CHEMISTRY OF
MATERIALS
Article

Chem. Mater. **2010,** *22,* 783–788 783
DOI:10.1021/cm901374u

Synthesis of A Novel Spirobisnitroxide Polymer and its Evaluation in an Organic Radical Battery[†]

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Received May 25, 2009. Revised Manuscript Received July 13, 2009

A straightforward synthesis of a novel spirobisnitroxide **6** has been developed. Cyclovoltammetry of **6** revealed two distinct reversible oxidation/reduction steps separated by ca. 740 mV indicating the formation of the corresponding oxoammonium cations. Rhodium-catalyzed polymerization of **6** afforded the polyacetylene polymer **7** bearing the pending spirobisnitroxide groups. Additionally, cross-linked **7** was prepared in the presence of 3 mol % of *N,N*′-diprop-2-ynyl-oxalamide. If oxidation of both nitroxide groups is considered, **7** possesses an unprecedented high theoretical charge capacity of 174 mA h g^{-1}. Evaluation of the cross-linked polymer **7** as a cathode material for an organic radical battery showed very good cycling stability when the potential was kept below the oxidation potential of the five-membered nitroxide subunit of **6**. A presumable irreversible degradation of the polymeric backbone of **7** occurred at higher potentials, limiting the experimentally obtained charge capacity to 73 mA h g^{-1}.

Introduction

Lithium-ion batteries are widely used in portable electronic devices and power tools, and a growing demand is expected from future electric vehicle applications. The increased use of transition metal compounds as cathode active material in these batteries will ultimately lead to an increase in material cost. In addition, the current cathode materials based on cobalt are toxic, and recycling problems are not yet solved. New materials based on organic compounds are therefore an attractive alternative. Recently, Nakahara and co-workers developed an organic radical battery in which an organic polymer poly(4-methacryloyloxy-2,2,6,6-tetramethylpiperidin-*N*-oxyl) (PTMA) bearing redox active nitroxide radicals is used as cathode material.[1−3] Thereby, a fully reversible one-electron oxidation of the 2,2,6,6-tetramethylpiperidin-*N*-oxyl (TEMPO)-nitroxide at a potential of ca. 3.6 V vs Li/Li$^+$ leads to formation of an oxoammonium cation (Scheme 1). Different workers have shown that batteries made from PTMA have a high rate capability and cycling stability.[4−11] The good rate capability predestinates batteries made from PTMA for use in applications where high power is needed for short times. Prototypes of organic radical batteries were used e.g. to safely shut down desktop computers in the case of power failure.[12,13] Another promising application may be flexible organic batteries.[14]

However, while the rate capability and cycle stability of this polymer is excellent, it suffers from rather low energy density. Thus, the theoretical charge capacity[15] of pure PTMA is 112 mA h g^{-1}, compared to > 140 mA h g^{-1} for transition metal based materials. In order to increase the energy density of radical batteries, it is necessary to increase the number of radical centers per weight unit and/or to increase the cell voltage by using radicals with more positive oxidation potentials. Several groups pursued this challenging target during the last years and reported new nitroxide bearing polymers. On one side, TEMPO-nitroxide was attached to different polymers such as polynorbornene,[16,17] poly(7-oxanorbornene),[18]

[†] Accepted as part of the 2010 "Materials Chemistry of Energy Conversion Special Issue".

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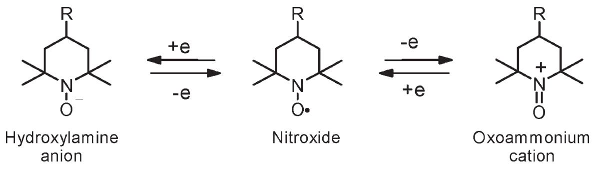
Scheme 1. Redox Behavior of Nitroxide Radicals



polyvinylether,[19−21] polyoxirane,[22,23] polyoxetane,[23] polyallene,[24] polyacetylene,[25,26] cellulose,[27] or even DNA.[28] On the other side, polymers substituted with nitroxides different than TEMPO were prepared such as for example poly(*p*-*tert*-butylaminoxy-styrene),[29] polyacetylene, polynorbornene, or cellulose bearing 2,2,5,5-tetramethyl-1-pyrrolidinyloxy moieties[26,27,30] or polyoxirane substituted with 2,2,5,5-tetramethyl-3-pyrroline-*N*-oxyls.[23] However the theoretical charge capacity of these new nitroxide polymers did not significantly surpass that of PTMA. In fact, the highest value (135 mA h g^{-1}) reached by poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl vinyl ether)[19] is still lower than that of the currently used $LiCoO_2$ (about 140 mA h g^{-1}). Moreover, the oxidation potential of nitroxides attached to the above cited polymers was practically the same as that of TEMPO (~0.88 V vs NHE).

In this paper, we describe the synthesis of novel spirobisnitroxides **6** and **6a** containing two nitroxide groups with significantly different oxidation potentials and very high theoretical charge capacity of 174 and 173 mA h g^{-1}, respectively (Scheme 2). Furthermore, **6** was transformed into the polyacetylene polymers **7** and **7a** of which the latter was evaluated as a cathode material for organic radical battery.

Experimental Section

Triacetonamine (>99%), was obtained from Ciba; all other reagents and solvents (>99%) were purchased from Fluka and used as received. The catalyst [Rh(norbornadiene)(B(C_6H_5)$_4$)] was prepared according ref 31, *N*,*N*′-diprop-2-ynyl-oxalamide, according to ref 32. The solid supported catalyst Fulcat 22B was obtained from Laporte, England. Other acid catalysts will work too.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 spectrometer (300 MHz for ^{1}H and 75.47 MHz for ^{13}C). Chemical shifts (δ) are given in parts per million downfield from an internal Me_4Si standard, and *J* values are in hertz. IR spectra were taken on Nicolet Magna-IR 750 spectrometer in attenuated total reflectance (ATR) mode, and MS spectra were taken on a Finnigan SSQ 710 apparatus. The electron spin resonance (ESR) spectra were acquired on an X-Band Miniscope MS 2000 spectrometer (Magnettech, Germany). Size exclusion chromatography (SEC) was carried out at a sample concentration of **7** of 1 g L^{-1} with degassed dimethylacetamide containing 3 g L^{-1} LiBr and 6 g L^{-1} CH_3COOH as eluent at a flow rate of 0.5 mL min^{-1} at 60 °C on a system consisting of a GPC_{max} pump (Viscotek, Houston), a set of two columns (GRAM 100, 300 mm × 8 mm, 10 μm, pore size 10 nm, and GRAM 30, 300 mm × 8 mm, 10 μm, pore size 3 nm, Polymer Standard Services, Germany), and a triple array detector TDA 302 (Viscotek, Houston). The system was calibrated in the range of 1140−300 300 g mol^{-1} with eight samples of poly(methyl methacrylate) (Polymer Standard Services, Germany). Electrodes for the use in coinlike test cells were prepared by coating aluminum current collectors with a slurry consisting of powdered nitroxide polymer **7a** (20 wt %), graphite (TIMREX KS4, TIMCAL SA, 34 wt %), carbon black (ENSACO 250, TIMCAL SA, 7 wt %), and binder (PVDF6020, Solvay SA, 39 wt %) dissolved in N-methyl-2-pyrrolidone (NMP). After casting the slurry by a doctor-blade method, the electrodes were dried for 12 h at 100 °C in vacuum and then transferred into an argon filled glovebox for cell assembly. Typical electrodes of 1.33 cm^2 geometric surface contained ca. 2 mg of nitroxide polymer. A solution of $LiPF_6$ (1M) in a 1:1 mixture of ethylene carbonate/dimethyl carbonate (EC/DMC) or propylene carbonate (PC) was used as electrolyte, and the counterelectrode was made from lithium foil. Galvanostatic cycling was performed at 25 (± 0.1) °C on a Batsmal battery measurement system (Astrol Electronic AG). Cyclic voltammograms were measured at a sweep rate of 0.1 V s^{-1} with an AMEL model 2049 potentiostat at 22 °C in acetonitrile containing 0.1 M Bu_4NBF_4. Platinum wires were used as the counter and working electrodes (20 mm^2), a silver wire was used as reference electrode, and potentials are given versus the ferrocene/ferricenium (Fc) redox system.

4-Amino-2,2,6,6-tetramethyl-piperidine-4-carbonitrile (**2**). A 750 mL four neck flask was charged with triacetonamine (155.2 g, 1 mol) and acetone cyanhydrin (154.4 g, 1.81 mol). The suspension was stirred at 75−80 °C during 1 h, and the acetone generated in the reaction was continuously distilled off. The mixture was then cooled to room temperature, and 100 mL of methyl-*t*-butyl ether were added. The slurry was cooled to 5 °C, filtered, washed with 150 mL cold methyl-*t*-butyl ether, and dried to afford 149.7 g (82%) of 4-hydroxy-2,2,6,6-tetramethyl-piperidine-4-carbonitrile as white crystals, mp 134−136 °C (literature[33] mp 136 °C). A 148.8 g portion (0.816 mol) of this material were added to a methanolic solution of NH_3 gas (230 g, 16.6% NH_3 by weight), and the mixture was stirred at room temperature during 19 h. The colorless solution was evaporated at 10 mbar and a maximum of 25 °C to afford 163 g of crude **2** as a colorless oil slowly crystallizing on standing. Sample recrystallized from hexanes had an mp 75−77 °C (literature[34] mp 75−76 °C). ^{1}H NMR (CD_3OD): 4.7 (bs, 3H),

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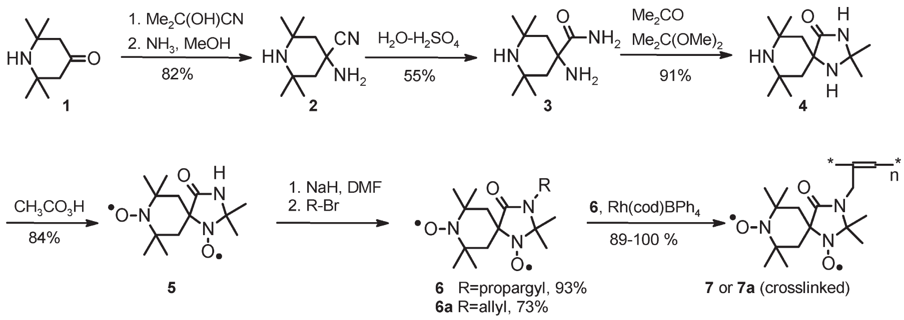
Scheme 2. Synthesis of Spirobisnitroxides 6 and 6a and of Polymers 7 and 7a



2.15 (d, 2H, $J = 13.8$ Hz), 1.41 (s, 6H), 1.34 (d, 2H, $J = 13.5$ Hz), 1.21 (s, 3H).

4-Amino-2,2,6,6-tetramethyl-piperidine-4-carboxylic Acid Amide (3). A 1500 mL flask was charged with water (16.8 mL) and H_2SO_4 (420 mL, 96%, 7.52 mol). The acid was cooled to 10 °C, and the crude 4-amino-2,2,6,6-tetramethyl-piperidine-4-carbonitrile **2** (160 g, about 0.8 mol) was added slowly with intense stirring during 1 h while keeping the temperature below 40 °C. The mixture was then stirred for 23 h at 50 °C, cooled to 35 °C, and poured on crushed ice (3.5 kg). Solid NaOH (640 g, 16 mol) was added and the solution was extracted with THF-EtOAc (1:1, 5× 400 mL). The combined extracts were washed with 100 mL of saturated NaCl, dried over K_2CO_3, and evaporated. The residue was triturated with cold EtOAc to afford 87.1 g (54.6%) of **3**, colorless crystals, mp 142−144 °C. ^1H NMR (CD_3OD): 4.9 (bs, 5H), 1.88 (d, 2H, $J = 14.4$ Hz), 1.46 (d, 2H, $J = 14.4$ Hz), 1.37 (s, 6H), 1.17 (s, 6H). ^{13}C NMR(CD_3OD): 182.9, 57.8, 44.1, 32.9, 30.7. MS (CI) for $C_{10}H_{21}N_3O$ (199.3) found: $m/z = 199$ (M^+). IR: 1605, 1666 (C=O), cm^{-1}.

2,2,7,7,9,9-Hexamethyl-1,3,8-triaza-spiro[4.5]decan-4-one (4). A 250 mL steel autoclave was charged with 4-amino-2,2,6,6-tetramethyl-piperidine-4-carboxylic acid amide **3** (40 g, 0.2 mol), acetone (46.4 g, 0.8 mol), acetone dimethylketal (25 g, 0.24 mol), and Fulcat 22B catalyst (4 g). The autoclave was heated 17 h at 150 °C, and then cooled, and the mixture was dissolved in methanol (800 mL) and filtered. The filtrate was evaporated on a rotary evaporator and the solid residue was stirred 30 min with EtOAc (300 mL) at 0 °C. The crystals were filtered off, washed with cold EtOAc (50 mL), and dried to afford 43.6 g (91%) of **4**. Colorless crystals, mp 247−250 °C. ^1H NMR (CD_3OD): 4.89 (bs, 3H), 1.61 (bs, 4H), 1.43 (s, 12H), 1.17 (s, 6H). ^{13}C NMR(CD_3OD): 180.2, 71.4, 63.2, 49.5, 43.6, 33.8, 29.6, 27.3. MS for $C_{13}H_{25}N_3O$ (239.36) found: $m/z = 239$(M^+). IR: 1686 (C=O), cm^{-1}.

2,2,7,7,9,9-Hexamethyl-1,3,8-triaza-spiro[4.5]decan-4-one-1,8-di-*N*-oxyl (5). A 4.5 L flask was charged with 2,2,7,7,9,9-hexamethyl-1,3,8-triaza-spiro[4.5]decan-4-one **4** (107.7 g, 0.45 mol), dichloromethane (800 mL), water (330 mL), and $NaHCO_3$ (227 g, 2.7 mol). Peracetic acid (394.3 g, 40% in acetic acid, 2.375 mol) was then added during 65 min dropwise to the stirred mixture kept at 5 °C. The red mixture was then stirred 29 h at room temperature (rt). The organic layer was separated, washed with 1 M NaOH (3 × 200 mL) and water (2 × 100 mL), dried over $MgSO_4$, and diluted with methanol (400 mL). The red solution was then concentrated on a rotary evaporator to a weight of approximately 225 g. The red slurry was stirred 1 h at 0 °C, the solid was filtered off, washed with cold methanol (50 mL), and dried to afford 101.4 g (83.7%) of **5**. Red crystals, mp 132−134 °C. Anal calcd for $C_{13}H_{23}N_3O_3$ (269.35) calcd: C 57.97; H 8.61; N 15.60. Found: C 57.80; H 8.49; N 15.66. MS (CI): $m/z = 269$ (M^+). IR: 1722 (C=O), cm^{-1}.

2,2,7,7,9,9-Hexamethyl-3-prop-2-ynyl-1,3,8-triaza-spiro[4.5]-decan-4-one-1,8-di-*N*-oxyl (6). Sodium hydride (4.6 g, 0.105 mol, 55% in mineral oil) was slowly added to a solution of 2,2,7,7,9,9-hexamethyl-1,3,8-triaza-spiro[4.5]decan-4-one-1,8-di-*N*-oxyl **5** (26.95 g, 0.1 mol) in dry dimethyl formamide (80 mL), and the mixture was stirred 1 h at 40 °C. It was then cooled to 3 °C, and propargyl bromide (13.1 g, 0.11 mol) was added slowly. The mixture was stirred 2 h at room temperature and then diluted with ice water (1000 mL). The precipitate was filtered off, dried, and recrystallized from dichloromethane−hexane to afford 28.64 g (93%) of **6**. Red crystals, mp 139−141 °C. Anal. calcd for $C_{16}H_{25}N_3O_3$ (307.4) calcd: C 62.52; H 8.20; N 13.67. Found C 62.75; H 8.30; N 13.67. MS (APCI): $m/z = 308$ (MH^+). IR: 3253 (—C≡C—H), 1705 (C=O), cm^{-1}.

2,2,7,7,9,9-Hexamethyl-3-allyl-1,3,8-triaza-spiro[4.5]decan-4-one-1,8-di-*N*-oxyl (6a). Sodium hydride (0.92 g, 0.021 mol, 55% in mineral oil) was slowly added to a solution of 2,2,7,7,9,9-hexamethyl-1,3,8-triaza-spiro[4.5]decan-4-one-1,8-di-*N*-oxyl **5** (5.38 g, 0.02 mol) in dry dimethyl formamide (20 mL), and the mixture was stirred 1 h at 40 °C. It was then cooled to 3 °C, and allyl bromide (2.66 g, 0.022 mol) was added slowly. The mixture was stirred 3 h at room temperature and then diluted with ice water (200 mL). The precipitate was filtered off, dried, and recrystallized from dichloromethane-hexane to afford 4.54 g (73.4%) of **6a**, red crystals, mp 93−5 °C. Anal. Calcd. for $C_{16}H_{27}N_3O_3$ (309.4) calcd. C 62.11; H 8.80; N 13.58; found C 61.77; H 8.67; N 13.42. MS(APCI) $m/z = 310$(MH^+). IR: 1709 (C=O), cm^{-1}.

Poly(2,2,7,7,9,9-hexamethyl-3-prop-2-ynyl-1,3,8-triaza-spiro-[4.5]decan-4-one-1,8-di-*N*-oxyl) (7). A solution of 2,2,7,7,9,9-hexamethyl-3-prop-2-ynyl-1,3,8-triaza-spiro[4.5]decan-4-one-1,8-di-*N*-oxyl **6** (3.074 g, 10 mmol) in dimethylformamide (30 mL) was purged with argon for 15 min. The catalyst, [Rh(norbornadiene)(B(C_6H_5)$_4$)] (51 mg, 0.1 mmol) was then added, and the mixture was stirred for 15 h under argon at 40 °C. The red viscous solution was then transferred into water (500 mL) and stirred for 30 min. The precipitate was filtered off, dispersed in methanol (300 mL), stirred for 30 min, filtered, washed with methanol and water, and dried to afford 2.75 g (89%) of **7** as an orange powder. IR: —C≡C—H absorption (3253 cm^{-1}) absent, >C=O at 1705 cm^{-1}. SEC: relative calibration $M_n = 42856$, $M_w = 118664$, absolute calibration $M_n = 46959$, $M_w = 136117$. ESR: see Figure 1. The cross-linked polymer **7a** was prepared following the same procedure but the cross-linker *N*,*N*′-diprop-2-ynyl-oxalamide (49.2 mg, 0.3 mmol) was added to **6** before addition of the catalyst. The mixture was stirred 23 h at rt, the resulting red gel was then stirred 3 h with water (500 mL), the solid was dispersed in methanol (500 mL), stirred 40 h at rt to remove any entrapped momomer, and dried to afford 3.08 g (~100%) of **7a** as an

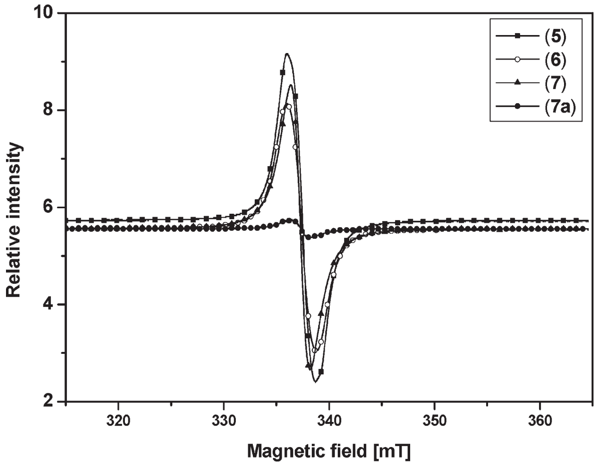


Figure 1. ESR spectra of bisnitroxides **5** and **6** and of polymers **7** and **7a** in CH_2Cl_2 (c = 1 g L^{-1}). The curve for **7a** corresponds to a saturated solution obtained by stirring 1 mg of **7a** with 1 mL CH_2Cl_2 for 1 h at rt and filtration.

orange powder. IR: —C≡C—H absorption (3253 cm^{-1}) absent, > C═O at 1705 cm^{-1}. ESR: see Figure 1.

Results and Discussion

The synthesis of the novel spirobisnitroxide acetylene monomer **6** and of the model compound **6a** (vide infra) starting from the cheap industrially available 2,2,6,6-tetramethyl-piperid-4-one (triacetonamine, **1**) is depicted in Scheme 2. Acetone cyanohydrin rather than KCN[34] and methanolic NH_3 were used to transform **1** into the aminonitrile **2**. Sulfuric acid promoted hydration of **2** afforded the novel aminoamide **3** in 45% yield (on **1**). Acid catalyzed cyclization[35] of **3** with mixture of acetone and acetone dimethylketal provided the hitherto unknown 2,2,7,7,9,9-hexamethyl-1,3,8-triaza-spiro[4.5]decan-4-one **4** (91%) which was oxidized with peracetic acid into the novel spirobisnitroxide **5** (84%). Alkylation of **5** with propargylbromide or allybromide and NaH furnished the propargylated bisnitroxide **6** (93%) and the allylated analog **6a** (73%). Transformation of **6** into the polymeric nitroxide **7** was accomplished using [Rh(norbornadiene)(B(C_6H_5)$_4$)] catalyst.[31] Synthesis of polyacetylenes bearing pending nitroxide groups via Rh-catalyzed polymerization of propargylated nitroxides and, importantly, compatibility of the nitroxide function with the polymerization conditions has been reported several times.[25,26,30,36,37] Polymerization of **6** with 1 mol % of the catalyst in DMF afforded the polymer **7** as a yellow powder (89%). The polymer **7** has very low solubility in THF, methanol, or $CHCl_3$ but is sufficiently soluble in *N*,*N*-dimethylacetamide which was used for determination of its molecular weight by size exclusion chromatography (SEC). The SEC results using relative (M_n = 42856, M_w = 118664) and absolute calibration (M_n = 46959, M_w = 136117) are in good agreement. Moreover, the characteristic absorption at 3253 cm^{-1} of the terminal acetylene group (—C≡C—H) observed in **6** was absent in **7** indicating a successful polymerization. The ESR spectrum of **7** in dichloromethane (1 mg ml^{-1}) shown in Figure 1 features only an unresolved band, characterictic for polymeric nitroxides.[38] The absence of hyperfine splitting in the spectra of the monomeric spirobisnitroxides **5** and **6** is very probably due to exchange interaction occurring between the two closely spaced nitroxide groups.[39] We have recently demonstrated on the example of cross-linked PTMA that insolubility of the nitroxide polymer in the battery electrolyte is crucial for cycling stability of the organic radical battery.[10] Thus, even though **7** is already a quite insoluble material we decided to further decrease its solubility via copolymerization with 3 mol % of a croslinker *N*,*N*′-diprop-2-ynyl-oxalamide. The cross-linked polymer **7a** was obtained in quantitative yield. The theoretical charge capacity of **7** amounts to 174 mA h g^{-1} which is unprecedented for a nitroxide polymer and higher than that of $LiCoO_2$ (about 140 mA h g^{-1}). The theoretical charge capacity of **7a** is, considering incorporation of 3 mol % of the electrochemically inert cross-linker, 172 mA h g^{-1}. The significantly diminished solubility of the cross-linked polymer **7a** is demonstrated by the low intensity of the ESR signal of its saturated dichloromethane solution (Figure 1) obtained by stirring 1 mg **7a** with 1 mL CH_2Cl_2 for 1 h at rt and filtration of the nondissolved material. Thermogravimetric analysis of **7a** (N_2, 10 °C min^{-1}) revealed its excellent stability up to 200 °C followed by a rapid decomposition starting sharply at about 220 °C which is presumably due to depolymerization known[40],41 to occur in some polyacetylenes around this temperature.

Cyclic voltammetry (CV) of the monomeric bisnitroxide **6** in acetonitrile solution shows two reversible redox processes occurring at 0.325 and 1.076 V ($E_{1/2}$ vs Fc/Fc^+), respectively (Figure 2, a CV of TEMPO acquired under the same conditions, is shown for comparison, $E_{1/2}$ = 0.227 V). The pair of redox peaks at lower potential is attributed to the reversible oxidation/reduction of the six-membered nitroxide. The oxidation of the five-membered nitroxide is shifted to more positive potentials, as expected for imidazolidinone *N*-oxyls.[42−44] The allyl analog **6a** behaves similarly. Cyclic voltammograms of both **6** and **6a** remain unchanged for at least 10 cycles.

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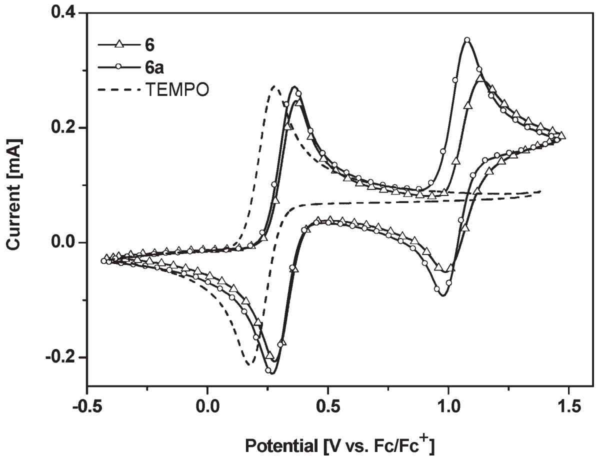

Figure 2. Cyclic voltammograms of bisnitroxides bearing propargyl-(**6**) and allyl-(**6a**) substituents recorded in acetonitrile/0.1 M nBu_4BF_4 solution: Pt working electrode; scan rate 100 mV s^{-1}.

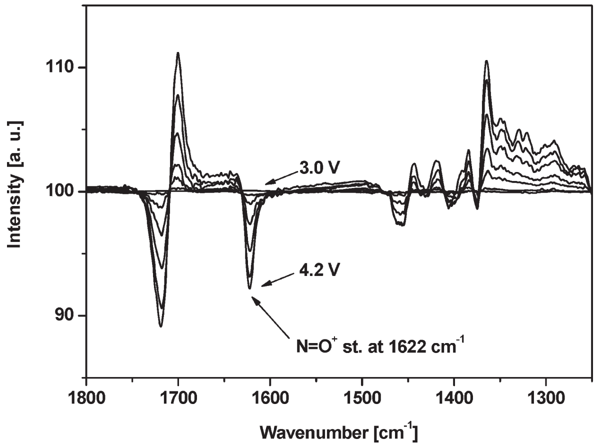

Figure 3. In situ difference FTIR spectra of **7a** acquired during charging from 3.0 to 4.2 V vs Li/Li$^+$. The difference spectra show changes with respect to the pristine material at 3.0 V. Characteristic for the oxidation of nitroxide is the appearance on a new N═O stretching band at 1622 cm^{-1}.

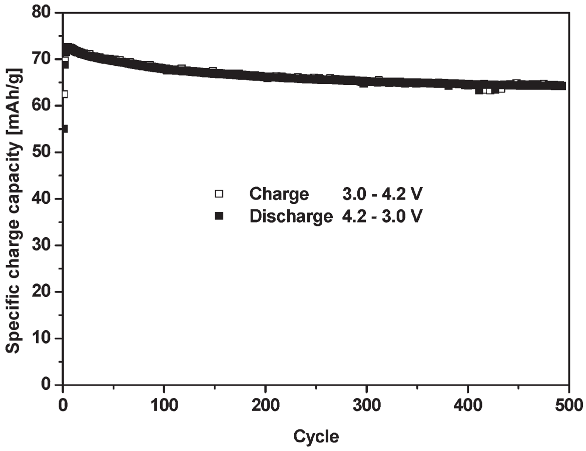

Figure 4. Galvanostatic cycling of model electrodes made from **7a** (20%), graphite KS4 (34%), soot ENSACO250 (7%), and PVDF binder (39%): counterelectrode metallic lithium; charge/discharge rate 1 C; electrolyte EC/DMC, 1 M $LiPF_6$.

To confirm the assigned mechanism of the electrochemical reactions, in situ Fourier transform infrared (FTIR) spectroscopy was used as an independent technique: The oxidation of nitroxides to oxoammonium cations involves an increase in the formal bond order of the nitrogen−oxygen bond from 1.5 in the reduced state to 2 in the oxidized state. This change is accompanied by a shortening of the N—O bond and an increase in its stretching frequency. These changes in the nitroxide polymer **7a** during electrochemical cycling were confirmed with in situ FTIR spectroscopy (Figure 3). The positive electrode of an organic radical battery was placed on a diamond ATR prism. Acetonitrile containing 1 M lithium perchlorate was chosen as an electrolyte with low infrared absorbance in the relevant spectral window, and $Li_4Ti_5O_{12}$ was used as the active material for the counterelectrode. The N—O stretching frequency of cyclic nitroxides is expected[45,46] in the range between 1450 and 1340 cm^{-1}, but an unambiguous assignment was not possible in this case. A series of spectra was acquired while the working electrode was stepwise charged to a potential of 4.2 V vs Li/Li$^+$. Figure 3 shows difference spectra illustrating the changes occurring during this charging. A new band emerging at 1622 cm^{-1} which is the characteristic stretching frequency[47] of the N═O$^+$ group proves the formation the oxoammonium ions.

To test the performance of polymer **7a** as cathode material in organic radical batteries, composite electrodes were prepared of the active material with conductive carbon additives and PVDF binder. These electrodes were galvanostatically cycled in half-cells vs metallic lithium, in an electrolyte consisting of $LiPF_6$ (1 M) in EC/DMC 1/1 (Figure 4). Thereby the electrodes show excellent cycling stability as long as the cell voltage is kept within the limits of 3.0 and 4.2 V. In this potential window, only the six-membered nitroxide of **7a** is expected to be reversibly oxidized to an oxoammonium ion. However, the measured specific charge capacity did not reach the theoretical value of 86 mA h g^{-1} corresponding to its quantitative and selective oxidation but only 73 mA h g^{-1}, possibly because a small part of the polymer had no contact to the conductive carbon in the electrode. In fact, the ratio of the nitroxide polymer to conductive carbon[48] and the thickness[49] of the electrode are known to influence the achievable charge capacity significantly. As the cutoff voltage for the charging step is increased to 4.4 V in order to oxidize both nitroxide groups, the cycling stability is low, and the specific discharge capacity drops from 90 mA h g^{-1} to less than 40 mA h g^{-1} within 15 cycles. The onset of degradation is shown in cyclic voltammograms of increasing sweep width (Figure 5). Substituting the

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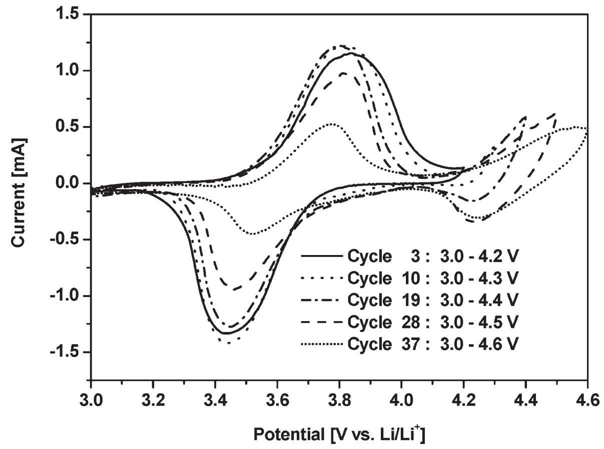

Figure 5. Cyclic voltammogram of composite electrode made from polymer **7a** in a coin-cell-like test cell: electrolyte PC, 1 M $LiPF_6$; counter/reference electrode lithium foil; scan rate 1 mV s^{-1}.

electrolyte solvents EC and DMC for the more oxidation stable propylene carbonate did not lead to an increased cycling stability. We assume therefore that side reactions involving oxidation of the polyacetylene backbone set in prior to oxidation of the second nitroxide group. The possibility[50] that the degradation is due to the oxidation of allylic positions of **7a** seems less probable because the monomeric model *N*-allyl-bisnitroxide **6a** shows reversible cyclovoltammetric behavior.

Conclusions

A straightforward synthesis of a novel spirobisnitroxide **6** with two electrochemically different nitroxide groups and possessing a very high theoretical charge capacity (174 mA h g^{-1}) was developed. Rhodium catalyzed polymerization of **6** afforded its polymer **7**. Evaluation of the cross-linked polymer **7a** in an organic radical battery suggests that the polyacetylene backbone of **7a** is not stable at potentials where the imidazolidinone nitroxide of **6** undergoes oxidation. Modification of the polymeric backbone to which the spirobisnitroxide unit of **6** is attached may lead to organic radical batteries with higher voltage and high charge capacity and cycle life.

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(50) The authors thank one reviewer for the suggestion to prepare **6a** and evaluate its electrochemical behavior.