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Environmentally benign batteries based on organic radical polymers*

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Abstract: A radical polymer is an aliphatic organic polymer bearing densely populated unpaired electrons in the pendant robust radical groups per repeating unit. These radicals' unpaired electrons are characterized by very fast electron-transfer reactivity, allowing reversible charging as the electrode-active materials for secondary batteries. Organic-based radical batteries have several advantages over conventional batteries, such as increased safety, adaptability to wet fabrication processes, easy disposability, and capability of fabrication from less-limited resources, which are described along the fashion of green chemistry.

Keywords: electrode-active materials; functional polymers; green chemistry; radical molecules; secondary batteries.

INTRODUCTION

Rechargeable secondary batteries are widely used in portable equipment. Ubiquitous electronic devices, such as smart cards, IC tags, and rollup displays, and power electric instruments, such as electric vehicles and robots, and solar-energy and wind-power storage, also require the development of secondary batteries. Among the secondary batteries, Li-ion batteries are becoming the most popular: Almost 6 billion battery cells worth US$8 billion were produced in Japan in 2007 [1], which corresponded to almost half of the world-wide production of Li-ion batteries.

The configuration of a conventional Li-ion battery is illustrated in Fig. 1. The cathode is composed of Li-ion-containing metal oxides, such as cobalt oxide, and the anode is graphitic carbon; during the charging process, Li-ions are eliminated from the lattice of the metal oxide cathode and intercalated into the carbon anode. During the discharging process, the lithium cobalt oxide is regenerated by the reduction reaction with Li-ions [2]. That is, the Li-ion battery is based on the rocking-chair-type intercalation reactions of Li-ions between the cathode and anode materials. Li is the smallest among the elements except for hydrogen and helium, and the very high electromotive force of the Li-ion ($Li_xC \rightarrow xLi^+ + xe^- + C$: –2.9 V vs. NHE) results in a high energy-density performance and the highest given voltage at the battery. However, the intercalating diffusion of Li-ions accompanied by transformation of the lattice- and layer-structure during the electrode reactions causes slow kinetics and heat generation in the charging and discharging processes, sometimes producing overheating and occasionally ignition. Indeed, in 2007 and 2008, Panasonic and Sony issued recalls of their 46 and 0.1 million Li-ion batteries for mobile phones and laptops, respectively, due to overheating accidents [3,4].

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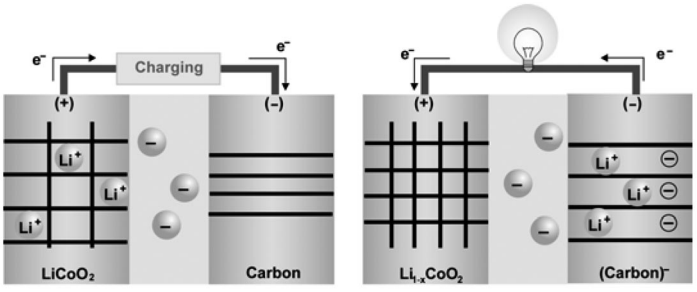


Fig. 1 Scheme of a conventional Li-ion battery.

The cathode- and anode-active materials of conventional primary and secondary batteries are usually metal-oxides, such as manganese-, silver-, lead-, nickel-, and, vanadium-oxides, and metals, such as zinc, lead, cadmium, and lithium [5]. That is, all the electrodes of conventional batteries are composed of such metals and metal oxides (except oxygen and carbon for the air battery cathode and the lithium battery anode, respectively), some of which come from limited resources.

Tedious waste processing of used batteries is another difficult and crucial issue of the metal- and metal oxide-based conventional batteries. Used batteries are, in these days of environmental concern, being collected and recycled. Among the recycling of used batteries, the Li-ion batteries are highly valued for their excellent collection yield of 60 % from personal computers and mobile phones [6]. The typical recycle processing of used Li-ion batteries, represented in Fig. 2, is reasonably working, at least in Japan, which includes several steps [7]. The first step is incineration at high temperature to open the batteries and burn out the electrolytes and separators. The residue is subsequently sieved and magnetically separated to obtain the steel and copper. The remaining powder is dissolved in acid, and the solvent extraction yields cobalt and other metal compounds. The recovered cobalt is re-introduced into the production cycle of batteries. However, the collection yields of used Li-ion batteries are somewhat decreasing because the batteries are being equipped in many varieties of small devices. Additionally, other used batteries are often found in landfill disposal or simply stand at the level at 60 kton/year even in Japan [8]. The conventional metal-based batteries involve several inherent unsolved issues from the standpoint of green chemistry.

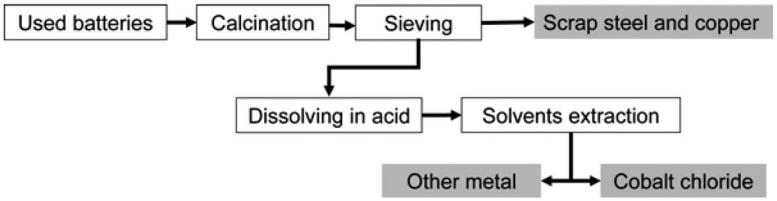


Fig. 2 Recyling of used Li-ion batteries in Japan.

ROBUST RADICAL MOLECULES

Organic functional polymers have been developed as alternatives of inorganic functional materials because of their light weight, flexibility, thin film-forming ability, processability, metal-free, or benign environmental aspects, and fewer limitations by organic resources. Organic-derived electrode-active battery materials have been studied since the 1980s. McDiarmid and Heeger, by extending their discovery of electrically conductive polyacetylene, reported in 1981 [9], the potential application of p- and n-doping processes in polyacetylene to rechargeable batteries in an all-organic device design. However, the

achievable doping degree of polyacetylene was limited to less than 10 % of the repeating units, which confined the energy-density of the battery to a low value. The chemical instability of both the virgin and doped polyacetylenes was the fatal flaw to practically applying the polyacetylenes to a battery device. In the late 1980s, disulfide compounds were intensively investigated as a cathode material [10]. However, their rate performance remains low due to the bimolecular redox reaction (2RS· ⇌ RS-SR). Additionally, the nasty odor of sulfur compounds is a problematic practical issue.

Our original plan to develop an organic polymer-based battery or a plastic battery using organic electrodes is being achieved by focusing on and utilizing robust organic radical molecules. The radical molecule is an organic molecular entity possessing one unpaired electron, which often appears as an intermediate during photochemical and thermal reactions and is also known to initiate and propagate polymerization and combustion reactions. They are usually short-lived and highly reactive, thus the organic radicals had been classified as unstable and intractable materials. However, organic radicals have been chemically modified into stable or robust compounds, existing for appreciable lengths of time under ambient conditions. Chemical stabilization has been 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 [11].

Some robust radicals are commercially available, and examples are shown in Fig. 3 (the dots symbolize an unpaired electron). They are widely used as spin labels for monitoring biomolecules and as spin traps or radical scavengers of organic materials and biological systems.

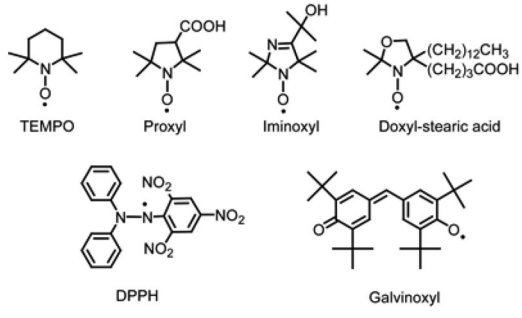


Fig. 3 Commercially available robust organic radicals as a spin-label and spin-trap.

Precursors of radical molecules are also produced in multi-ton quantities as antioxidants and as light-stabilizers for plastics and commodity materials (Fig. 4). 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 short, organic molecular radicals and their precursors have been utilized in commodity materials and biomedical applications, and have been examined and guaranteed as nontoxic materials.

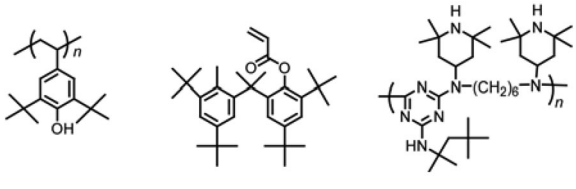


Fig. 4 Radical precursors as an antioxidant and a light-stabilizer.

Robust organic radicals have also been extended to their polymeric radical analogs (Fig. 5). The radical polymers were extensively studied in the 1970s as redox reagents or redox resins, which catalyze the oxidative and/or reductive reactions of organic compounds. For example, poly(acrylate)-combined TEMPOs were synthesized and studied as a catalytic reagent for the oxidation of alcohols into aldehydes and ketones (TEMPO: 2,2,6,6-tetramethylpiperidine-1-oxyl) [12]. The organic radical-based or metal-free redox reagents have been recently reexamined from the perspective of green or environmentally compatible chemical reaction processes.

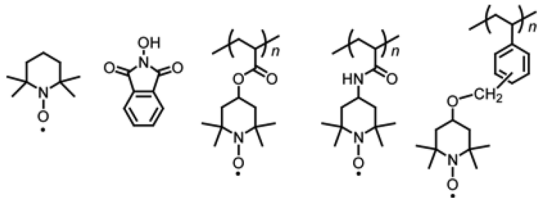


Fig. 5 Nitroxide radicals as a redox catalyst.

ELECTRON-TRANSFER PROCESS OF RADICAL POLYMERS

Why do the radical polymers work as redox catalysts? Important electrochemical studies have revealed that the nitroxide radical displays a reversible redox behavior attributable to the one-electron oxidation of the nitroxide radical and reduction of the corresponding oxoammonium to the original nitroxide (the left-hand reaction in Fig. 6). This reversible oxidation corresponds to the p-type doping of the radical material. On the other hand, a phenoxyl radical is one-electron reduced to form the corresponding anion and oxidized back to the phenoxyl radical (the right-hand reaction in Fig. 6), leading to the n-type doping of the material. However, there has been no report, except for our work, in which organic radical molecules and polymers have been utilized as the electrode-active or charge-storage component for a secondary battery [13–15]. Our idea is that the redox couple of the nitroxide radical and of the phenoxyl radical are applicable for the cathode and anode reaction of a secondary battery, respectively, as illustrated in Fig. 9 (described later).

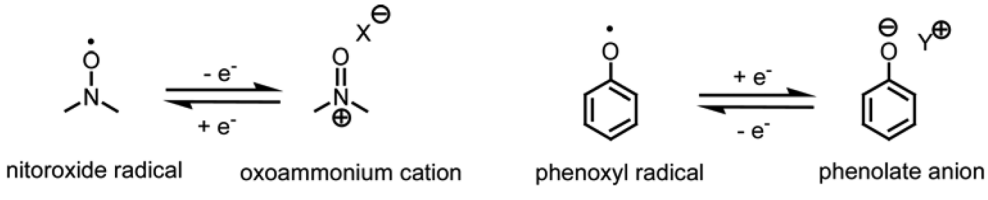


Fig. 6 Redox couple of a nitroxide radical and a phenoxyl radical.

Not only radical molecules, but also their oxidized (p-doped) and reduced (n-doped) forms play important roles in battery electrode performance. For example, the oxidized form of the TEMPO radical, that is, the oxoammonium cation salt, was isolated, which was robust as well as the radical molecule under ambient conditions. Chemical stability of both the radical and the doped forms is essential for durability of the charging and discharging processes of the battery. Figure 7 shows the crystallographic structures and IR data of the TEMPO derivative and its oxoammonium compound [16]. The latter was characterized by the double-band nature of N–O and almost planar C_2O plane due to the sp^2 character of the nitrogen atom. However, the structural change between the radical and the oxoammo-

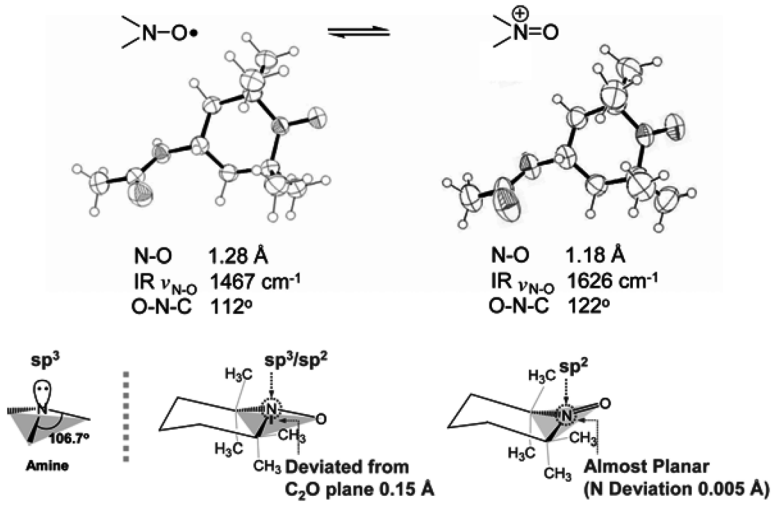
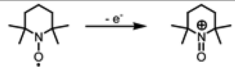
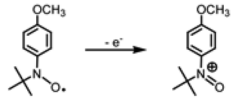
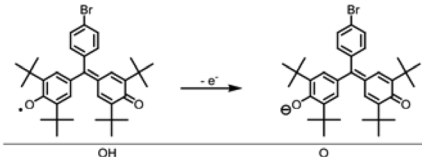
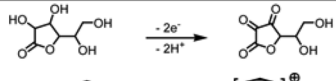
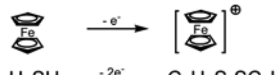


Fig. 7 Structures of the nitroxide radical and oxoammonium cation of a TEMPO derivative.

nium was very slight, which could be responsible for the rapid electron-transfer reaction of the radical molecule.

Electron-transfer rate constants (k_0) for the nitroxide radicals and the phenoxyl radical in solution were estimated to be on the order of 10^{-1} cm/s [17] (Table 1). This rapid electron-transfer rate for the radical redoxes is the most important feature when compared to the slow rates for the other organic redox reactions (e.g., the electron-transfer rate constants of 10^{-4} and 10^{-8} cm/s for the ascorbic acid oxidation and thional oxidation to form a disulfide, respectively). The electron-transfer reactions of the radical molecules are rather faster than that for the ferrocene, well known as a standard molecule in electrochemical reactivity, and are almost comparable to that for the copper ion.

Table 1 Electron-transfer rate constant (k_0) of radical molecules.

Oxidation reaction	k_0(cm/s)
	1.0×10^{-1}
	1.7×10^{-1}
	0.38×10^{-1}
	$\sim 10^{-4}$
	$\sim 10^{-2}$
$2\ C_4H_9SH \xrightarrow[-2H^+]{-2e^-} C_4H_9S\text{-}SC_4H_9$	$\sim 10^{-8}$
$Cu \xrightarrow{-e^-} Cu^{\oplus}$	$\sim 10^{-1}$

The radical polymer electrode was prepared by coating the polymer on a current collector, such as an indium tin oxide-polyester (ITO-PET) film and glassy carbon substrate. In the radical polymer layer, an electron is hopping or a charge is transferred (or propagated) via the redox reaction of the neighboring radical moieties on the polymer (or the geared cycles of the radicals' redoxes) (Fig. 8). The redox process is accompanied by incorporation and transfer of a counter ion (here an anion) to compensate the charge, which would be the rate-determining step of the charge propagation. The diffusion coefficient (D) of the electron- or the charge-propagation in the radical polymer layer was on the order of 10^{-9} cm^2/s [18], which was comparable to those of preciously reported redox-active polymers, such as poly(vinylferrocene) ($D = 10^{-9}$ cm^2/s). The amorphous, solvated, and slightly swollen structure of the radical polymer in the electrode ensures a fast counter ion mobility during the charge-transfer process. These features afford a high power-rate performance for the charging and discharging during battery applications of the radical polymers.

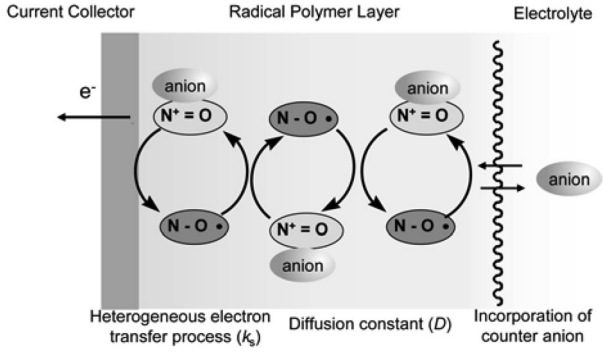


Fig. 8 Charge-propagation in the radical polymer layer.

PERFORMANCE OF TOTALLY ORGANIC RADICAL POLYMER BATTERY

Radical polymers with different redox potentials can be employed as the cathode- and anode-active materials in an all organic-based battery [19] (Fig. 9). A representative combination is the poly(methacrylate)-combined TEMPO, poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate), shown in the upper left section of Fig. 11, as the cathode and the poly(galvinoxylstyrene) (the third listing in the lower column of Fig. 12) as the anode. These two polymers were synthesized via the radical polymerization of the corresponding nonradical precursor methacrylate and styrene derivatives followed by chemical oxidation to generate the radical polymers. The radical density of each polymer was >0.9 unpaired electrons per monomer unit. Solutions of the radical polymers were coated as thin films on an ITO-PET substrate as the current collectors. The coated radical polymers were suitably modified via a cross-linking reaction to impede their dissolution into the electrolyte solution which causes self-discharging of the battery. A microporous separator film containing the electrolyte solution, such as ethylenecarbonate containing tetrabutylammonium chloride, was sandwiched between two radical polymer films coated on the current collectors, in order to fabricate the all-organic battery consisting of radical polymer electrodes, namely, an all-organic "radical battery" [20].

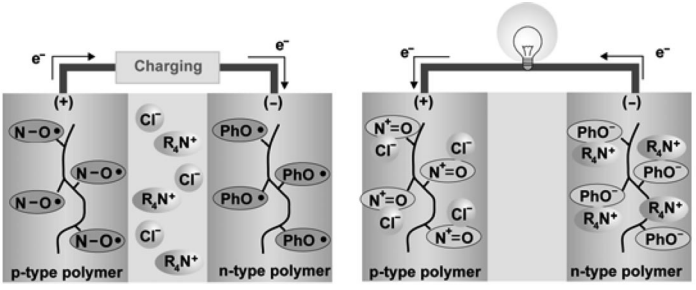


Fig. 9 Totally organic radical polymer battery (Li-ion-free secondary battery).

Figure 10 is a picture of the paper-like and flexible, totally organic radical battery [19]. The blue color in the charged state results from the galvinolate anion that dramatically reverted to a light yellow color of the galvinoxyl radical in the discharged state. In a see-through battery, the color change, accompanied by radical redox reactions, can be used as an indicator of the charging level. The organic radical battery composed of the radical polymer electrodes has several advantages [15,20]: (1) a high-charging and -discharging capacity (>100 mAh/g), ascribed to the stoichiometric redox of the radical moieties, (2) a high-charging and -discharging rate performance resulting from the rapid electron-transfer process of the radical species and from the amorphous state of the radical polymers, and (3) a long cycle life, often exceeding 1000 cycles, derived from the chemical stability of the radicals and from the amorphous electrode structure.

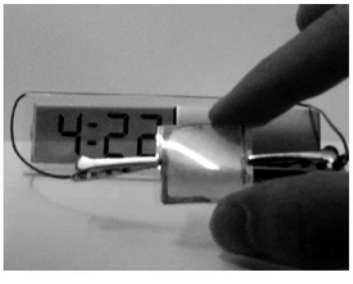


Fig. 10 Flexible plastic battery totally composed of organic radical polymers.

A series of radical polymers has been synthesized, and Figs. 11 and 12 depict the radical polymers previously reported by our groups [13–24]. A variety of polymer backbones have been employed to bear the pendant radical groups, such as poly(meth)acrylates, polystyrene, poly(vinyl ether)s, polyethers, and poly(norbornene)s. For example, the backbones with a lower glass transition temperature or rubbery polymers often produced a higher rate performance during the charging and discharging processes.

We have extensively explored the n-type redox-active radical polymers (Fig. 12), for example, introducing an electron-withdrawing group, such as a carbonyl and trifluorometyl group, on the neighboring position of the nitroxide group in order to stabilize the n-type redox pair and to tune the redox potential. The molecular design and synthesis based on green chemistry are powerful strategies for developing organic functional materials including the organic radical polymers.

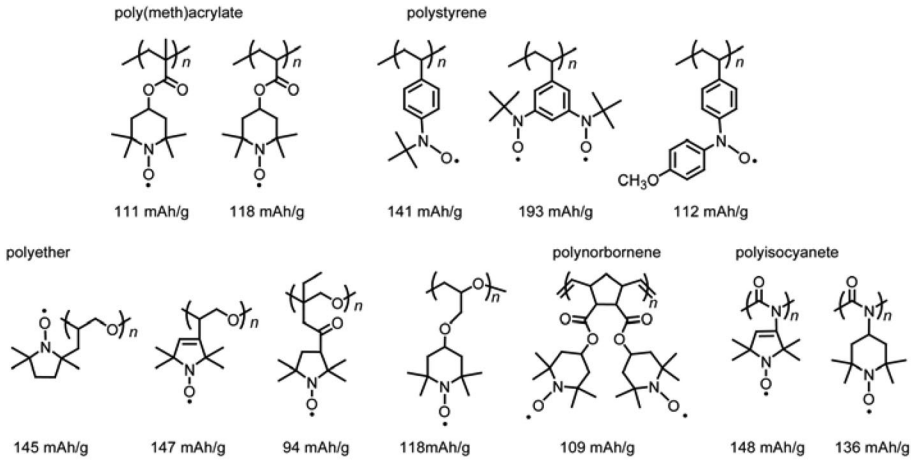


Fig. 11 Nitroxide radical polymers based on various polymer backbones.

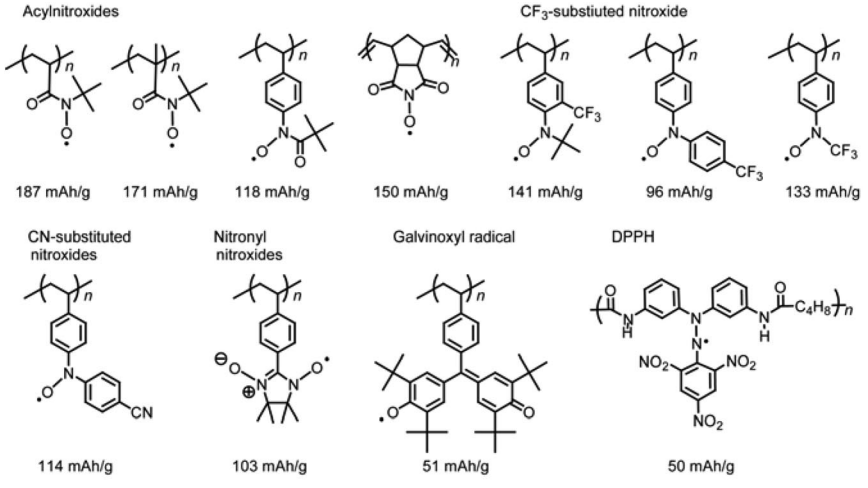


Fig. 12 n-Type radical polymers.

AQUEOUS ELECTROLYTE-TYPE RADICAL POLYMER BATTERY

The radical polymers shown in Figs. 11 and 12 are lypophilic, and organic electrolytes are generally used for the battery. Safety (ignition risk-free) of the radical battery and sustainability both of the battery and during its fabrication process could be improved by using aqueous electrolytes in the radical battery. Radical polymers for use in an aqueous electrolyte-type battery have been designed [25]: These radical polymers are composed of a hydrophilic polymer backbone and a redox-active pendant even in aqueous electrolytes. Such examples are poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl vinylether) and poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl acrylamide) (Fig. 13), the hydrophilic polyvinylether and polyacrylamide bearing the robust TEMPO as the redox-active pendant, respectively. The polyvinylether-TEMPO displayed a chemically reversible redox at 0.73 V (vs. Ag/AgCl) in 0.1 M NaCl (in the pH range of 1–8) under air. The capacity of the radical polymer electrode was proportional to the polymer film on the current collector and reached 45 mC/cm^2 for the film with a thickness of 1 μm. Additionally, the combination of the hydrophilic radical polymer and the aqueous electrolyte has allowed a high charging–discharging rate performance. The charging-rate performance of the battery fab-

ricated with the polyvinylether-TEMPO electrode is shown in Fig. 14. The capacity of the cell charged even at 1200 C (The 1C rate is defined as the current density at which the charging or discharging of the cell takes 1 h. 1200 C corresponds to the full charging for 3 s) was retained at 97 % of the calculated capacity. Ultrafast and quantitative full charging was demonstrated for the aqueous electrolyte-based battery. The battery capacity was almost maintained even after 1000 charging–discharging cycles (inset of Fig. 14). This excellent battery performance was ascribed to the synergistic effect of the homogeneously solvated hydrophilic radical polymer and the aqueous electrolyte which possesses a high equivalent electrical conductivity on the order of 10^{-2}~10^{-3} m^2S/mol. In addition to the environmentally benign features when using aqueous electrolytes (such as an aqueous sodium chloride solution for the battery), the molecular designing of battery materials along the guidance of green chemistry allowed an ultrafast charging capability of the battery in as short as 3 s for full charging.

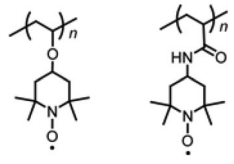


Fig. 13 Polyvinylether- and polyacrylamide-TEMPO radicals.

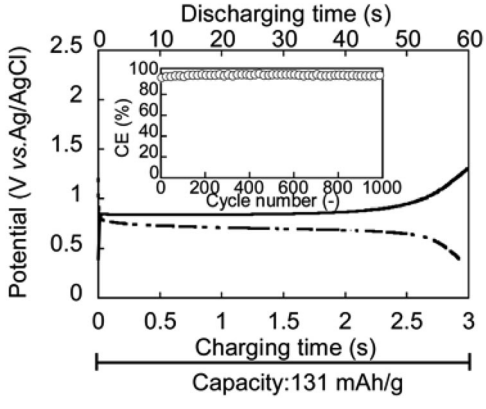


Fig. 14 Charging–discharging property of the aqueous electrolyte-type radical polymer battery. Solid line: charging; dashed line: discharging. Inset: Columbic efficiency of the aqueous electrolyte type-radical polymer battery.

The organic-based and Li-ion-free radical batteries have several advantages over the conventional batteries, that is, (1) a higher safety in avoiding ignitable and toxic substances such as lithium and lead, (2) an adoptability to less energy-consuming wet fabrication processes during battery manufacturing, (3) an easy disposability such as incineration without any toxic gas and ash formation, and (4) the capability of fabrication from less-limited resources. We envision a slim and flexible paper-like battery, a battery-on-chip, and a battery-on-package in the not-too-distant future. Current portable equipment and power instruments are accelerating the demands for a battery with a high capacity, high power rate, and light weight, and the organic radical battery appears to fulfill these criteria. Organic radical polymers are becoming a new class of functional materials (vs. metal- and silicon-based materials) that are relevant to the application of electric and energy devices.

ACKNOWLEDGMENTS

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