doi:10.1246/cl.2011.222

Highlight Review

Organic Radical Battery Approaching Practical Use

Kentaro Nakahara, Kenichi Oyaizu, and Hiroyuki Nishide*

(Received December 1, 2010; CL-108014)

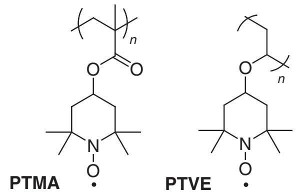
Abstract

The electrochemical redox reactions of organic polymers bearing robust unpaired electrons were investigated to determine the applicability of these polymers to rechargeable batteries. Such an “organic radical battery” would be environmentally friendly and have high-power characteristics. This highlight review describes the performance of a battery using a nitroxyl radical polymer as the cathode active material. The electron-transfer mechanism and recent developments that should lead to the practical application of the organic radical battery are also described.

◆ 1. Introduction

Lithium-ion batteries are widely used power sources for portable electric devices such as cellular phones and laptop computers because of their high-energy density and long life. Application of these batteries is expanding to electric vehicles and domestic energy storage.[1–5] In these batteries, a lithium transition-metal oxide cathode and a graphite anode are used as energy storage electrodes. Since the lithium transition-metal oxide cathode comprises the main part of a lithium ion battery, the lithium transition-metal oxide mainly determines the battery’s energy density and capacity. The lithium transition-metal oxide is charged/discharged electrochemically in accordance with de-intercalation/intercalation of the lithium ions and oxidation/reduction of the transition-metal ions. Although toxicity, safety, and resource availability are known problems with lithium transition-metal oxide, alternatives have been hardly reported except for conducting polymers and disulfide compounds.[6,7]

Radical polymers are candidates for replacing lithium transition-metal oxide.[8–11] We call a polymer which has unpaired electrons a radical polymer. The disappearance of the unpaired electrons due to chemical bond formation can be suppressed by a precisely designed chemical structure through a combination of the resonance effect of the electrons and the sterically hindered effect of the substituent groups. Chemical groups such as nitroxyl, phenoxyl, and hydrazyl are robust structures with less-reactive unpaired electrons in the uncharged state. Radical polymers with alicyclic nitroxyl such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) and 2,2,5,5-tetramethylpyrrolidine-1-oxyl (PROXYL) in particular have been studied in detail.[8–12] Two previously synthesized nitroxyl radical polymers, poly(2,2,6,6-tetramethylpiperidine-4-yl-1-oxyl methacrylate) (PTMA)[8,9] and poly(2,2,6,6-tetramethylpiperidine-4-yl-1-oxyl vinyl ether) (PTVE),[12] are promising candidates because they provide sufficient stability, high voltage, and high specific capacity for battery use (Scheme 1).[8,9]



Scheme 1. Molecular structures of PTMA and PTVE.

Radical polymers show reversible redox electrochemical reactions in aprotic solutions.[8] Preparing a polymer composite electrode with carbon materials significantly enhances the electrochemical activity.[8,9] A previous study[8] showed that a lithium battery with a radical polymer composite cathode has an operating voltage of 3.5 V with cyclability comparable to that of a conventional lithium ion battery. We call these new batteries “organic radical batteries.” The highest theoretical capacity of the nitroxyl radical polymers is 147 mA h g^{-1},[13,14] which is comparable to the practical specific capacity of $LiCoO_2$ (140 mA h g^{-1}).[1,2] The organic radical battery is a promising environmentally friendly and high-power rechargeable battery.[15]

This highlight review mainly describes the performance of organic radical batteries using a nitroxyl radical polymer as the cathode active material. The redox reactions of the radical polymer, the electron-transfer mechanism in the composite electrode, and recent developments in its practical use are also described.

◆ 2. Radical Polymers for Rechargeable Battery Electrode

Most radical polymers consist of two main components: a robust radical pendant and a backbone polymer. For use in rechargeable batteries, a radical polymer must be robust over a long period of time, possess insolubility in but affinity to electrolyte, and support high energy density.

To be robust in an electrochemical cell for a long period of time, the unpaired electrons in the polymer must be sufficiently unreactive in the electrolyte. This is an essential and difficult-to-achieve requirement for molecular design. Typical structures of the radical pendants are alicyclic nitroxyls such as TEMPO and PROXYL. For example, unpaired electrons in the TEMPO structure can survive for more than a year in aprotic solution containing 1.0 M lithium hexafluorophosphate ($LiPF_6$).

Mr. Kentaro Nakahara,[1,2] Prof. Kenichi Oyaizu,[1] and Prof. Hiroyuki Nishide*[1]
[1]Department of Applied Chemistry, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555
[2]Green Innovation Research Laboratories, NEC Corporation, 34 Miyukigaoka, Tsukuba, Ibaraki 350-8501
E-mail: nishide@waseda.jp

The structures of the backbone polymer affect insolubility in and affinity to the electrolyte. To prevent the radical polymer from contacting the opposite electrode, the polymer should be insoluble in the electrolyte. The polymer should also have affinity for the electrolyte to support the ionic conductivity. To date, various backbone polymers, such as polymethacrylate,[8,9] poly(vinyl ether),[12] polystyrene,[16,17] polyether,[13] polynorbornene,[18–20] polysiloxane,[21] polyacetylene,[22,23] cellulose,[24] and DNA complexes[25] have been reported. The polymer used must be dense in a thick electrode to obtain sufficient capacity. From the viewpoints of processability and mechanical strength, backbone polymers such as polymethacrylate, poly(vinyl ether), and polyether, are promising backbone structures for the radical polymers.

The energy density of a battery is represented by the product of the voltage and the capacity. The reaction voltage of radical polymers is affected by the type of redox reaction. Radical polymers cause two types of redox reactions, between a radical and a cation (p-type) and between a radical and an anion (n-type).[8–11] Although both types of reactions can be used as an alternative to the reaction of lithium transition-metal oxide, the voltage of a p-type reaction tends to be higher than that of an n-type reaction. Using a p-type reaction is thus better for obtaining high energy density.

The theoretical capacity of a radical polymer is inversely proportional to the molecular weight of the monomer unit. High theoretical capacity is thus obtained from a compact unit structure. A polyether bearing 2,2,5,5-tetramethyl-2,5-dihydro-1*H*-pyrrol-1-oxyl-3-yl has a theoretical capacity of 147 $\mathrm{mA\,h\,g^{-1}}$,[13,14] the highest theoretical capacity for radical polymers to date, when a one-electron redox reaction is assumed.

The energy density of an organic radical battery can be calculated by assuming that it has a radical polymer cathode and a lithium metal anode. Such calculation shows that the p-type reaction of nitroxyl radical polymers has an energy density of 400–550 $\mathrm{mW\,h\,g^{-1}}$ (Figure 1). In contrast, the energy density of an n-type reaction in a modified nitroxyl radical polymer and in a poly(galvinoxylstyrene) is 250 and 150 $\mathrm{mW\,h\,g^{-1}}$, respectively. The p-type reaction of nitroxyl radical polymers means that they are now considered to be the closest to a practical alternative to lithium transition-metal oxides.

◆ 3. Electron Transfer in Radical Polymer Electrode

The working mechanism of the organic radical electrode is thought to have two electron transfer steps (Figure 2).[26] The first step is heterogeneous electron transfer from a current collector to the radical component. The second step is homogeneous electron transfer among the radical components.

For the first step, the standard rate constant (k_0) of the TEMPO structure on a platinum surface was investigated using electrochemical methods such as cyclic voltammetry, chronoamperometry, and AC impedance spectroscopy[27] and was found to be ca. $10^{-1}\,\mathrm{cm\,s^{-1}}$ with each method. The rate constant is thus almost of the same order as that for the redox reactions of transition-metal ions ($\mathrm{Co^{2+}/Co^{3+}}$: ca. $10^{-2}\,\mathrm{cm\,s^{-1}}$)[28] and is several orders larger than that of disulfide compounds (ca. $10^{-8}\,\mathrm{cm\,s^{-1}}$).[28] The conformation of the molecule is almost unchanged during the electron-transfer process, which promotes fast electron transfer. The rate of the electrochemical reaction is determined completely by the diffusion rate of the molecules onto the platinum surface.

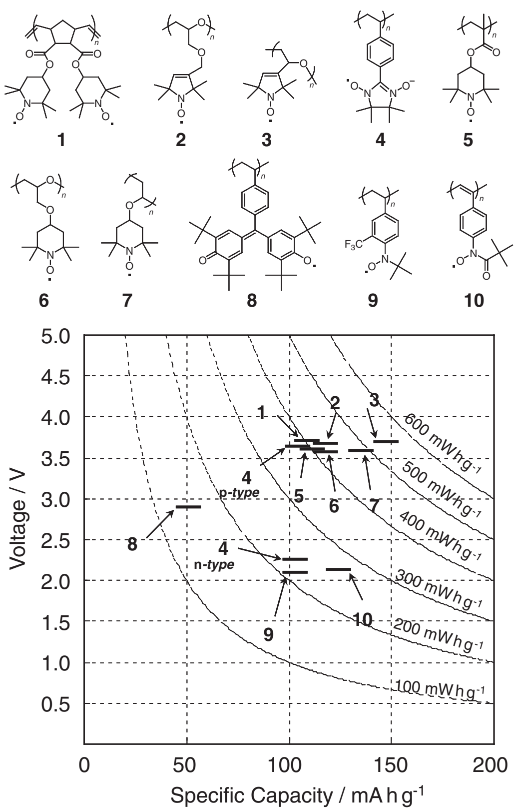


Figure 1. Operating voltage vs. specific capacity of radical polymers.

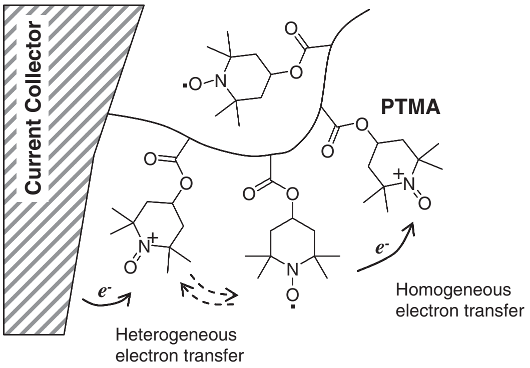


Figure 2. Electron-transfer profile in a radical polymer electrode.

We investigated in detail the homogeneous step of the reaction by using a crosslinkable polynorbornene bearing TEMPO components.[29] In this step, electron transfers are apparently driven by the concentration gradient through an electron self-exchange reaction between neighboring radicals. The bimolecular rate constant (k_{ex}) of the self-exchange reaction was estimated to be $1.8 \times 10^5\,\mathrm{M^{-1}\,s^{-1}}$. Although the polymer does not contain any transition metals, the rate constant is almost the same as that of transition metal containing polymers such as poly(vinylferrocene) (ca. $10^5\,M^{-1}\,s^{-1}$).[30] The relatively fast self-exchange reaction causes Nernstian adsorbate-like behavior in even 10 to 100 nm-thick layers. The diffusion constant of the polymer electrode is reported to be $5.3 \times 10^{-10}\,cm^2\,s^{-1}$.[29] The electron transfer in radical polymer electrodes is determined completely by the fast self-exchange reaction in the polymer. Radical polymer electrodes are thus promising for application to rechargeable batteries. The radical polymers can be viewed as electro-active polymers although their working mechanism is different from that of π-conjugated polymers.

♦ 4. Radical Polymer/Carbon Composite Electrodes

In the organic radical battery, polymer/carbon composite electrodes can be used to further the conductivity of the radical polymer electrodes.[8,9] A radical polymer/carbon electrode is fabricated by first finely pulverizing the radical polymer.[31] The polymer particles are typically made smaller than 50 µm because their size affects the capacity and rate capability of the composite electrode. The pulverized polymer is mixed homogeneously with carbon and a binder. The mixture is dispersed in water to form composite slurry. The slurry is spread on aluminum foil using a doctor blade. Drying of the slurry at 100 °C results in a radical polymer/carbon electrode. The SEM image in Figure 3a clearly shows the homogeneous dispersion of a PTMA/vapor-grown carbon fiber (VGCF) electrode. Many types of carbon, such as Ketjen black, acetylene black, and carbon fiber, have been investigated for use as a composite electrode. Among them, carbon fiber is the most promising due to its mechanical strength and the long-distance-electron conductivity of the composite electrode resulting from the high aspect ratio of the carbon fiber.[32]

The ratio at which the radical polymers and carbon are mixed significantly affects the capacity and the resistance of the electrode. Generally, the higher the ratio of polymers, the higher the capacity and resistance.[33] However, a radical-polymer-rich electrode (80 wt % PTVE and 15 wt % VGCF) coped with both high capacity and low resistance.[34] The electrochemical properties of a composite electrode can be improved by revising the fabrication. Also important for obtaining a homogeneously dispersed electrode is the selection of the binder and slurry solvent.

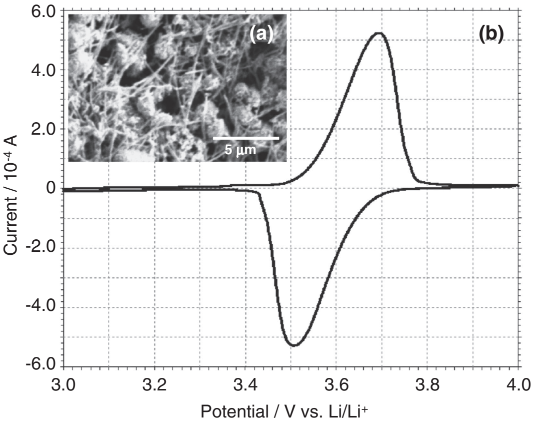


Figure 3. (a) SEM image of PTMA/VGCF composite electrode. (b) Cyclic voltammogram of PTMA/VGCF composite electrode. Platinum wire and lithium metal were used as counter and reference electrodes. Electrolyte was 1.0 M $LiPF_6$ EC/DEC = 3/7. Sweep speed was $1\,mV\,s^{-1}$.

The electrochemical properties of a PTMA/VGCF composite electrode were investigated[31] by using a platinum wire as a counter electrode and lithium metal as a reference electrode. As shown in Figure 3b, the cyclic voltammogram obtained for the electrode in an aprotic electrolyte displayed a pair of current peaks at the standard redox potential of 3.58 V vs. Li/Li^+. The peaks were remarkably sharp, and their separation was quite narrow. This indicates that the redox reaction of PTMA was homogenous and that the redox reaction at each site was almost independent. The densely populated radical components brought about high capacity without any limitations.

♦ 5. Cell Performance of PTMA/Carbon Composite Cathode

The half-cell performance of a PTMA/VGCF composite cathode was investigated[31] for a cathode comprising 50 wt % PTMA powder, 45 wt % VGCF, 4 wt % carboxymethyl cellulose, and 1 wt % poly(tetrafluoroethylene). The cathode was 130–180 µm thick. The electrolyte in the half-cell was an ethylene carbonate and diethyl carbonate solvent mixture containing 1.0 M $LiPF_6$. The cell was a 2320 coin-type cell with a lithium metal anode.

5.1 Capacity and Voltage of Li/PTMA Coin Cell

The charging and discharging curves obtained for the voltage range 2.6–4.5 V displayed obvious plateaus. The discharge plateau showed average discharge voltage of 3.51 V. The specific capacity of the PTMA was $110\,mA\,h\,g^{-1}$, nearly equal to the theoretical capacity ($111\,mA\,h\,g^{-1}$), indicating that almost all the nitroxyl radical components contributed to the charge storage. This is evidence that the composite electrode allowed delivering of electrons to all radical components in the oxidized state during discharge and that electro-neutralization with electrolyte counter-ions occurred throughout the radical polymers.

The rate dependence of the discharge curve for this electrode was investigated[31] for 1–20 C at 45 °C (Figure 4b). A discharge current of 1 C corresponded to a current density of $0.27\,mA\,cm^{-2}$. The discharge capacity at 20 C was 78% that at a 1 C. The capacity decrease at a high discharge rate (Figure 4a) was caused by an increase in the number of inert radical components in the radical polymers rather than an increase in the direct current resistance. The increase in the number of inert radical components was due to the limitation of the kinetics of the self-exchange reaction between neighboring radical components. The capacity decrease at the high rate can be reduced by improving dispersivity in the composite electrode by using an effective dispersing solvent for the PTMA, such as *N*-methyl-2-pyrrolidone. A composite electrode with highly dispersed PTMA should thus be effective for reducing the thickness of the homogeneous electron-transfer layer.[35]

5.2 Stability of Li/PTMA Coin Cell

Sample Li/PTMA coin cells were tested[31] by charging and discharging them at a temperature of 20, 45, or 60 °C, a voltage

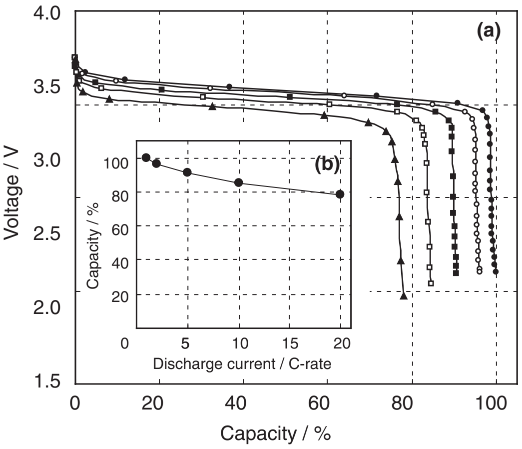


Figure 4. (a) Rate dependence of the discharge curves at 1 (-●-), 2 (-○-), 5 (-■-), 10 (-□-), and 20 C rate (-▲-) at 45 °C. All charges were carried out at the 1 C rate. (b) Rate dependences of discharge capacity.

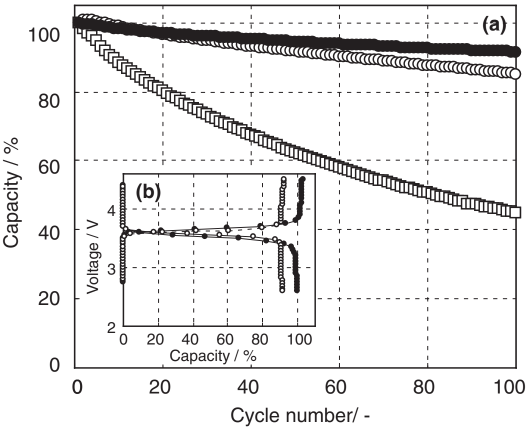


Figure 5. (a) Cycling performance of half-cell measured for 2.6–4.5 V (●: 20 °C, ○: 45 °C, □: 60 °C). (b) Charge and discharge curves for 1st (-●-) and 100th (-○-) cycle obtained at 20 °C.

of 2.6–4.5 V, and 1 C rate (Figure 5a). As shown in Figure 5b, at 20 °C, the capacity after 100 cycles was 91% of the initial capacity. Another test[35] showed that a composite electrode with highly dispersed PTMA retained 98% of its initial capacity after 500 cycles. These results demonstrate that PTMA is sufficiently stable during cycling at 20 °C. The higher temperatures, however, caused faster deterioration of the cell capacity. In particular, at 60 °C, almost 50% of the initial capacity was lost during the first 100 cycles. This is attributed to degradation of the lithium metal anode at high temperatures. The use of a graphite anode may suppress this deterioration.

A previous report[31] pointed out that fast self-discharge is a problem with PTMA/VGCF electrodes. Although the capacity almost completely recovered, 38% of the charged capacity was lost after one week of storage at 20 °C. Dissolution of the radical polymers apparently caused the self-discharge. Cross-linking of the radical polymers effectively suppressed the self-discharge.[36]

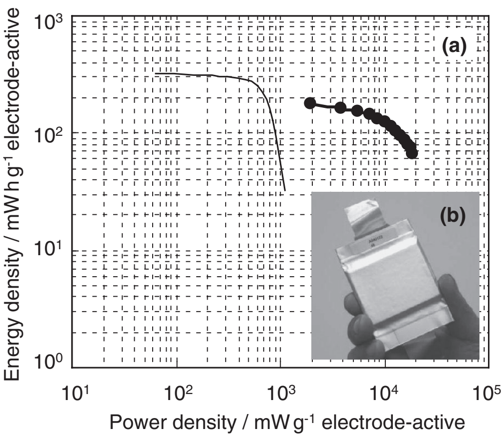


Figure 6. (a) Ragone-plots for organic radical battery (-●-) and a conventional lithium ion battery (—). Energy density and power density were calculated from weight of electrode active materials. (b) The photograph of the 100 mA h-class organic radical battery.

♦ 6. Recent Developments for Practical Application of Organic Radical Battery

The organic radical battery is being developed for sub-battery and smart card applications as the main target at NEC Corporation. Because of their high-power characteristic, organic radical batteries in a compact battery pack should be able to power a desktop computer as a sub-battery for emergency use. Their environmental friendliness makes them well suited for powering smart cards.

6.1 Sub-battery for Desktop Computer Emergency Use

A 100 mA h-class aluminum-laminated-film-packaged organic radical battery with a PTMA/carbon cathode and a graphite anode has been fabricated.[15] The composite electrode consists of 50 wt % PTMA and 45 wt % VGCF. The composite electrode and graphite anode are 180 and 20 µm thick, respectively. The electrode is 45 × 55 mm^2, about half the size of a business card. The fabricated battery weighs 22 g and is 4.3 mm thick. A battery pack consisting of four such batteries connected in series operated a 200 W-class desktop computer without additional power input, so the battery is suitable for emergency use as a sub-battery. The battery pack is compact enough to be installed in an expansion slot of a desktop computer. A rate capability test demonstrated that the battery pack has a 13 A (130 C-rate) discharge although the capacity decreased to half that at a lower rate. Organic radical batteries could also be used as high-power energy sources, such as sub-batteries for electronic devices and motor assistance for electric vehicles, replacing the electric double-layer capacitors and nickel metal hydride batteries.

A Ragone plot for an organic radical battery is compared with one for a conventional lithium ion battery in Figure 6a and a photograph of a 100 mA h-class organic radical battery is shown in Figure 6b.[15] The power density and energy density were calculated on the basis of the weight of the electrode active materials. Although the energy density of the organic radical battery was smaller, power density was quite superior to that of a lithium ion battery.

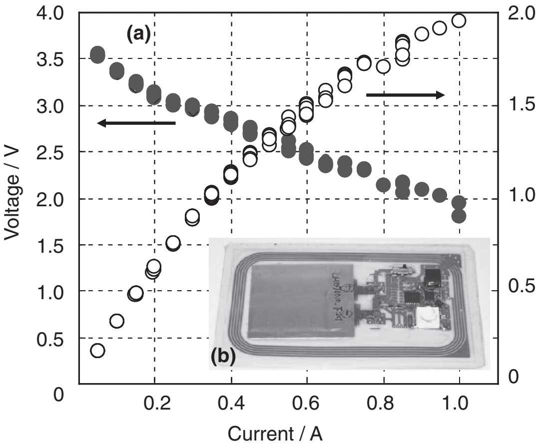


Figure 7. (a) *I*–*V* characteristic of thin organic radical battery at 20 °C. Voltages obtained at various currents after 1 s discharge (●) and output power of battery (○). (b) Photograph of prototype thin organic radical battery embedded in smartcard.

6.2 Thin Batteries as Smart-card Power Source

Thin organic radical batteries are being developed for application to smart cards. A prototype battery with a thickness of 800 µm was fabricated and tested. It had a composite electrode containing 70 wt % PTVE and a lithium metal anode. The electrode was 24 × 22 mm^2. The discharge capacity of the battery was 6.0 mA h. The *I*–*V* characteristics were investigated using a 1-s pulse discharge. The direct current resistance of the battery was only 1.5 Ω, and as shown in Figure 7a, the maximum power output was 2.0 W. This output power is considered sufficient for high-power applications such as for the luminescence of an LED flash device. A photograph of the prototype battery embedded in a smart card is shown in Figure 7b.

The pulse cyclability of the battery was examined by subjecting it to 5 mA (5 s) pulse discharges once a minute. Almost no deterioration was observed up to 10000 pulse cycles even at 40 °C. This stability further supports the practical application of the organic radical battery.

◆ 7. Future Perspectives

Organic radical batteries with a nitroxyl radical polymer composite cathode and a graphite anode are close to becoming practical. Because of their low volumetric energy density, they are not suitable as the main battery in mobile phones or laptop computers. However, more specialized applications, such as a sub-battery for desktop-computer-emergency use and as a smart-card power source, are realistic. The remaining issues to be resolved to achieve commercialization are long-term stability for more than years and cost reduction. Our approach to resolving these issues is to modify the production processes.

Research on a rocking-chair-type organic radical battery is in progress. Since the electrolyte salt concentration does not change during charging and discharging, the energy density of the battery should be high. The n-type reaction of the radical polymers is critical to the rocking-chair-type battery, but this reaction is more susceptible to side reactions than the p-type reaction. However, the n-type reaction can be controlled by altering the electron-withdrawing characteristics of the substituents on the poly(nitroxylstyrene).[16] Another type of n-type reaction has been demonstrated in poly(galvinoxylstyrene).[37] These polymers are thus attractive as the cathode active material for the rocking-chair-type battery.

Radical polymers have been used not only as an alternative to lithium transition-metal oxide but also as the electrode active material for various types of rechargeable devices. A totally organic polymer-based rechargeable battery with a poly(TEMPO-substituted norbornene) cathode and a poly(galvinoxylstyrene) anode has been reported[37] as well as an aqueous-electrolyte rechargeable battery with a PTVE cathode and a zinc anode.[38] These batteries are attractive as flexible, printable, and green batteries.[39–41] Furthermore, radical polymers have been used not only for rechargeable batteries but also for diodes,[42] nonvolatile memories,[43,44] and electrochromic devices.[45] The use of radical polymers is thus spreading as they become used as electro-active polymers for new functional devices.

Radical polymers are a promising alternative to lithium transition-metal oxides in lithium-ion batteries. Nitroxyl radical polymers are a particularly attractive candidate for cathode active material from the viewpoints of high power density and environmental friendliness. Other radical polymers may be applicable to next-generation batteries, such as an all-plastic battery. The practical use of the polymers in organic radical batteries may thus be near at hand.

This work was partially supported by the New Energy and Industrial Technology Development Organization (NEDO), Japan. This work was also partially supported by Grant-in-Aid for Scientific Research (No. 19105003), and the Waseda University Global COE Program from MEXT, Japan. We are grateful to Dr. Shigeyuki Iwasa, Dr. Masahiro Suguro, Mr. Jiro Iriyama (NEC Corporation), and Dr. Takeo Suga (Waseda University) for their technical discussions.

References

1 J.-M. Tarascon, M. Armand, *Nature* **2001**, *414*, 359.
2 A. S. Aricò, P. Bruce, B. Scrosati, J.-M. Tarascon, W. V. Schalkwijk, *Nat. Mater.* **2005**, *4*, 366.
3 P. Bruce, B. Scrosati, J.-M. Tarascon, *Angew. Chem., Int. Ed.* **2008**, *47*, 2930.
4 B. Scrosati, J. Garche, *J. Power Sources* **2010**, *195*, 2419.
5 M. Wakihara, *Mater. Sci. Eng., R* **2001**, *33*, 109.
6 P. J. Nigrey, D. MacInnes, Jr., D. P. Nairns, A. G. MacDiarmid, A. J. Heeger, *J. Electrochem. Soc.* **1981**, *128*, 1651.
7 S. J. Visco, M. Liu, L. C. De Jonghe, *J. Electrochem. Soc.* **1990**, *137*, 1191.
8 K. Nakahara, S. Iwasa, M. Satoh, Y. Morioka, J. Iriyama, M. Suguro, E. Hasegawa, *Chem. Phys. Lett.* **2002**, *359*, 351.
9 H. Nishide, S. Iwasa, Y.-J. Pu, T. Suga, K. Nakahara, M. Satoh, *Electrochim. Acta* **2004**, *50*, 827.
10 J. Iriyama, K. Nakahara, S. Iwasa, Y. Morioka, M. Suguro, M. Satoh, *IEICE Trans.* **2002**, *E85-C*, 1256.
11 H. Nishide, T. Suga, *Electrochem. Soc. Interface* **2005**, *14*, No. 4, 32.
12 M. Suguro, S. Iwasa, Y. Kusachi, Y. Morioka, K. Nakahara, *Macromol. Rapid Commun.* **2007**, *28*, 1929.
13 K. Oyaizu, T. Suga, K. Yoshimura, H. Nishide, *Macro-*

molecules **2008**, *41*, 6646.
14 K. Oyaizu, T. Kawamoto, T. Suga, H. Nishide, *Macromolecules* **2010**, *43*, 10382.
15 K. Nakahara, J. Iriyama, S. Iwasa, M. Suguro, M. Satoh, E. J. Cairns, *J. Power Sources* **2007**, *163*, 1110.
16 T. Suga, Y.-J. Pu, S. Kasatori, H. Nishide, *Macromolecules* **2007**, *40*, 3167.
17 T. Suga, S. Sugita, H. Ohshiro, K. Oyaizu, H. Nishide, *Adv. Mater.*, in press. DOI:10.1002/adma.201003525
18 T. Suga, H. Konishi, H. Nishide, *Chem. Commun.* **2007**, 1730.
19 J. Qu, T. Katsumata, M. Satoh, J. Wada, T. Masuda, *Polymer* **2009**, *50*, 391.
20 T. Katsumata, M. Satoh, J. Wada, M. Shiotsuki, F. Sanda, T. Masuda, *Macromol. Rapid Commun.* **2006**, *27*, 1206.
21 M. Suguro, A. Mori, S. Iwasa, K. Nakahara, K. Nakano, *Macromol. Chem. Phys.* **2009**, *210*, 1402.
22 J. Qu, T. Katsumata, M. Satoh, J. Wada, J. Igarashi, K. Mizoguchi, T. Masuda, *Chem.—Eur. J.* **2007**, *13*, 7965.
23 K. Oyaizu, T. Sukegawa, H. Nishide, *Chem. Lett.* **2011**, *40*, 184.
24 J. Qu, R. Morita, M. Satoh, J. Wada, F. Terakura, K. Mizoguchi, N. Ogata, T. Masuda, *Chem.—Eur. J.* **2008**, *14*, 3250.
25 J. Qu, F. Z. Khan, M. Satoh, J. Wada, H. Hayashi, K. Mizoguchi, T. Masuda, *Polymer* **2008**, *49*, 1490.
26 K. Oyaizu, H. Nishide, *Adv. Mater.* **2009**, *21*, 2339.
27 T. Suga, Y.-J. Pu, K. Oyaizu, H. Nishide, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 2203.
28 M. Satoh, K. Nakahara, J. Iriyama, S. Iwasa, M. Suguro, *IEICE Trans.* **2004**, *E87-C*, 2076.
29 K. Oyaizu, Y. Ando, H. Konishi, H. Nishide, *J. Am. Chem. Soc.* **2008**, *130*, 14459.
30 M. G. Sullivan, R. W. Murray, *J. Phys. Chem.* **1994**, *98*, 4343.
31 K. Nakahara, J. Iriyama, S. Iwasa, M. Suguro, M. Satoh, E. J. Cairns, *J. Power Sources* **2007**, *165*, 398.
32 S. Yoshihara, H. Isozumi, M. Kasai, H. Yonehara, Y. Ando, K. Oyaizu, H. Nishide, *J. Phys. Chem. B* **2010**, *114*, 8335.
33 J.-K. Kim, G. Cheruvally, J.-H. Ahn, Y.-G. Seo, D. S. Choi, S.-H. Lee, C. E. Song, *J. Ind. Eng. Chem.* **2008**, *14*, 371.
34 M. Suguro, S. Iwasa, K. Nakahara, *Macromol. Rapid Commun.* **2008**, *29*, 1635.
35 K. Nakahara, J. Iriyama, S. Iwasa, M. Suguro, M. Satoh, E. J. Cairns, *J. Power Sources* **2007**, *165*, 870.
36 L. Bugnon, C. J. H. Morton, P. Novak, J. Vetter, P. Nesvadba, *Chem. Mater.* **2007**, *19*, 2910.
37 T. Suga, H. Ohshiro, S. Sugita, K. Oyaizu, H. Nishide, *Adv. Mater.* **2009**, *21*, 1627.
38 K. Koshika, N. Sano, K. Oyaizu, H. Nishide, *Macromol. Chem. Phys.* **2009**, *210*, 1989.
39 H. Nishide, K. Oyaizu, *Science* **2008**, *319*, 737.
40 H. Nishide, K. Koshika, K. Oyaizu, *Pure Appl. Chem.* **2009**, *81*, 1961.
41 K. Koshika, N. Chikushi, N. Sano, K. Oyaizu, H. Nishide, *Green Chem.* **2010**, *12*, 1573.
42 T. Suga, S. Takeuchi, T. Ozaki, M. Sakata, K. Oyaizu, H. Nishide, *Chem. Lett.* **2009**, *38*, 1160.
43 Y. Yonekuta, K. Susuki, K. Oyaizu, K. Honda, H. Nishide, *J. Am. Chem. Soc.* **2007**, *129*, 14128.
44 Y. Yonekuta, K. Honda, H. Nishide, *Polym. Adv. Technol.* **2008**, *19*, 281.
45 Y. Takahashi, N. Hayashi, K. Oyaizu, K. Honda, H. Nishide, *Polym. J.* **2008**, *40*, 763.