

Organic Radical Battery

by Hiroyuki Nishide and Takeo Suga

Organic Molecular Radicals—An organic molecular radical is a molecular entity possessing one unpaired electron such as $\cdot\text{CH}_3$ and $\cdot\text{CCl}_3$, in which the dot symbolizes an unpaired electron. Organic radicals often appear as intermediates in photochemical and thermal reactions and are also known to initiate and propagate polymerization and combustion reactions. They are usually short-lived and highly reactive, being converted to stable molecules through dimerization or redox reactions with other molecules, solvents, or molecular oxygen. For example, the methyl radical easily forms ethane ($2\text{CH}_3\cdot \rightarrow \text{CH}_3\text{-CH}_3$) by dimerization. Thus the organic molecular radicals had been hitherto classified as unstable and intractable materials.

However, organic radicals can be chemically modified into stable compounds, existing for appreciable lengths of time under ambient conditions. Chemical stabilization is achieved via sterically protected structures around the radical centers or the unpaired electrons and/or by resonance structures involving the unpaired electrons. Based on these chemical modifications, hundreds of stable organic radicals are now known.¹ Examples are contained in Fig. 1. Tris(pentachlorophenyl)methyl and bis(diphenylenepropenyl)phenylmethyl are carbon-centered radicals. Diphenylpicrylhydrazyl (DPPH) and triphenylaminium cationic radicals are examples of nitrogen-centered radicals. Oxygen-centered species involve molecular radicals such as 2,4,6-tri-*t*-butylphenoxyl, galvinoxyl, nitronyl nitroxide, and 2,2,6,6-tetramethyl-1-piperidinyl-1-oxyl (TEMPO).²

Some stable radicals such as TEMPO and their derivatives are

commercially available and widely used as spin labels for monitoring biomolecules and as spin traps or radical scavengers of organic materials and biological systems. Precursors of radical molecules are also produced in ton level quantities as antioxidants and as light-stabilizers for plastics and commodity materials. For example, hindered amines (and polyamines) and hindered phenols (and polyphenols) act as antioxidants to reductively remove oxygen and radical contaminants, yielding stable radical species through the abstraction of hydrogen. In summary, organic molecular radicals and their precursors have been utilized in commodity stuffs, and have been examined and guaranteed as nontoxic materials.

Stable organic radicals have been extended to their polymeric radical analogs as well. The radical polymers were studied extensively in the 1970s as redox reagents or redox resins, which catalyze the oxidative

and/or reductive reactions of organic compounds. For example, poly(acrylic acid)-combined TEMPOs were synthesized and studied as a catalytic reagent for the oxidation of alcohols into aldehydes and ketones. The organic radical-based or metal-free redox reagents have been reexamined recently from the perspective of green or environmentally compatible chemical reaction processes.

Why do nitroxide radical polymers work as catalysts? Electrochemical studies of these polymers have revealed that the nitroxide center displays reversible redox behavior attributable to oxidation of the nitroxide radical and reduction of the corresponding oxoammonium form. However, there has been no report, except for our work, in which organic radical polymers have been utilized as the electrode-active or charge-storage component for a secondary battery.^{3, 4} A battery composed of the radical polymer electrode is a so-called organic radical battery here.

Redox Couples of the Nitroxide Radical Leading to an Organic Radical Battery

A nitroxide radical is a typical oxygen-centered stable radical with spin-density localization on the oxygen atom, and involves the resonance structure shown in Fig. 2 that contributes to the high stability of the radical. A nitroxide radical is also characterized by its significantly small molecular weight per the radical moiety ($\text{N-O} =$ formula weight 30) and its compact molecular size.

The nitroxide radical displays two redox couples as illustrated in Fig. 3. On the anodic side, the nitroxide radical is oxidized to form the corresponding oxoammonium cation. For example, an oxoammonium phosphorus hexafluoride salt is formed in the presence of LiPF_6 which has been isolated as a stable salt. The oxidation process of the radical is reversible and leads to p-type doping of the radical material. On the cathodic side, the nitroxide radical is reduced to the aminoxy anion (e.g., the lithium alcoholate amine formation in LiPF_6), leading to n-type doping of the material. Our idea is that the anodic redox couple of the nitroxide radical and the cathodic couple are applicable to cathode and anode reaction of a secondary lithium-ion battery, respectively. We have synthesized a series of nitroxide polymers: The polymer involves the radical moiety with a high density and allows molding of electrodes. Figure 4 shows the

charging and discharging mechanism of a prototype organic radical-based lithium-ion battery where the p-type nitroxide radical polymer forms a cathode operated in conjunction with a carbon anode. 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 reduction of the oxoammonium.

A typical example of the nitroxide radical polymer is poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate) (PTMA, Fig. 5). This polymer is a derivative of a conventional plastic, polymethacrylate, and has a TEMPO radical in the repeating unit. PTMA is obtained by the polymerization of 2,2,6,6-tetramethylpiperidine methacrylate, a material known as a light stabilizer, followed by the oxidation reaction of the precursor polymer. PTMA is also prepared by the anionic polymerization of the radical monomer, 4-methacryloyl-2,2,6,6-tetramethylpiperidinyloxy. The molecular weight of PTMA is $>10^4$, and the radical content is almost 100% as shown by the chemical structure of PTMA in Fig. 5. PTMA is an amorphous polymer that exists in a glassy state at room temperature, with a glass transition temperature (T_g) to change to a rubbery state of 70°C . This is comparable to that of poly(alkyl methacrylate), which suggests that PTMA may have good processability and molding ability. PTMA is thermally stable at high temperature: A 10% weight decrease in the whole polymer occurs at 263°C . The radicals on the PTMA are almost stable up to this thermal decomposition temperature of the polymer. This radical concentration remains unchanged for over 1 year under ambient conditions. This polymer displays appropriate solubility in organic solvents and is insoluble in electrolyte solutions such as ethylene carbonate and diethyl carbonate with LiPF_6 .

Battery Fabrication and Performance

The radical polymer PTMA itself does not show sufficient electric conductivity; therefore, PTMA is mixed with 20-50 wt % graphite fibers to give a cathode electrode. A scanning electron microscopy (SEM) image of the composite electrode (Fig. 6) reveals that a graphite nanofiber with a diameter of 150 nm is thoroughly covered with a thin (50-100 nm thick) PTMA layer. Figure 7 shows a cyclic voltammogram

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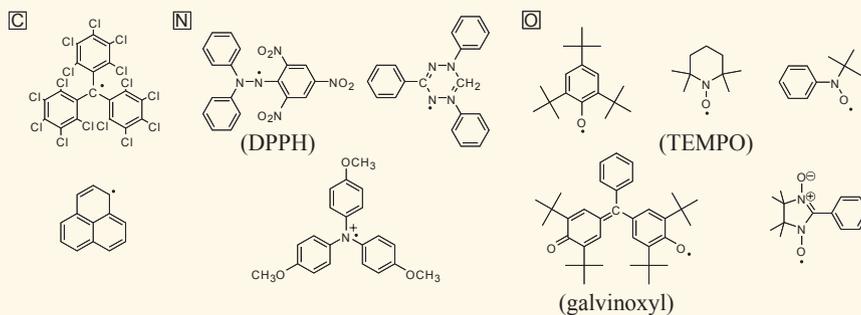


FIG. 1. Stable radical molecules. In the chemical formulae the unpaired electron is indicated by a dot.



FIG. 2. Resonance structures for a nitroxide radical.

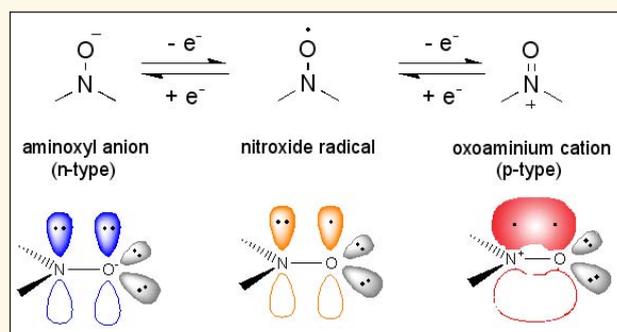


FIG. 3. Redox processes involving the nitroxide radical.

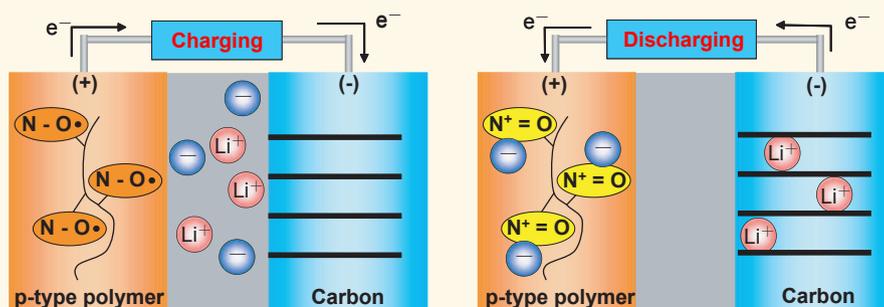


FIG. 4. A lithium-ion battery based on a radical polymer cathode.

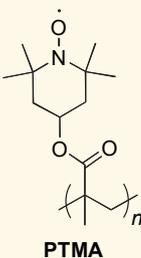


FIG. 5. The radical polymer, PTMA (see text).

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of the PTMA/carbon composite electrode. *In situ* electron spin resonance (ESR) signals (also shown in Fig. 7) support ESR-silent oxoammonium formation on the anodic side and regeneration of the nitroxide radical with very high concentration on the cathodic side. The redox potential of the PTMA electrode is 0.76 V vs. Ag/AgCl (3.58 V vs. Li/Li⁺). The narrow peak separation of the redox waves of the radical polymer even in the form of the electrode (Fig. 7) is attributable to fast electrode reaction kinetics, which affords the capability for a high power rate in the charging and discharging processes of the battery.

The test cell was fabricated by stacking the radical polymer electrode with a separator film and lithium metal or a graphite carbon as the anode (Fig. 4). Ethylene carbonate containing LiPF₆ was used as the electrolyte.

The charge-discharge curves for the fabricated PTMA lithium battery display a plateau voltage at almost 3.5 V, which agrees with the redox potential of the PTMA radical polymer. The charge and discharge capacities were very similar and were 110 mAh/g based on the PTMA weight at a current density of 0.1 mA/cm² (1 C), which is close to 100% of the theoretical capacity based on the amount of PTMA present on the electrode (111 mAh/g). The high current efficiency may be ascribed to the simple one-electron transfer reaction in the nanometer-size polymer layer of the electrode.

There was no self-discharge in the battery via eluting out of the radical polymer into the electrolyte solution. At a current density of 1.0 mA/cm² (10 C), the charging capacity still retained *ca.* 95% of that at 0.1 mA/cm² (1 C). A current density of 1.0 mA/cm² is much greater than those of conventional batteries, and only 5 min was needed to fully charge this battery. In another aspect (Fig. 8), almost no voltage drop and no capacity decrease were observed during the discharging process at a current density as high as 50 C rate. Such rapid charging and high power discharging behavior of the radical polymer battery is caused by rapid electron-transfer of the organic radical in the nanometer-size polymer layer (see above).

The cycle performance during charging and discharging in the range from 3.0 to 4.0 V of the fabricated battery has been tested; no significant deterioration in the capacity was observed for more than 1000 cycles. This surprisingly long cyclability may be ascribed to the chemical stability of the nitroxide radical, the simple one-electron transfer reaction of the radical, and to the amorphous electrode structure. The charging and discharging processes of this battery do not involve any structural change in the organic polymer or the electrode-active material, bringing about the strikingly long cycle life.

Previously Studied Organic Batteries

Organic functional polymers have been developed as alternatives of inorganic materials because of their light weight, flexibility, thin film-forming ability, processability, metal-free or benign environmental aspects, and no limitation

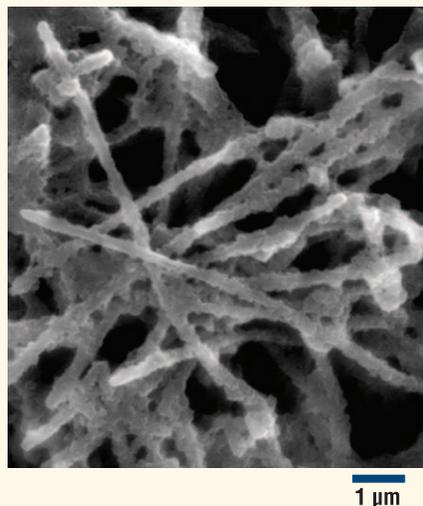


Fig. 6. A SEM image of the radical polymer (PTMA)/carbon composite cathode.

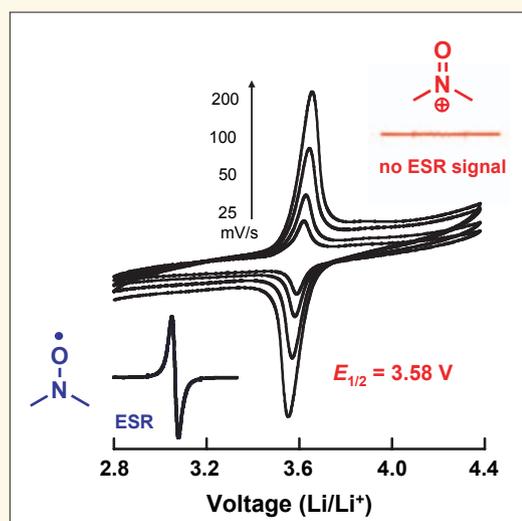


Fig. 7. Cyclic voltammogram of the radical polymer (PTMA) as the composite electrode.

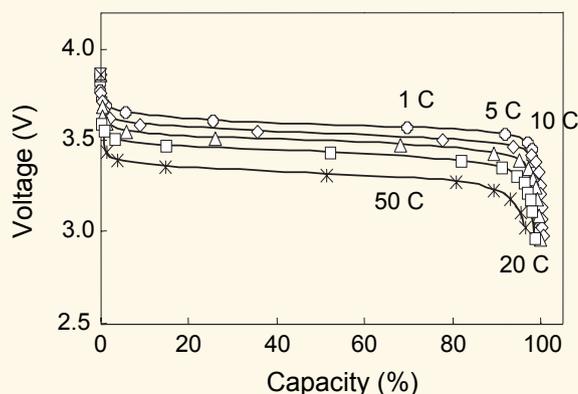


Fig. 8. Example of discharging curves for the organic radical battery.

in organic resources. Organic-derived electrode-active battery materials have been studied since the 1980s. MacInnes *et al.*, by extending their discovery of electrically conductive polyacetylene, reported in 1981,⁵ the potential application of p- and n-doping processes in polyacetylene to a rechargeable battery in an all-organic device design. However, the achievable doping degree of polyacetylene was limited to less than 10% of the repeating unit due to delocalized unpaired electrons on the π -conjugated backbone, which confined the energy-density of the battery to a low value. Relatively slow electrochemical kinetics during the doping/dedoping of polyacetylene, due to the slow diffusion of dopant ions in the polymer, also affected battery performance deleteriously. The cell voltage was not constant and dependent on the doping degree. The chemical instability of both the virgin and doped polyacetylenes was the fatal flaw to practically applying doped polyacetylene to a battery device.

Some electrically conducting polymers such as polythiophene, polypyrrole, and polyaniline have also been investigated as electrode materials. However, their doping and dedoping processes do not satisfy the requisites for a battery. The fluctuation problem of the cell voltage has not yet been solved. In the late 1980s, disulfide compounds were investigated intensively as a cathode material.^{6,7} However, their rate performance remains low due to the bimolecular redox reaction ($2RS\cdot \rightleftharpoons RS-SR$). Additionally, the nasty odor of sulfur compounds is a problematic practical issue.

Why the Nitroxide Radical Polymer?

The organic nitroxide radical has the following characteristics as an electroactive or charge storage material for batteries. One characteristic is the small molecular weight (formula weight) per active site among the redox active organic molecules, for example, 30, 64, and 186 for N-O, S-S, and ferrocene, respectively. That is, the specific capacity as an electrode may be enhanced by designing the molecular structure of the nitroxide derivative. Second, the repeating unit structure bearing a localized unpaired electron provides a high density of unpaired electrons in the radical polymer, that is, a deeply (almost quantitative) doped state. This is in contrast to the so-called polymer electrodes composed of π -conjugated conductive polymers.

The electron-transfer rate constant for the nitroxide radical in solution is estimated to be on the order of $>10^{-1}$ cm/s.⁸ This rapid electron-transfer rate for the nitroxide radical redox is the most important feature in comparison with the slow rates for the other organic redox couples (*e.g.*, the electron-transfer rate constant of 10^{-8} cm/s for a disulfide redox). The diffusion coefficient (D_{app}) of the redox or charge transfer in the radical polymer layer, using the PTMA-modified electrode: $D_{app} = 10^{-8}$ cm²/s, is comparable to those of previously reported redox-active polymers such as poly(vinylferrocene) ($D_{app} = 10^{-8}$ cm²/s). The amorphous, solvated, and slightly swollen structure of the radical polymer in the composite electrode ensures good counterion mobility during the electrode process. These features afford a high power-rate performance for the charge and discharge processes during battery applications.

The battery performance based on the PTMA cathode is projected on the energy and power density diagram for conventional batteries and capacitors (Fig. 9). The performance of the radical battery is characterized by both remarkably high power density and high energy density (or high capacity), and they are almost comparable to those of capacitors and conventional secondary batteries, respectively. By utilizing its high power performance and relatively high capacity, the radical battery is

now being tested, for example, as an uninterruptible power supply system (UPS) for the backup or shutdown of personal computers and computer servers during power failure.

Molecular Design toward an All-Organic Radical Battery

An ongoing issue with the organic radical battery is the enhancement of the energy density or the capacity. The theoretical capacity of PTMA as the cathode active material is 111 mAh/g, which is around two-thirds of the capacity of the cathode material (150-170 mAh/g) in conventional Li-ion batteries. Along with designing the molecular structure of the nitroxide derivative, we have proposed and synthesized a series of radical polymers with a compact molecular structure and a small molecular weight per active nitroxide site (Fig. 10). As shown in this diagram, some of these candidates are expected to display energy density or capacity beyond 200 mAh/g.

In addition to such a high energy density, it may be possible to synthesize radical polymers with intrinsic electrical conductivity (**6**) which could contribute to further improvements of the rate property or power density of the radical battery.

Based on our recent work, the radical polymer may be switched from p-type or cathode active material to n-type or anode active material. A typical example is the nitroxide-

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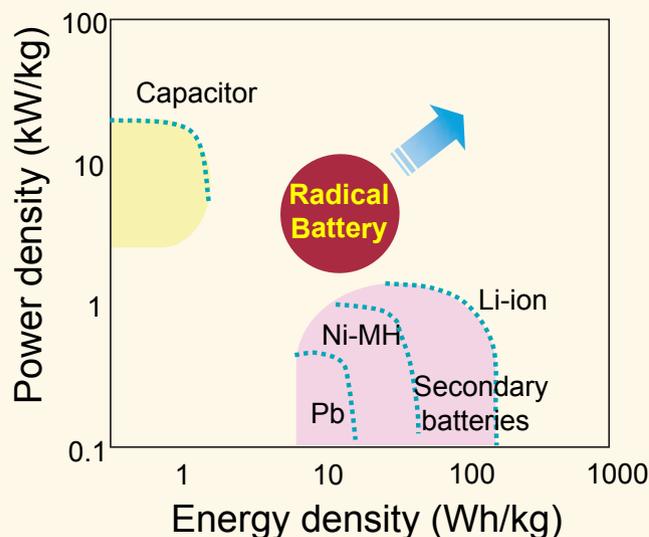


Fig. 9. Battery performance of the organic radical battery based on the PTMA cathode relative to conventional charge storage devices.

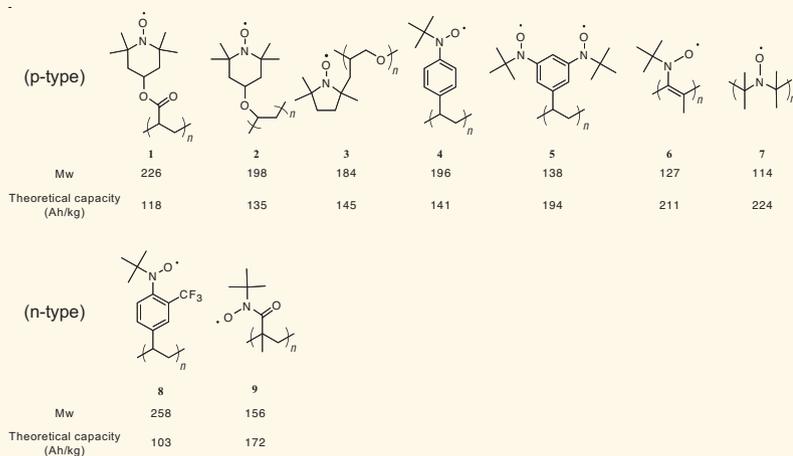


Fig. 10. Examples of radical polymers.

substituted polystyrenes: **4** displays p-type redox behavior, and polymer **8** shows n-type redox behavior. **8** bears a trifluoromethyl (CF_3) group, which acts as an electron-withdrawing group, to stabilize the n-type redox pair between the nitroxide radical and the aminoxy anion. The redox potential (cell voltage) also may be tuned via molecular design. For example, the redox potential of the nitroxide radical is tuned from 0.7 V (vs. Ag/AgCl) for PTMA to 1.0 V (vs. Ag/AgCl) for **3**. Such potential tuning is impossible for inorganic-derived materials. These possibilities with the radical polymers promise an all-organic battery as illustrated in Fig. 11. Molecular design and synthesis are powerful strategies for organic functional materials including the organic radical polymers.

The nitroxide radical polymer is completely burned to yield only carbon dioxide, water, and a small amount of nitrogen oxide, and undergoes thermal runaway with no odor or ash formation. The radical polymers are not toxic. These environmentally benign characteristics of the radical polymers are strong advantages vs. metal-based conventional (e.g., NiCd) or sulfur-based battery electrodes.

The organic radical polymer has solvent solubility and processability, which facilitates battery manufacture via a wet, printable, and rollable process. We envision a slim and flexible paper battery, a battery-on-chip, and a battery-on-package in the not-too-distant future. Current portable instruments are accelerating demands for a battery with a high capacity, high power rate, and light weight and the organic radical battery appears to fulfill these criteria. ■

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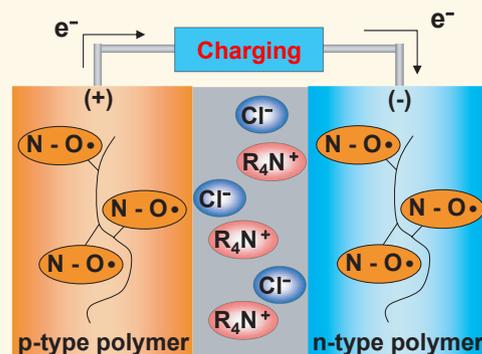


Fig. 11. Schematic diagram of an all-organic radical battery.

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