A TEMPO-substituted polyacrylamide as a new cathode material: an organic rechargeable device composed of polymer electrodes and aqueous electrolyte†

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Poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl acrylamide) was designed and synthesized as an electrode-active polymer for an organic rechargeable device containing an aqueous electrolyte. The device demonstrated a 1.2 V output voltage, exceeded 2000 charging–discharging cycles, and had a high charging rate performance within 1 min.

Polyacrylamide is a well-known hydrophilic soft matter widely used in cell culture, drug delivery, and soil amendment.[1–4] Its applications have been vigorously studied in the biological, medical and agricultural fields. On the other hand, the study of the electronic energy related application has been minor and limited to polymer electrolyte fuel cells.[5] We now report a new application of polyacrylamide as an electrode-active material in organic rechargeable devices.

Organic-based electrode-active materials have been paid considerable attention because of their potential to overcome the inherent disadvantages of metal-based electrodes, such as limited raw-material resource and tedious waste process. We have focused on the reversible redox reaction of radical species, such as nitroxide, phenoxyl and galvinoxyl radicals, synthesizing a series of aliphatic polymers bearing pendant radical groups (we call them "radical polymer"), and utilizing them as an electrode-active or charge-storage material in a rechargeable device.[6–13] A typical example of a radical polymer is poly(2,2,6,6-tetramethylpiperidinyloy-4-yl norbornene).[10] This polymer contains 2,2,6,6-tetramethylpiperidin-1-oxyl-4-yl (TEMPO) groups which are rapidly, reversibly, and stoichiometrically oxidized to the corresponding oxoammonium cation. The poly(TEMPO-substituted norbornene) was used as the positive electrode (the cathode)‡ and coupled with a lithium metal negative electrode (an anode)‡ in a semi-organic rechargeable device containing a $LiPF_6$ ethylene carbonate/diethyl carbonate (1/1) solution. The device demonstrated a high charging–discharging performance, such as a 3.6 V output voltage, rapid charging within 1 min, and exceeded 1000 charging–discharging cycles.[12] In addition, a test cell composed of the poly(TEMPO-substituted norbornene) cathode, poly(galvinoxylstyrene) anode and $(C_4H_9)_4NClO_4$ ace-

tonitrile solution, suggests the potential of a totally organic rechargeable device.[11]

Safety is one of the most fundamental requirements for their practical use. Generally, a flammable or ignition risk of organic electrolytes in energy storage devices, such as a Li-ion battery and organic electrolyte-type electric double-layer capacitor, is strictly controlled by several safety systems.[14] To improve the safety concerns with organic rechargeable devices, we have tried to replace the organic electrolytes with aqueous electrolytes. This is a more preferable and green benign approach than to install safety systems in the devices for risk reduction.[15,16] However, previously reported radical polymer electrodes insufficiently worked in aqueous electrolytes due to their hydrophobic property.[10–12] We designed and synthesized poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl vinylether) (PTVE) as a hydrophilic polyvinylether backboned radical polymer for use with an aqueous electrolyte.[9,13] The PTVE film electrode showed a reversible redox even in an aqueous electrolyte and demonstrated a charging–discharging operation, for the first time, as a cathode coupled with a zinc anode. However, there remained limitations for a long cycle charging–discharging operation and working film thickness; the reasons could be attributed to the slow dissolution of the low molecular weight polymer and insufficient hydrophilicity of the polyvinylether-backbone generating defective parts within the thick film. In this paper, we report, for the first time, a polyacrylamide backboned radical polymer and its application in an aqueous electrolyte-type totally organic rechargeable device which provides a constant output voltage like batteries. Such a rechargeable device composed of two hydrophilic polymer electrodes and aqueous electrolyte has never been reported (except a few reports[17–19] on the supercapacitors using conducting polymers). The heavy metal-free and organic solvent-free design would lead to significant advantages not only in the device fabrication process and waste disposal process, but also in expanding their application.

Poly(2,2,6,6-tetramethylpiperidinyloy-4-yl acrylamide) (PTAm) was designed as a water-insoluble, but sufficiently water-swellable electrode-active polymer. PTAm with a molecular weight of $M_w = 1\,100\,000$ ($M_w/M_n = 4.9$) and unpaired electron content of 0.96 per monomer unit (a maximum effective charging–discharging capacity per weight of 114 mAh g^{-1}) was prepared by the radical polymerization of 2,2,6,6-tetramethylpiperidine-4-yl acrylamide followed by oxidation of the precursor polymer (Scheme 1). The polymer was soluble in THF, acetonitrile and DMF, but insoluble in water. The volume swell ratio of the PTAm was 1.4 in water.

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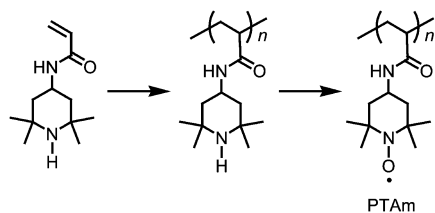
Scheme 1 Synthesis of the TEMPO-substituted polyacrylamide.

This higher molecular weight and higher volume swell ratio, compared to the previously reported PTVE,[13] would lead to an excellent film formability, long cycle life and high capacity per area. The THF solutions of PTAm (10 to 50 g L^{-1}) were spin-coated or cast on a current collector, such as a glassy carbon substrate, followed by drying at 70 °C for 12 h under vacuum, to yield the PTAm film with a thickness of 50 nm to 3.2 μm. An AFM analysis revealed that the surface of the obtained polymer film was smooth with a roughness of ±0.2 nm (Fig. S3†). The cyclic voltammogram of the PTAm film repeatedly displayed a redox wave of over 1000 times at 0.68 V (*vs.* Ag/AgCl) in a 0.5 M NaBF$_4$ aqueous solution (pH *ca.* 4.3 in air), which was assigned to the one-electron oxidation of the nitroxide to the corresponding oxoammonium cation salt. After 1000 electrochemical redox reactions, the polymer electrode surface remained smooth (a roughness <±2 nm) without any significant defects, cracks or pores (Fig. 2b, c). In the experiment using another PTAm sample with a lower molecular weight of $M_w = 90\,000$ ($M_w/M_n = 1.7$), the film thickness decreased to *ca.* 15% of its initial value, and its surface roughness increased to <±10 nm.

These results indicated that both the PTAm and PTAm cation salt, regardless of their polarities, were practically insoluble in the aqueous electrolyte, which would suppress the charging–discharging capacity decrease *versus* cycle number. The redox capacity of the PTAm film was in agreement with the capacity calculated based on the dry film thickness and polymer density of *ca.* 1 g cm^{-3}. The redox capacity was proportional to the film thickness and reached 123 mC cm^{-2} for the film with a thickness of 3.2 μm, even in the absence of conductive additives which are frequently employed in polymer electrodes. These results mean that the PTAm film was homogeneously solvated with the aqueous electrolyte and that the TEMPO group of the PTAm quantitatively worked as the redox site, even for micrometre-order thick films which were easily obtained by the wet fabrication process. The results of this electrochemical study suggested that the PTAm has a sufficient potential for developing an aqueous electrolyte-type totally organic rechargeable device with another hydrophilic redox polymer electrode.

To evaluate its electrode performance in a full-cell, a test-cell was fabricated with a PTAm film (100 nm) cathode, poly(*N*-4,4′-bipyridinium-*N*-decamethylene dibromide) (PV10) film anode (150 nm), and 0.1 M NaBF$_4$ aq. PV10 was selected as a suitable anode for coupling with the PTAm because PV10 is a well-studied polyviologen derivative that displays a reversible redox at −0.55 V (*vs.* Ag/AgCl) in an aqueous electrolyte.[20,21] The potential gap between the PTAm and PV10 will provide an output voltage of more than 1.0 V. The test-cell was charged

and discharged at a C-rate§ of 60 C (corresponding to the full charging and discharging for 1 min). The charging–discharging curves of the fabricated cell displayed a plateau voltage at 1.2 V, which agreed with the difference in the redox potentials (inset of Fig. 3). The charging process corresponded to the oxidation of the nitroxide radical at the cathode and the reduction of the viologen dication to the radical cation at the anode (Fig. 1). The charging capacity (110 mAh g^{-1}) agreed well with the calculated capacity obtained in Fig. 2 (2.8 mC cm^{-2} × 100 nm thickness).
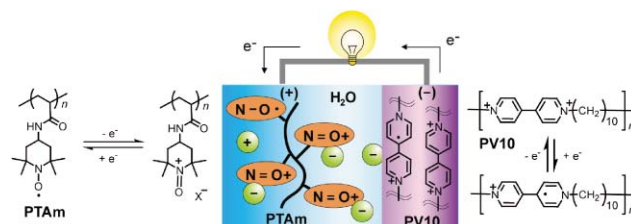

Fig. 1 Test-cell configuration of the organic rechargeable device: redox schemes for PTAm and PV10.
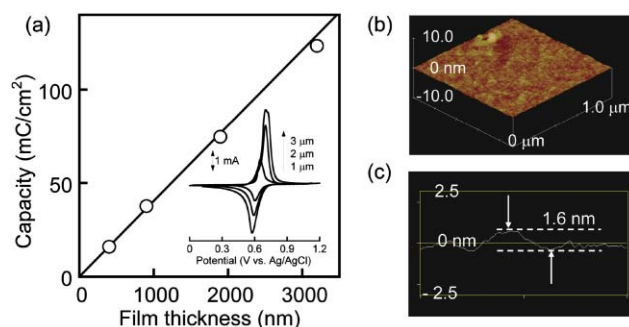
Fig. 2 (a) Redox capacity per area for the PTAm film with a thickness of 50 nm–3 μm. The solid line represents the calculated redox capacity with the coating amount. Inset: cyclic voltammograms of the PTAm films of different thicknesses at the scan rate of 1 mV s^{-1} in 0.5 M aqueous NaBF$_4$. (b), (c) AFM image of PTAm film surface after the electrochemical measurements (500 nm).

The coulombic efficiency, *i.e.*, discharging capacity *vs.* charging capacity, was almost quantitative (*ca.* 95%) indicating that the charged species, the oxoammonium form of the PTAm, stoichiometrically contributed to the following discharging process. The cycle performance of the test-cell during the repeated charging–discharging process was recorded at the cut-off voltages of 1.0–1.4 V and C-rate of 60 C. The relative capacity, *i.e.*, the obtained discharging capacity *vs.* the initial discharging capacity, *vs.* the cycle number for the test-cell is shown in Fig. 3 (closed circle plots). The discharging capacities of the test-cell were maintained at *ca.* 80% of initial capacity after 2000 cycles without any significant deterioration. This long cycle performance can be ascribed to the long cycling of PTAm (Fig. S5†), and a chemically reversible anode reaction without generating any by-product materials that inhibit the cathode reaction. In another experiment using a semi-organic test cell composed of the PTAm film (100 nm) cathode, zinc anode and 0.1 M ZnCl$_2$–NH$_4$Cl aq., the discharging capacities abruptly decrease to 65% of the initial capacity after 1000 cycles (open
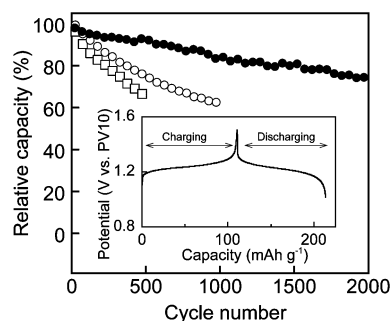
Fig. 3 Charging–discharging cycle performance of the test-cells fabricated with (●) PTAm-PV10, (○) PTAm-Zn and (□) PTVE-Zn at the C-rate of 60 C. Inset: charging–discharging curves of the test-cell fabricated with PTAm-PV10.

circle plots). The reason for the abrupt capacity decrease was attributed to the precipitation of $Zn(OH)_2$ which was generated during the discharging process of the zinc anode. The precipitate gradually accumulated on the PTAm film electrode, decreasing the charging–discharging capacities. These results indicated that the combination of PTAm and PV10 allowed a heavy metal-free device design and long cycle performance at the same time.

In summary, PTAm provided a new class of organic rechargeable devices characterized by a safe design, heavy metal-free design, rapid charging–discharging performance and long cycle life. Such organic rechargeable devices could be used in next generation IC tags and smart cards which are produced in large quantities and require a high cost for recycling.

Acknowledgements

Notes and references

‡ The technical terms "cathode" and "anode" were used in the senses of "positive electrode" and "negative electrode", respectively in this manuscript, for following the often-used terms in the literatures for lithium ion batteries.
§ The 1 C rate is defined as the current density at which the charging or discharging of the cell takes 1 h. Conventional secondary batteries, such as lithium-ion, are usually charged at a rate of 1–2 C.

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