

An ultrafast chargeable polymer electrode based on the combination of nitroxide radical and aqueous electrolyte

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Received (in Cambridge, UK) 14th October 2008, Accepted 26th November 2008

First published as an Advance Article on the web 15th December 2008

DOI: 10.1039/b818087c

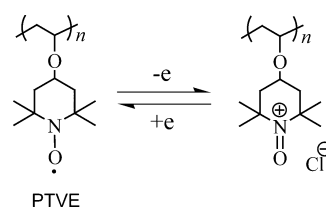
A film of poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl vinyl ether) coated on a current collector displayed a rapid and reversible electrochemical response in aqueous electrolytes, and allowed an ultrafast full charging of 3 mC cm⁻² in as short as 3 seconds by virtue of the combination of the hydrophilic radical polymer and the aqueous electrolyte possessing a high electrical conductivity.

Some nitroxide radical molecules, such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), are robust and known to show a reversible redox ability in organic and aqueous solutions,¹ and they have often been studied as a redox mediator in sensors and catalysts.^{2,3} We have synthesized a series of aliphatic polymers bearing pendant nitroxide radical groups and utilized them as an electrode-active or charge-storage material for use in secondary or rechargeable batteries.^{4–13} The “radical polymer battery” fabricated with the nitroxide radical polymer as the cathode showed the following features: high charging–discharging capacity ascribed to the stoichiometric redox of the nitroxide radical, high charging–discharging rate resulting from the rapid electron-transfer process of the nitroxide radical, and long cycle-life derived from the chemical stability of the nitroxide radical.^{4,8}

Rapid charging is one of the most important performances of secondary batteries; a short charging time would lead to significant advantages in our use of portable electric devices equipped with a secondary battery. Conventional Li-ion batteries cannot be rapidly charged because the charging process involves the slow de-intercalation of lithium ions from the metal oxide cathode, often taking more than 30 minutes for full charging. On the other hand, our previously reported radical polymer battery, which was composed of a lipophilic radical polymer as the cathode active material and an organic electrolyte containing a lithium salt, such as ethylene carbonate containing LiPF₆, performed a rapid full charging in *ca.* 1 minute.⁶ However, there remained a limitation for even more rapid charging; the reasons could be attributed to insufficient electrochemical kinetics of the redox reaction involving lithium ions and/or the moderate electric conductivity of the organic electrolytes. It has been known that aqueous electrolytes possess a high equivalent electrical conductivity on the order of 10⁻²–10⁻³ m² S mol⁻¹.¹⁴ However, aqueous electrolytes have never been studied as the electrolyte of an organic polymer battery,^{9,12} which would also impart environmentally benign characteristics and reduce the risk of ignition and explosion to improve the safety of the battery.

In this paper, we report, for the first time, an aqueous electrolyte-based radical polymer battery that has very fast charging characteristics. We have designed poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl vinyl ether) (PTVE) as an electrode-active and hydrophilic polyvinylether-backboned polymer bearing a TEMPO pendant group (Scheme 1), which shows a reversible one-electron oxidation capability even in aqueous electrolytes. This functionality and compact molecular designing of PTVE allowed a high formula-weight-based charging–discharging capacity per weight of 135 mAh g⁻¹, which has improved from those of conventional redox polymers, such as polyvinylferrocene¹⁵ and polybutylviologen dibromide,¹⁶ and was even higher than that of the previously reported poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate) (PTMA)¹² (111 mAh g⁻¹) by our group.

PTVE with a molecular weight of $M_n = 78\,000$ ($M_w/M_n = 1.2$) and unpaired electron content of 0.97 per monomer unit (a maximum effective charging–discharging capacity per weight of 131 mAh g⁻¹) was prepared by the cationic polymerization of 2,2,6,6-tetramethylpiperidinyloxy vinyl ether¹⁷ using trifluoroborane–diethylether as the initiator. The polymer was soluble in acetonitrile, but swollen and not soluble in water.† The acetonitrile solutions of PTVE (10–50 g/L) 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 thickness of 35 nm–1 μm, respectively. The cyclic voltammogram of the PTVE film repeatedly displayed a chemically reversible redox wave at 0.73 V vs. Ag/AgCl (Inset of Fig. 1) in a 0.1 M NaCl aqueous solution (pH *ca.* 6.8 in air),‡ which was assigned to the one-electron oxidation of the nitroxide to the corresponding oxoammonium cation salt (Scheme 1).§ The redox wave gave a narrow peak-to-peak separation ($\Delta E = 16$ mV) for the film with a thickness of <35 nm, which arose both from the fast electrode kinetics and the rapid diffusion of counter ions, leading to a Nernstian adsorbate-like behavior despite the substantial thickness of the polymer.¶ The anodic or oxidation peak was sharper than the cathodic or reduction peak, although the oxidation and reduction capacities or the peak areas almost coincided with each other. This redox



Scheme 1 Redox couple of PTVE.

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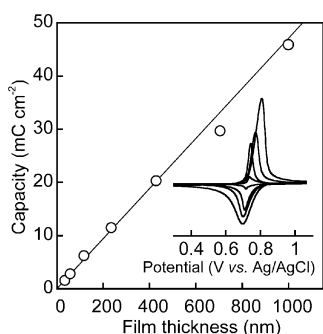


Fig. 1 Redox capacity per area for the PTVE film with the thickness of 35 nm–1 μm . The solid line represents the calculated redox capacity with the coating amount. Inset: Cyclic voltammograms of the PTVE films with different thicknesses (35, 60, 120 and 240 nm) at the scan rate of 1 mV s^{-1} , the working electrode: PTVE on glassy carbon, in 0.1 M aqueous NaCl.

behavior was similar to that of the polyvinylferrocene redox in aqueous electrolytes. The redox capacity of the PTVE film was also in agreement with the capacity calculated with the film thickness and polymer density of *ca.* 1 g cm^{-3} . The redox capacity was proportional to the film thickness (Fig. 1) and reached 45 mC cm^{-2} for the film with a thickness of $1 \mu\text{m}$,** even in the absence of conductive additives which are frequently employed in battery electrodes. These results mean that the PTVE polymer was homogeneously solvated with aqueous electrolyte, such that counter ions were sufficiently supplied to the TEMPO radical's redox site from the aqueous electrolyte phase to compensate the charge, and that the TEMPO group of the PTVE quantitatively worked as the redox site. These results also suggested that the polymer film fabricated by the solution-based, *e.g.*, spin-coating, process did not involve any structural defects to decrease the capacity and to prevent the charge transfer within the polymer.

A half-cell was fabricated using the PTVE film with a thickness of 62 nm as the working electrode, and Pt wire and Ag/AgCl, as the counter and reference electrodes, respectively. The charging–discharging curves of the half-cell

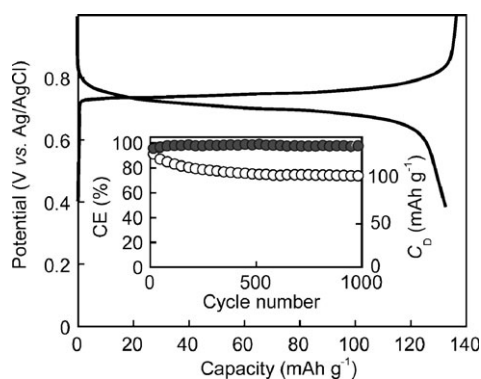


Fig. 2 Charging–discharging curves (capacity vs. potential of the cell) for the half-cell composed of the PTVE cathode. The counter and reference electrodes were a Pt wire and Ag/AgCl, respectively, in 0.1 M NaCl aq. at the charging–discharging rate of 60 C ($45 \mu\text{A cm}^{-2}$). Inset: Columbic efficiency (CE) (●) and discharging capacity (C_D) (○) for the half-cell on the charging–discharging cycle number.

exhibited a plateau voltage at $0.71\text{--}0.75 \text{ V vs. Ag/AgCl}$ (Fig. 2), which agreed with the redox potential of the PTVE film (0.73 V) given in inset of Fig. 1. The charging–discharging capacity almost coincided with each other at *ca.* 131 mAh g^{-1} and agreed with the calculated capacity obtained in Fig. 1 ($2.8 \text{ mC cm}^{-2} \times 60 \text{ nm thickness}$). The charging state survived for half a day, indicating no significant self-discharge in an appropriate period. The cycle performance of the charging–discharging at the cut-off voltages of $0.6\text{--}1.0 \text{ V}$ and C-rate†† of 60 C is shown in the inset of Fig. 2. The columbic efficiency, *i.e.*, discharging capacity vs. charging capacity, is maintained at almost 100% even after 1000 charging–discharging cycles, indicating that the charged species, the oxoammonium form of PTVE, stoichiometrically contributed to the following discharging process. However, the discharging capacity decreases to *ca.* 75% of the initial after 1000 cycles, suggesting partial elution out of the PTVE polymer into the electrolyte (which could be impeded through slight cross-linking of the polymer).

The PTVE half-cell was charged at the $60\text{--}2400 \text{ C-rate}$, and its (discharging) capacity was measured (at 60 C) to examine the charging rate performance (Fig. 3). The capacity of the cell charged even at 1200 C (corresponding to the full charging for 3 seconds) was retained at 97% (127 mAh g^{-1}) of the calculated capacity. Ultrafast and quantitative full charging was demonstrated for the aqueous electrolyte-based PTVE cell.

The open circle plots in the inset of Fig. 3 show the effect of the charging rate on the discharging capacity for a half-cell composed of the same PTVE cathode but using a 0.1 M $(\text{C}_4\text{H}_9)_4\text{NCl}$ ethylene carbonate–diethylene carbonate ($50 : 50 \text{ v/v}$) electrolyte as a control experiment. The capacity of the reference cell charged at 1200 C gives only 55% (72 mAh g^{-1}) of the calculated capacity.

A test full-cell was fabricated using the PTVE cathode and a zinc anode in the aqueous solution of 0.1 M ZnCl_2 and 0.1 M NH_4Cl . The charging–discharging curves for the fabricated cell displayed a plateau voltage at $1.73 \text{ V (vs. Zn/Zn}^{2+})$ with the capacity of 124 mAh g^{-1} , which supported the

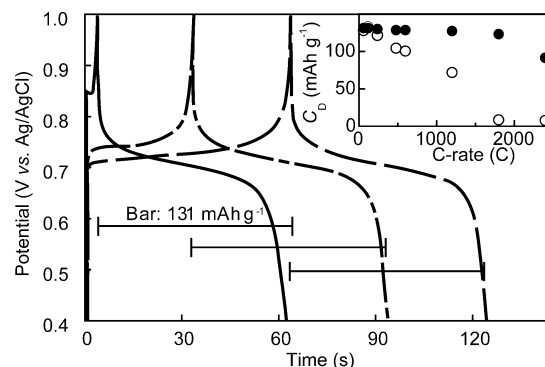


Fig. 3 Charging–discharging of the half-cell composed of PTVE cathode in 0.1 M NaCl aq. at the charging rate of 60 (— —), 120 (— · —) and 1200 (—) C and constant discharge rate of 60 C . Inset: Effect of charging rate on the discharging capacity (C_D) for the half-cell of the PTVE film in 0.1 M NaCl aq. (●) and 0.1 M $(\text{C}_4\text{H}_9)_4\text{NCl}$ ethylene carbonate–diethylene carbonate ($50 : 50 \text{ v/v}$) electrolyte (○).

potential of the aqueous electrolyte-based organic radical polymer battery.

This work was partially supported by Grants-in-Aid for Scientific Research (no. 19105003 and 19655043) from MEXT, Japan, and the Research Project "Radical Polymers" at the Advanced Research Institute for Science & Engineering at Waseda University.

Notes and references

† Elemental analysis data of PTVE: (Found: C, 65.9; H, 9.9; N, 6.8. $C_{11}H_{20}NO_2$ requires C, 66.6; H, 10.1; N, 7.1%). The PTVE was chemically reduced with phenylhydrazine, and characterized by NMR spectroscopy. δ_H (500 MHz; CD_3CN ; Me₄Si) 3.85 (1 H, m, piperidine CH), 3.68 (1 H, br s, OCHCH₂), 1.93 (2 H, m, piperidine CH₂), 1.79 (2 H, m, piperidine CH₂), 1.32 (2 H, br s, OCHCH₂), 1.11 (6 H, s, 2 × CH₃), 1.10 (6 H, s, 2 × CH₃); δ_C (500 MHz; CD_3CN ; Me₄Si) 20.7, 33.1, 48.9, 59.6, 63.1, 74.8, 75.6.

‡ The cyclic voltammogram was not significantly affected by the supporting electrolyte species, such as KCl and Na₂SO₄. The chemical reversibility of the voltammograms was observed in the pH range of 1–8.

§ The corresponding oxoammonium cation derived from the PTVE (Scheme 1) was slightly soluble in water.

¶ The peak current was proportional to the scan rate in the range of 1–20 mV s⁻¹.

|| Jureviciute *et al.*¹⁸ discussed that the sharp oxidation peak was ascribed to a rapid incorporation of counter ions and the broaden reduction peak would be caused by a slow releasing of hydrated counter ions.

** An observed concentration of the redox site of *ca.* 4.7 M, calculated with the quoted charge density, the film thickness under dry conditions, and the Faraday constant, was in good agreement with the concentration of the redox site of *ca.* 4.9 M which was derived from the molar mass of the monomer unit, the quoted density, and the unpaired electron concentration determined independently by a SQUID measurement. Preliminary microscopic analysis of the polymer volume before and after the swelling in water indicated that the degree of swelling under equilibrated conditions was *ca.* 1.2 (v/v), which corresponded to the increase of only 5% in the thickness and

suggested that the high site concentration was maintained in the swollen layer.

†† The 1 C rate is defined as the current density at which the charging or discharging of the cell takes 1 h.

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