher discharge potentials of 3–4 V versus Li/Li⁺, but usually lower specific capacities. However, as demonstrated above, superior rate capabilities and cycling stabilities at fast C-rates can be obtained with p-type radical polymers or redox polymers based on heteroaromatics. It should furthermore be mentioned that organic-based cells can show impressive temperature performance down to -70 °C.⁶⁸ In all cases structural modification allows adjustment of the redox potential of the polymer. Polymer backbone engineering significantly influences battery performance, as demonstrated for **P(PT-T2)** and **P(NDI2OD-T2)** with a semiconducting backbone structure or for **PVMPT** and **X-PVMPT**, where cross-linking changed the charge/discharge mechanism. Challenges in the future will be to develop novel redox-active polymers with high cycling stability, rate performance and specific capacity, to lower the amount of conductive additive required in the composite electrode in order to obtain higher specific capacities and to improve the performance of all-organic batteries.

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