Photocrosslinked nitroxide polymer cathode-active materials for application in an organic-based paper battery†

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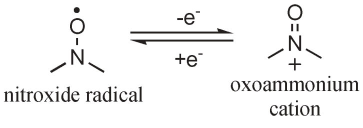
A nitroxide radical functional polymer was photocrosslinked for the first time without significant side reactions, producing a cathode-active thin film, leading to an organic-based paper battery.

Prompted by the remarkable development of portable or ubiquitous electronic devices, the demand for smaller and more flexible batteries has increased in recent years.[1,2] Particularly, due to their utility in nanoelectronics, such as microsensors, micro-actuators, and memory chips, a slim, "paper-like" battery enables design flexibility for integration with electronic devices; *i.e.*, battery-on-chip and battery-on-device. While nanostructured metal or metal oxide electrode materials for small Li-ion batteries such as $LiCoO_2$, $LiMnO_2$ and V_2O_5 have been prepared by sequential deposition,[2] block copolymer-templated,[3] or self-assembly methods,[1,4] organic-based electrodes have several inherent advantages: lightness, environmentally-benign characteristics, mechanical flexibility, and processing compatibility, leading to a solution-based or wet processing such as roll-to-roll and inkjet printing;[5,6] these advantages could also be applicable for battery fabrication.

Organic functional polymers such as polyacetylene, polyaniline, and disulfide derivatives have been investigated as potential alternatives to inorganic-based electrode-active materials.[7,8] However, batteries composed of these organic-based materials face problematic practical issues such as the limited degree of doping, slow electrochemical process, and fluctuating voltage. Recently, we have explored the use of organic radical species,[9,10] particularly pendant nitroxide radical polymers, as a cathode-active, charge-storage material for secondary Li-ion batteries.[11] A typical example of a nitroxide polymer is poly(2,2,6,6-tetramethyl-piperidinyloxy-4-yl methacrylate) (PTMA).[12] This polymer contains a 2,2,6,6-tetramethylpiperidinyl-*N*-oxy (TEMPO) radical moiety, which is chemically robust, as well as being rapidly, reversibly, and stoichiometrically oxidized to the corresponding oxoammonium cation *via* chemical or electrochemical oxidation (Scheme 1). The organic radical battery composed of the radical polymer cathode has several advantages over other organic-based batteries: (1) high charge/discharge capacity (*ca.* 100 mAh g^{-1}), ascribed to the stoichiometric redox of the nitroxide radical, in contrast to the limited doping level of π-conjugated polymers, (2) high-charging and discharging rate performance resulting from the rapid electron-transfer process of the nitroxide radical,[13] (3) long cycle life, often exceeding 1000 cycles, derived from the chemical stability of the nitroxide radical and from the amorphous electrode structure.

In the use of radical polymers as electrode-active materials, it is crucial to eliminate dissolving of the radical polymer into the electrolyte solution, which results in self-discharging of the battery. However, this requirement conflicts with processing compatibility such as solution-based fabrication to develop a paper-like battery. Furthermore, existing radical polymers such as PTMA lack any molding ability and film forming ability. To address this issue, photocrosslinking, widely used in photoresists, was chosen as a method for providing tunable solubility of the polymer, increasing mechanical toughness of the film, improving design flexibility and enabling patterning on the device. However, due to the sensitivity of most radical crosslinking reactions to nitroxide radical, the development of successful crosslinking chemistry has proved challenging. In this study, we report, for the first time, photocrosslinking of the radical containing polymers through careful design of the polymer backbone and the crosslinker structure, yielding a flexible, cathode-active material. A polynorbornene backbone provides not only good film formability and compatibility with the current collectors but also contains sites for potential photocrosslinking after molding. We carefully chose a bis(azide) derivative **3** among a series of photocrosslinkers, with the hypothesis that the photo-induced nitrene radical (–N:) would remain unreactive with the nitroxide radical due to the thermodynamically unfavored N–O–N bonding, and would selectively react with the olefinic moiety of polynorbornene backbone. The rapid electron transfer in the obtained film and the cell performance are also demonstrated.

The TEMPO-substituted norbornene monomer, 2,3-bis(2′,2′,6′,6′-tetramethylpiperidinyl-*N*-oxyl-4′-oxycarbonyl)-5-norbornene **2**,[14] was prepared *via* the esterification of 5-norbornene-2,3-dicarboxylic anhydride. Ring-opening metathesis polymerization of the norbornene monomer **2** with the Grubbs second generation catalyst yielded the corresponding norbornene polymer **1a** with high molecular weight (*e.g.*, $M_n = 1.3 \times 10^4$, $M_w/M_n = 1.2$). The radical density of **1a** remained unchanged even after the polymerization; *e.g.*, 1.95 and 1.98 radicals per monomer unit, estimated from the intensity of the ESR signal and from SQUID



Scheme 1 Redox couple of a nitroxide derivative.

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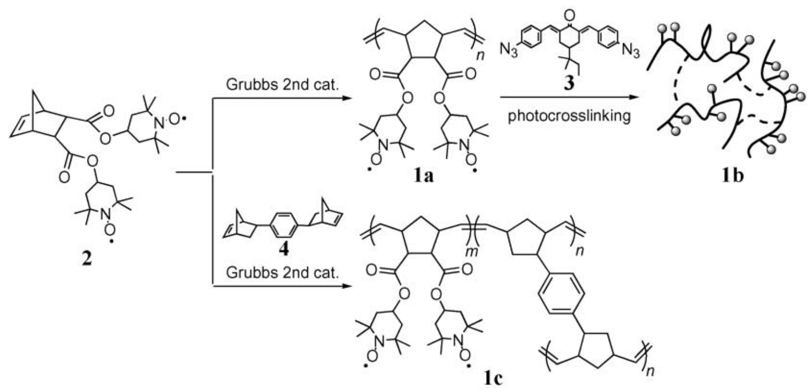

Scheme 2 Synthesis of the TEMPO-substituted polynorbornenes **1a–c**.

(superconducting quantum interference device) measurement, respectively. The radical polymer **1a** was chemically reduced to the corresponding hydroxyamine with phenylhydrazine and characterized by NMR spectroscopy, which revealed that the norbornene monomer was polymerized without any side reactions to yield **1a** as represented in Scheme 2 (see ESI).‡ The obtained polymer **1a** displayed good solubility in common organic solvents, such as chloroform, ethyl lactate, and also in typical battery electrolytes.

A toluene–ethyl lactate solution of **1a** and a small amount of the bis(azide) derivative **3** were spin-coated on an ITO glass substrate. UV irradiation (40 mJ cm^{-2}) induced nitrene formation, which resulted in reaction with the olefinic moieties of the polynorbornene backbone to afford the crosslinked film (Fig. 1). A patterned crosslinked film **1b** was prepared using UV irradiation and a photo-mask, followed by washing with chloroform to remove the unreacted soluble part. The obtained film **1b** was insoluble, but slightly swollen in organic solvents. The crosslinked part became slightly yellowish due to the azo-crosslinker. The contact stylus profile on the obtained film showed a flat (roughness < 4 nm) and uniform surface, with a thickness of 50–500 nm, after tuning the film formation conditions such as the solution concentration. The SQUID measurement gave 1.97 radicals per monomer unit in the film **1b**, which revealed that no side reactions on the TEMPO radical moiety occurred during the photocrosslinking. The use of photo-radical initiator or photo acid generator (10 mol%) also resulted in crosslinked polymer, however, the radical densities decreased significantly (1.2 and 0.9 radicals per monomer, respectively). A flexible radical film **1b** on an ITO–polyethylene terephthalate (PET) substrate was prepared as well (Fig. 1). Crosslinking copolymerization with a bifunctional monomer **4** also yielded the radical film **1c** on an ITO glass substrate.[15]

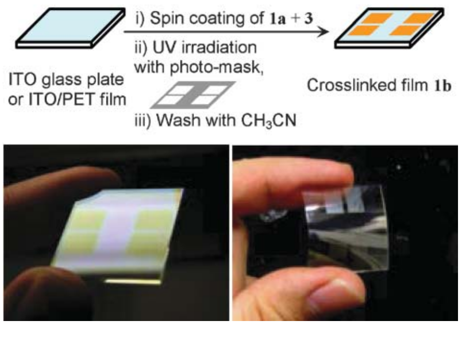

Fig. 1 The radical polymer thin film on an ITO glass and an ITO–PET substrate.

The cyclic voltammogram of the film **1b** on ITO displayed a reversible redox wave at 0.84 V *vs.* Ag/AgCl (Fig. 2a), which was assigned to the oxidation of the nitroxide to the corresponding oxoammonium cation. Electrolytic *in situ* ESR spectroscopy supported ESR-silent oxoammonium formation under the applied potential at 1.1 V and nitroxide radical regeneration at 0.6 V. The redox couple (Fig. 2a) produced a symmetric, narrow, peak-to-peak separation (ΔE = 26 mV) for the film with a thickness of 50–260 nm, which is a typical redox profile for a surface-confined species.[16] In this film thickness range, the peak current is proportional to the sweep rate, suggesting a fast electron transfer process in the film. This surface-confined and rapid electron transfer process could lead to a high power rate capability of the battery fabricated with this cathode. Beyond the thickness of 260 nm, the redox behavior changed to a diffusion-controlled profile (Fig. 2b). The number of electroactive sites in the film **1b** was coulometrically estimated from the charge Q (mC) by integrating the current obtained at the slow potential scan rate of 1 mV s^{-1}.[16,17] The charge, Q was proportional to the film thickness in the range 0–250 nm (Fig. 2b), which indicated

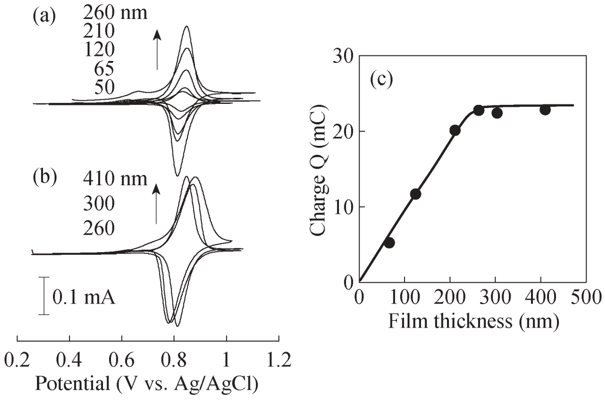

Fig. 2 Cyclic voltammograms of the half-cell, the working electrode: **1b** on the ITO glass substrate in 0.1 M acetonitrile solution of $(C_4H_9)_4NClO_4$ (a) for the film thickness: 50, 65, 120, 210 and 260 nm, (b) for the film thickness: 260, 300 and 410 nm, the counter electrode: Pt wire, the reference electrode: Ag/AgCl, scan rate = 1 mV s^{-1}. (c) Plots of the charge Q for the redox site of the loaded film **1b** *vs.* the film thickness.

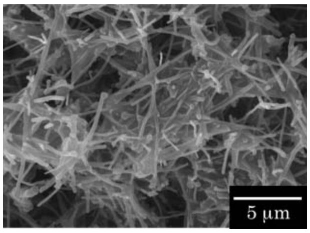

Fig. 3 SEM image of the **1b**–carbon nanofiber composite electrode prepared by UV irradiation after the molding.

quantitative electron transfer (94% of the loaded radical moiety in the film contributed to the redox process, calculated with Q and the loaded amount of **1b** on the ITO substrate). These results revealed the applicability of **1b** cathode to a thin-film battery without any carbon current collector.

The cell performance was tested using a conventional-size battery. A radical polymer–carbon composite electrode was prepared by the photocrosslinking of **1a**, in which the carbon nanofiber acted as a current collector. An ethyl lactate–toluene solution of **1a** and **3** was mixed with a carbon nanofiber, molded into the electrode, and photocrosslinked. An SEM image revealed that the carbon nanofiber was well-dispersed and uniformly coated with the radical polymer **1b** with a polymer thickness of 200 nm (Fig. 3).

The half-cell was fabricated using this polymer–carbon composite electrode, Pt wire, and Ag/AgCl as the working, counter, and reference electrode, respectively. The charge–discharge curves of the half-cell exhibited a plateau voltage at 0.84 V *vs.* Ag/AgCl, and the specific capacity was 106 mAh g^{-1}, which agreed well with the theoretical capacity (109 mAh g^{-1}), calculated from the molecular weight of the radical moiety in the the polymer **1a**. Fig. 4 also shows the charge–discharge curve at a higher current density. The capacity was even maintained at a current rate of 50 C, which enables a surprisingly rapid charging time (about 1 min) and a high power rate performance of the cell.§ A test full-cell was also fabricated by stacking the radical polymer–carbon composite cathode with a separator film and lithium metal as the anode. The charge–discharge curves for the fabricated cell displayed a plateau voltage at 3.60 V (*vs.* Li/Li^+), corresponding to the redox potential (0.84 V *vs.* Ag/AgCl) for **1b** in Fig. 2a, which revealed that **1b** served as a cathode-active material. The cycle performance during charging and discharging at the cut-off voltages of 3.0 and 4.2 V, respectively, displayed no significant deterioration in capacity up to 1000 cycles. This significantly stable cyclability can be ascribed to the simple one-electron transfer of the nitroxide radical and amorphous electrode structure.

In summary, a photocrosslinked TEMPO-substituted polynorbornene **1a** was obtained using a bis(azide) crosslinker, which was carefully designed to eliminate side reactions on the nitroxide moiety. The obtained radical film exhibited a rapid and reversible redox and served as a cathode-active material. This approach facilitated battery manufacture *via* a wet, printable and rollable process, leading to an organic-based, flexible paper battery, or a battery-on-chip in the not-too-distant future.

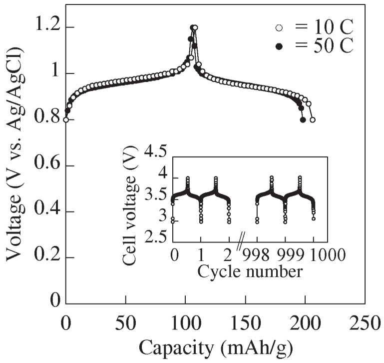

Fig. 4 Charge–discharge curves of the half-cell of polymer **1b**–carbon composite cathode, the counter electrode: Pt wire, the reference electrode: Ag/AgCl, in 0.1 M acetonitrile solution of $(C_4H_9)_4NClO_4$. Inset: cycle performance of the cell fabricated with polymer **1b**–carbon cathode and Li anode.

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Notes and references

‡ There have been several reports that the ring opening metathesis polymerization proceeds even in the presence of propagating radical species with a Ru-based tandem catalyst (C. W. Bielowski *et al.*, *J. Am. Chem. Soc.*, 2000, **122**, 12872), however, there is no report of the ring-opening metathesis polymerization of a radical containing monomer.

§ 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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