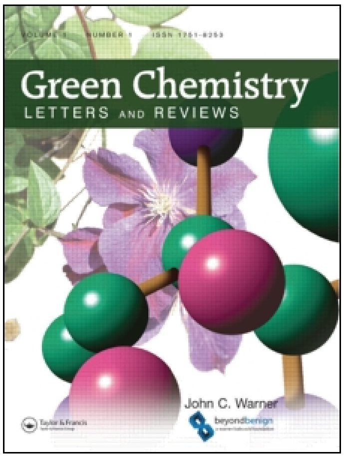

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RESEARCH LETTER

A rechargeable battery based on hydrophilic radical polymer electrode and its green assessment

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A hydrophilic radical polymer electrode-based rechargeable battery was designed along the concept of green chemistry. A hydrophilic radical polymer, poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl vinylether), was synthesized as an electrode-active material; its battery demonstrated a high charging–discharging rate and long cycle life. The combination of the hydrophilic polymer electrode and an aqueous electrolyte for the battery fabrication was expected to provide safety improvements such as a low ignition risk besides the high battery performance. The green characteristics were studied using the "i-Messe," an evaluation method proposed by the committee of the Green Sustainable Chemistry Network, Japan. The electrode-active polymer was evaluated for substantial improvements in disaster safety and health safety.

Keywords: secondary battery; redox polymer; radical polymer; aqueous electrolyte; safety assessment

Introduction

Research on devices for electrical energy storage has currently received significant attention (*1–4*). Rechargeable or secondary batteries, such as lithium ion batteries, are very popular and being used in portable electronic devices, such as mobile phones, laptop PCs, and digital cameras, and could also be used in electric vehicles, for electric storage and in solar and wind-energy converters. Secondary batteries have been regarded as an environmentally benign technology because of their rechargeability which contributes to reducing the amount of discarded primary batteries. However, secondary batteries still remain immature from the view points of green chemistry, i.e. limited metal resources, tedious waste treatment processes, and safety concerns (disaster and health). Some electrode-active materials in conventional batteries have been made from rare metals such as cobalt, manganese, and nickel (*3*). The used batteries were collected in large amounts at least in Japan, but most of them have been landfilled (only part of them was recycled for the metals) (*5,6*). Secondary batteries, such as Li ion and Ni-Cd, are encountering over-heating problems and the tightening of regulation issues of hazardous substances, respectively. The over-heating problems were caused by the combination of the exothermic electrode reaction and the ion conduction in organic electrolytes. Sometimes the heat ignited the organic electrolytes, resulting in a series of ignition accidents (*4*). Indeed, in 2007 and 2008, Panasonic and Sony encountered serious recalls of their 46 and 0.1 million Li ion batteries for mobile phones and laptops, respectively (*7,8*). The regulations against hazardous substances have become stricter on a global scale. In the European Union, Restriction on Hazardous Substances (RoHS) restricted the use of six hazardous materials, such as lead, mercury, and cadmium, in the manufacture of various types of electronic and electrical equipment (except batteries) in 2003. The directive 2006/66/EC then restricted the amount of mercury and cadmium contained in batteries in 2006. After the start of the directive, most batteries with a certain mercury or cadmium content will be prohibited from the market. Many manufacturers dealing with such hazardous substances started to prepare for their replacement.

We have studied electrode-active polymers using robust radicals for organic-based secondary batteries as one of the solutions to the problems (*9–11*). We have focused our attention on the redox property of the robust radicals, synthesizing a series of aliphatic polymers bearing the pendant robust radical groups (we called them radical polymers) and utilizing them as organic electrode-active materials (*12–18*).

The radical polymers, synthesized from less limited petroleum feedstock, have the possibility to alleviate the above resource problem and to allow a simple treatment process by incineration disposal. However, previously reported battery configurations

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with radical polymers and an organic electrolyte, such as poly(2,2,6,6,-tetramethylpiperidinyloxy-4-yl methacrylate) (PTMA) and an acetonitrile solution containing tetrabutylammonium (*18*) still retained the potential risk of ignition, thus requiring a built-in safety system like the lithium ion battery (*4*). This is because the previously reported radical polymers showed a hydrophobic character, not working in aqueous electrolytes.

According to the 12 principles of green chemistry, it is better to prevent waste than to treat or clean up waste after it is formed (*19,20*). Recently, we designed a hydrophilic radical polymer, poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl vinylether) (PTVE), which sufficiently functioned even in an aqueous electrolyte, and reported the following electrode performance (*21,22*): (i) high charging and discharging capacity of 131 mAh g^{-1} ascribed to the stoichiometric redox of the radical moieties; (ii) long cycle life, often exceeding 1000 cycles, derived from the chemical stability of the radicals and from the amorphous electrode structure; and (iii) high charging–discharging rate performance (1200 C) resulting from the rapid electron-transfer process of the radical moiety and the high equivalent electrical conductivity of the aqueous electrolyte on the order of 10^{-2} to 10^{-3} m^2 S mol^{-1}, which is 10 times higher than that of organic electrolytes (*23*). (The rate of 1 C is defined as the current density at which the charging or discharging of the cell takes in 1 h. Most conventional batteries function during the charging or discharging at 1–2 C.) An important issue described in this report is that a combination of hydrophilic radical polymer and aqueous electrolyte allowed an organic electrolyte-free battery design and a rapid charging–discharging performance at the same time. Previous papers (*21,22*) have discussed only the electrode performance, without evaluating the safety of the radical polymer electrode. One could assume that such a battery configuration has inherent advantages in terms of many aspect of green chemistry. In this paper, we report, for the first time, the disaster and health safeties of the hydrophilic radical polymer. The goal of this preliminary assessment at the early development stage is to recognize potential risk of the radical polymer electrode and its battery application. The safety was assessed qualitatively using the i-Messe (*24,25*), an evaluation method proposed by the committee of the Green Sustainable Chemistry Network, Japan (Figure 1).

Results and discussion

According to the i-Messe, the disaster safety and health safety of the hydrophilic radical polymer (PTVE) were evaluated from the perspective of "production, use and disposal" and "raw material," respectively. Two electrode-active materials, PTMA and lithium cobalt oxide, were also evaluated as the control experiment. PTMA is one of the most well studied hydrophobic radical polymers in our previous reports (*18*). Lithium cobalt oxide is one of the most popular cathode-active materials used in conventional lithium ion batteries (Figure 2).

Disaster safety

Evaluation of electrode-active materials during their use and disposal

PTVE and PTMA were basically considered to be low potential risks to cause disaster hazards. Thus, PTVE and PTMA are chemically stable, unexplosive, and non-flammable. The polymers have a sufficiently low reactivity toward oxygen and water, remaining unchanged without decomposition and deactivation under ambient conditions for over half a year. The polymers are also thermally stable. Their 10% decomposition temperatures are higher than 200°C (*18,21*). This is sufficiently higher than the envisioned operating temperatures of the battery.

The polymers also have low potential risks during their use and disposal. Unlike lithium cobalt oxide, the charging–discharging process of the polymers is low exothermic. The charging–discharging

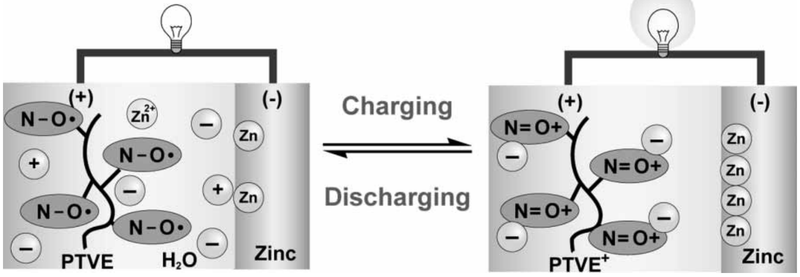


Figure 1. Aqueous electrolyte-type radical polymer battery 55 × 20 mm (600 × 600 DPI).

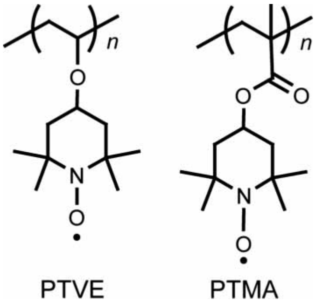
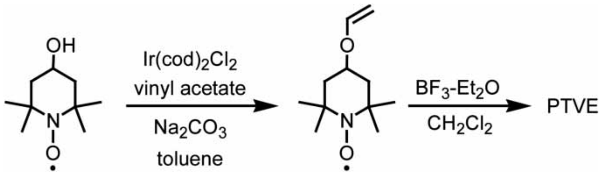


Figure 2. Typical electrode-active polymers for radical polymer batteries 30 × 24 mm (600 × 600 DPI).

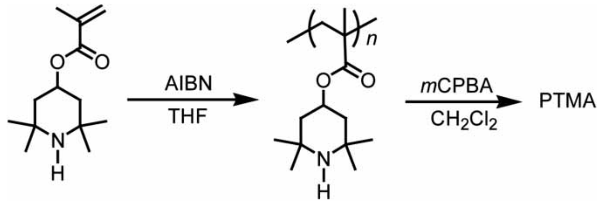
process of lithium cobalt oxide includes a lattice transformation with heat generation (*4*). On the other hand, the structural change of the TEMPO unit between the nitroxide radical and the oxidized form, oxoammonium cation, is not significant (*26*). This slight structural change suppresses heat generation of electrode, reducing the risk of overheating. In addition, considering the combination of the electrolyte solution, PTVE was the lowest risk potential of ignition and explosion due to the combination of a low exothermic electrode and aqueous electrolyte solutions. The polymers demonstrated a quantitative coulombic efficiency and high rechargeability (*18,22*). These results suggested that the redox reaction of TEMPO has no side reactions and both polymers in the charging state and discharging state have a low reactivity toward the electrolyte salts and solutions. Therefore, the PTVE and PTMA have a low possibility to generate heat, gases, and explosive materials. During their disposal, the polymers are simply burned and generate CO2, NO2, and H2O. Lithium cobalt oxide is landfilled and unchanged to any disaster materials. It was estimated that there is essentially not much difference in their disaster risk between the radical polymer cathodes and conventional lithium cobalt oxide (Table 1).

Materials used for the synthesis

In this study, the electrode-active materials, PTVE, PTMA, and lithium cobalt, were synthesized by the following three steps as shown in Schemes 1–3.



Scheme 1. Synthesis of PTVE 63 × 17 mm (600 × 600 DPI).



Scheme 2. Synthesis of PTMA 62 × 20 mm (600 × 600 DPI).

$$LiCO_3 \xrightarrow{Co_3O_4} LiCoO_2$$

Scheme 3. Synthesis of lithium cobalt oxide 29 × 5 mm (600 × 600 DPI).

Among the raw materials, the organic solvent was considered to have the highest disaster risk. For the polymer synthesis process, organic solvents were used as the reaction solvent. Some organic solvents, such as tetrahydrofuran (THF) and toluene, showed the risk phrase of R-11 (highly flammable). They require careful handling, however, we estimated that the actual ignition risk was within an acceptable range because they are often used in chemical industries (*27*).

Health safety

Electrode-active materials during their use and disposal

PTVE and PTMA were basically considered to be non-toxic and have low potential risks causing health hazards during their use and disposal. PTVE and PTMA have a low bioavailability as well as most of the general polymers (*19*). The polymers are non-volatile and insoluble in most general solvents except for a few types of organic solvents such as acetonitrile, dimethyl sulfoxide (DMSO), i.e. the polymers

Table 1. Potential risk of ignition 160 × 44 mm (600 × 600 DPI).

Cathode	Risk of ignition	Heat generation in charging–discharging process	Electrolyte solution
PTVE	Lowest	Lower exothermic	Non-flammable
PTMA	Lower	Lower exothermic	Flammable
Lithium cobalt oxide	Ignition accidents were reported	Exothermic	Flammable

have a low possibility of entering the human body through the respiratory tract and skin. During their use, the polymers have a low possibility of generating secondary toxic materials because of their stability as already described. For disposal, they are burned and generate NOx. However, NOx gases are converted to N2 and H2O by catalytic denitration method using a zeolite and alumina-based catalyst (*28*).

Materials used for the synthesis

Among the raw materials, boron trifluoride diethyl etherate, bis(1,5-cyclooctadiene) diiridium(I) dichloride and 3-chloroperbenzoic acid had 47, 33, and 34 Toxic Potential Indicator (TPI by Fraunhofer Institute IZM) mg–1 ratings, respectively. The other raw materials were lower than 20 TPI mg–1. Boron trifluoride diethyl etherate and bis(1,5-cyclooctadiene) diiridium(I) dichloride were used as an initiator and catalyst, i.e. their amounts were as low as 2 mol% of the monomer and main reactant, respectively. We estimated that the actual toxicity of boron trifluoride diethyl etherate and bis(1,5-cyclooctadiene) diiridium(I) dichloride were within the acceptable range. On the other hand, 3-chloroperbenzoic acid was used as a quantitative oxidant. A lower amount or change to a lower toxic oxidant was recommended.

Experimental

Synthetic procedures poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl vinylether) (PTVE)

2,2,6,6-tetramethylpiperidne-*N*-oxyl-4-vinyl, synthesizedas the monomer, was prepared using the coupling reaction of 4-hydroxy-2,2,6,6-tetramethylpiperidne-4-oxyl and vinyl acetate with catalyst of bis(1,5-cyclooctadiene) diiridium(I) dichloride and 3-chloroperbenzoic acid, according to a previous paper (*21,22,29,30*). The vinyl monomer was polymerized via cationic polymerization in dichloromethane with boron trifluoride diethyl etherate as the initiator at –25°C.

Poly(2,2,6,6,-tetramethylpiperidinyloxy-4-yl methacrylate) (PTMA)

The precursor of the PTMA monomer (2,2,6,6,-tetramethylpiperidine methacrylate) was polymerized by radical polymerization in THF with 2,2′-azobisisobutyronitrile as the radical initiator at 80°C. The precursor polymer was treated with 3-chloroperoxybenzoic acid to yield PTMA at room temperature.

Lithium cobalt oxide

Lithium cobalt oxide was prepared by heating a stoichiometric mixture of lithium carbonate and cobalt(II, III) oxide at 800°C in air for 20 h (*31*).

Formulation and preparation of electrode

Poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl vinylether) (PTVE) cathode

A film electrode was prepared by the following procedure. The acetonitrile solutions of PTVE were spin-coated on a current collector, such as a glassy carbon substrate, followed by drying at 80°C for 24 h under vacuum to yield the PTVE film with a 60 nm thickness.

Poly(2,2,6,6,-tetramethylpiperidinyloxy-4-yl methacrylate) (PTMA) cathode

A carbon-composite electrode (1.2 mg/cm2) was prepared by the following procedure.

A 10 mg of the radical polymer, PTMA, and 80 mg of graphite (carbon fiber prepared in gas-phase: VGCF, Showa Denko Co.) were mixed with 10 mg of binder powder (polyvinylidenefluoride resin: KF polymer, Kureha Chemical Co.) in the presence of a solvent. The resulting black clay was spread on a current collector, such as an aluminum plate, followed by drying at 80°C for 24 h under vacuum.

Evaluation of performances as cathode

The cathode performance of the PTVE was compared with those prepared with PTMA and lithium cobalt oxide by measuring the charging–discharging rate, rechargeable cycling and electromotive force vs. the standard reference anode. As for the performance of lithium ion battery, the specifications given by the relevant literature was used and listed for the purpose of having the appropriate level of performance (*32*).

Table 2. Comparison of cathode performances 199 × 44 mm (600 × 600 DPI).

Cathode	Charging–discharging rate performance	Rechargeable number	Electromotive force	Developmental stage (analysis condition)
PTVE	1200 C	1000 cycles	1.7 V vs. Zn/Zn^{2+}	Primary lab stage (beaker cell)
PTMA	12 C	1000 cycles	3.6 V vs. Li/Li^{+}	Performance test stage (coin cell)
Lithium cobalt oxide	2 C	500 cycles	3.7 V vs. C/CLi^{+}	Commercial stage (completed cell)

Aqueous electrolyte-type radical polymer battery cathode: poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl vinylether) (PTVE)

The chemical structure of PTVE is composed of a hydrophilic polyvinyl ether-backboned polymer and TEMPO pendant group. It has a reversible one-electron oxidation capability even in aqueous electrolytes. The PTVE prepared and used in this study gave a redox wave at 1.7 V vs. Zn/Zn^{2+}. The capacity of the PTVE remained at more than 80% of the initial level after 1000 charging–discharging cycles. The charging–discharging rate performance of the PTVE was 1200 C (corresponding to the full charging and discharging for 3 sec).

Organic electrolyte type radical polymer battery cathode: poly(2,2,6,6,-tetramethylpiperidinyloxy-4-yl methacrylate) (PTMA)

PTMA is composed of a hydrophobic polymethacylate-backboned polymer and TEMPO pendant group. The PTMA used in this study gave a redox wave at 3.6 V vs. $Li/Li+$. The capacity of the PTMA remained at more than 95% of the initial level after 1000 charging–discharging cycles. The charging–discharging rate performance of PTMA was 12 C (corresponding to the full charging and discharging for 5 minutes).

Li ion battery cathode: lithium cobalt oxide

Lithium cobalt oxide has a 3.7 V of electromotive force vs. graphite carbon. The capacity remained at more than 75% of initial capacity after 500 charging–discharging cycles. The charging–discharging rate performance was 2 C (corresponding to the full charging and discharging for 30 minutes) (Table 2).

Conclusion

A hydrophilic radical polymer cathode was designed, prepared, and evaluated, based on the concept of Green Chemistry. A preliminary evaluation, along the i-Messe, showed substantial improvements in disaster safety and health safety. These results strongly supported that the fact an aqueous electrolyte-type radical polymer battery promises to be safer and as the next generation secondary battery with a highly improved Green Chemistry profile and electrode performance. We will report an aqueous electrolyte-type rechargeable battery composed of radical polymers by replacing the zinc anode with a hydrophilic radical polymer with reversible redox at –0.5 V (vs. Ag/AgCl).

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