Synthesis of Poly(4-methacryloyloxy-TEMPO) via Group-Transfer Polymerization and Its Evaluation in Organic Radical Battery

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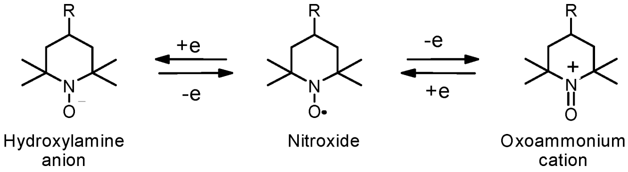
Novel group-transfer polymerization (GTP) of 4-methacryloyloxy-TEMPO for the preparation of poly-(4-methacryloyloxy-TEMPO) (PTMA) has been developed. The new PTMA has been tested as an active electrode material in rechargeable organic radical battery (ORB). The advantage of the GTP method is that it affords PTMA containing the theoretical amount of nitroxide groups. Furthermore, cross-linked PTMA was prepared in the presence of small amounts of ethylene glycol dimethacrylate. Cyclic voltammetry of this PTMA showed a single, highly reversible redox couple at a potential of ca. 3.6 V (vs Li/Li$^+$). This potential is similar to the potential of materials (e.g., $LiCoO_2$) used for the positive electrode in lithium-ion batteries. In galvanostatic cycling experiments between 3.0 and 4.0 V in a half-cell setup vs metallic Li as counter and reference electrode a reversible specific charge of ca. 103 Ah kg^{-1} at current rates up to 1 C was obtained with the cross-linked PTMA. The useable charge capacity is very stable with cycling, showing only a slight decrease after 200 full charge−discharge cycles at 2 C.

Introduction

Nitroxide radicals, the best-known example being 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO), show a unique redox behavior. One-electron reduction leads to the hydroxylamine anions, whereas one-electron oxidation generates the oxoammonium cations (Scheme 1).[1,2] Oxoammonium cations often form stable salts, whereas the hydroxylamine anions can be protonated under certain pH conditions to give the neutral hydroxylamines. The respective oxidation and reduction potentials depend somewhat on the nitroxide structure:[2−13] for example, with TEMPO the estimated standard redox potential[5] E_0 (vs NHE) by cyclic voltammetry of the redox couples is 0.87 V for the nitroxide−oxoammonium cation and 0.11 V for the nitroxide−hydroxylamine anion. The reversible oxidation of nitroxides into oxoammonium cations and their back-reduction into nitroxides is the underlying principle for their use as a positive electrode material in the recently reported organic radical battery (ORB).[10,11,14−16]

Scheme 1. Redox Behavior of Nitroxide Radicals



The setup of an ORB is similar to that of a classical[17] secondary Li-ion battery; however, the positive electrode material (e.g., $LiCoO_2$) used in lithium-ion batteries is replaced by a suitable nitroxide compound. ORB offers numerous advantages over lithium-ion batteries; in particular, the absence of heavy metals makes it more environmentally friendly and safe, it can be charged and discharged quickly, and it has a practically identical voltage (∼3.6 V). To be suitable for use in an ORB the nitroxide compound must satisfy several requirements. Fast and reversible redox behavior is a prerequisite for obtaining a large number of battery charge/discharge cycles. This is not the case for the redox couple nitroxide/hydroxylamine anion.[5] Hence, ORB employs only the nitroxide/oxoammonium cation couple which is reversible for many but not all types of nitroxides.[4]

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The concentration of nitroxide groups per electrode weight unit must be as high as possible in order to obtain high charge and energy density. Both the nitroxide and the related oxoammonium salt must have very low solubility or ideally be insoluble in the battery electrolyte, e.g., ethylene carbonate, in order to prevent their migration to the negative electrode. The requirement of low solubility is currently at best fulfilled with polymers bearing TEMPO substituents on the polymeric backbone.[10,11,15,16]

Poly(4-methacryloyloxy-2,2,6,6-tetramethylpiperidin-*N*-oxyl) (PTMA) was the first nitroxide polymer used in ORB. Reported syntheses of PTMA introduce the nitroxide function in the last step by oxidation of polymers obtained via free-radical polymerization of either 4-methacryloyloxy-2,2,6,6-tetramethylpiperidine[11,15,18,19] or 4-methacryloyloxy-*N*-hydroxy-2,2,6,6-tetramethylpiperidine.[20]

Unfortunately, this polymer analogous oxidation reaction never proceeds to 100% conversion and affords PTMA containing typically only 65% to at most 81% of the theoretically possible amount of nitroxide groups.[11,18] This low nitroxide content diminishes the charge capacity of the nitroxide positive electrode material to the same extent—at best a 90.3 Ah kg^{-1} capacity material can be obtained with PTMA containing 81% nitroxide groups[11] instead of the 111.5 Ah kg^{-1} theoretically[21] possible for 100% pure PTMA. In addition, the residual nonoxidized $-$NH$-$ or $-$N(OH)$-$ groups may undergo side reactions[2] with the oxoammonium cations, which is detrimental to the redox reversibility. Therefore, methods affording nitroxide polymers containing the theoretical amount of nitroxide groups are highly desirable.

Nitroxide polymers for ORB, prepared via rhodium-catalyzed polymerization of TEMPO-bearing acetylene monomers or via ring-opening metathesis polymerization of TEMPO-containing norbornene monomers, were very recently reported.[14] However, these materials did not approach the charge capacity theoretically obtainable with PTMA. The well-known high reactivity[1] of nitroxide radicals with carbon-centered radicals excludes the use of free-radical polymerization of nitroxide-containing monomers. Anionic polymerization of 4-methacryloyloxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl[22] or 4-acryloyloxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl[23] is known; however, the stringent experimental requirements of anionic polymerization make this method rather difficult. Here we report the hitherto unknown application of the experimentally much less demanding group-transfer polymerization[24] (GTP) for synthesis of PTMA with 100% of theoretically possible nitroxide content. Preparation of cross-linked and hence insoluble PTMA via GTP was successful as well. Evaluation of the new GTP-PTMA materials in ORB was then performed.

Experimental Section

All purchased reagents and solvents were, unless stated otherwise, used as received: 1-methoxy-2-methyl-1-trimethylsilyloxy-propene (techn. >90%, Fluka), tetrabutylammonium fluoride (1 M in THF, ~5 wt % H_2O, Aldrich), ethylene glycol dimethacrylate (98%, Aldrich), 4-hydroxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl (98%, Ciba SC), methacryloyl chloride (97%, Fluka, distilled before use), triethyl amine (99.5%, Fluka, distilled from CaH_2), THF (>99.5%, Fluka, dried by refluxing over sodium—benzophenone and subsequent distillation under argon), *N*-methyl-pyrrolidone (NMP, >99%, Fluka), dimethyl carbonate (DMC, >99%, Fluka), ethylene carbonate (EC, >99%, Fluka), and $LiPF_6$ (>98%, Aldrich). 4-Acetoxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl reference for UV spectroscopy was prepared according to ref 25 and purified by recrystallization from hexane to >99.8% purity (GC); mp 54−55 °C, UV (CH_2Cl_2, 1 cm cuvette, against CH_2Cl_2 blank): $c = 5.151$ g L^{-1}, $\lambda_{max} = 461.5$ nm, $\epsilon = 11.495$ L mol^{-1} cm^{-1}, $c = 10.016$ g L^{-1}, $\lambda_{max} = 461.3$ nm, $\epsilon = 11.378$ L mol^{-1} cm^{-1}.

The relative GPC analysis of the polymers was performed on a set of 2 PL-Gel 300 × 7.5 mm (5 μm) mixed C columns + 1 PL-Gel guard column using a Spark Holland Basic Marathon sampler and a Flux RHEOS 4000 pump with inline ERC 1215 α degasser, coupled with a ERC 7515A refractometer and ERC7217 UV detector. The column temperature was 40 °C; the detector temperature was 30 °C. Tetrahydrofuran was used as eluent (1 mL/min). Polystyrene standards were used for the calibration. The absolute GPC measurements were carried out using a PL-GPC 220 instrument with 2× PL-Gel Mix-B LS column set (2 × 30 cm) equipped with refractive index, viscosity, and light scattering (15° and 90° angle) detectors. DMF + 1 g L^{-1} LiBr at 80 °C was used as eluent. Universal calibration was done using PMMA standards in a range of $M_p = 2680-3\,900\,000$ (Polymer Labs Ltd, U.K.). Gas chromatography was performed on an Agilent 6850 Series chromatograph on a HP-1 methyl siloxane capillary column (30 m × 320 μm × 0.25 μm) with He carrier gas (3 mL min^{-1}) and a FID detector: injector temperature 250 °C, starting temperature 100 °C, gradient 20° min^{-1} to 300 °C.

4-Methacryloyloxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl (1). 4-Hydroxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl (172.2 g. 1 mol) and triethylamine (111.3 g, 1.1 mol) were dissolved in toluene (1600 mL). Methacryloyl chloride (115.0 g, 1.1 mol) was added dropwise over 20 min to the stirred solution while keeping the temperature below 30 °C. The mixture was then stirred at 50 °C for 2 h and then 10 h at 40 °C. Water (300 mL) was then added; the organic phase was separated, washed with water (3 × 100 mL), dried over $MgSO_4$, and evaporated under reduced pressure. The solid residue was dissolved in hot ethanol (220 mL, 94%), and the solution was diluted with water (220 mL). The slurry of red crystals was cooled to 0 °C, filtered, washed with cold ethanol—water mixture (100 mL), and dried at 50 °C/100 mbar to afford 169 g of red crystals (yield 70.3%) with a purity by GC of 97.7%. Recrystallization from hexanes (280 mL) afforded 148.4 g of 99.4% (GC) pure material. Recrystallization of this crop (124 g) from hexanes (600 mL) afforded 87.25 g of 99.6% pure material; mp 88−89 °C (lit.[22] mp 91−92 °C). This crop was dried for 10 h at 50 °C/100 mbar over P_4O_{10} prior its GTP polymerization.

Poly(4-methacryloyloxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl) (GTP-PTMA). An apparatus consisting of a 250 mL three-

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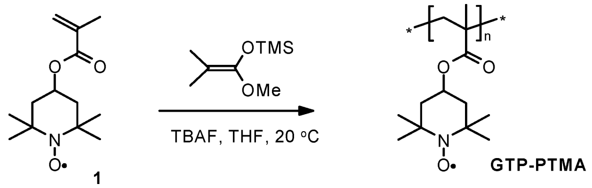
neck flask equipped with a magnetic stirrer, thermometer, rubber septum, and reflux condenser was dried overnight at 105 °C/100 mbar and assembled under argon while still hot. 4-Methacryloyloxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl (12.016 g. 50 mmol) was then charged into the flask under a stream of argon followed by freshly distilled THF (40 mL). 1-Methoxy-2-methyl-1-trimethylsilyloxypropene (0.22 mL, 1 mmol) was then added via syringe. To the very rapidly stirred solution was then added the solution (1 M in THF) of tetrabutylammonium fluoride (0.04 mL, 0.04 mmol). An exothermic reaction occurred immediately, and the temperature rose from 21 to 47 °C within 1 min. The viscous mixture was then stirred at 20 °C for 12 h, and methanol (5 mL) was then added. The mixture was stirred 5 min and then slowly poured onto vigorously stirred hexanes (500 mL). The orange precipitate was filtered off, washed with hexanes, and dried for 90 h at 50 °C/100 mbar to afford 11.5 g of orange powder (yield 95.7%). Anal. Calcd for $C_{13}H_{22}NO_3$ (240.33): C, 64.97; H, 9.23; N, 5.83. Found: C, 64.80; H, 9.23; N, 5.72. GPC (PSt calibration): $M_n = 13\,881$, $M_w = 41\,221$. GPC (Universal calibration): $M_n = 17\,972$, $M_w = 56\,583$. Nitroxide concentration [NO*] (as percent of the theoretically possible amount) by UV spectroscopy (see discussion) in CH_2Cl_2, (1 cm cuvette, against CH_2Cl_2 blank): $c = 5.088$ g L^{-1}, $\lambda_{max} = 461.4$ nm, $A = 0.2420$, [NO*] = 99.45%; $c = 10.09$ g L^{-1}, $\lambda_{max} = 462$ nm, $A = 0.4828$, [NO*] = 101.07%, average [NO*] = 100.26%.

Cross-Linked Poly(4-methacryloyloxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl) (X-GTP-PTMA). The same experimental setup as described for the synthesis of non-cross-linked PTMA was used. 4-Methacryloyloxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl (12.016 g, 50 mmol), 1-methoxy-2-methyl-1-trimethylsilyloxypropene (0.22 mL, 1 mmol), and ethylene glycol dimethacrylate (0.385 g, 1.94 mmol) were dissolved in freshly distilled THF (40 mL). To the very rapidly stirred solution was then added a solution (1 M in THF) of tetrabutylammonium fluoride (0.1 mL, 0.1 mmol). An exothermic reaction occurred immediately, and the temperature rose from 22 to 44 °C within 1 min. The low-viscosity solution transformed into a compact gel approximately 10 s after injection of the fluoride solution. After 1 h at room temperature the gelled reaction mixture was crushed and transferred into ethyl acetate (330 mL) and methanol (1 mL). The red suspension was intensively stirred for 1 h and then filtered. The swollen filter residue was dispersed in ethyl acetate (400 mL), stirred for 1 h, filtered, and then dispersed in dichloromethane (600 mL). The suspension was intensively stirred at room temperature for 10 h and then filtered, washed with dichloromethane (300 mL), and dried at 60 °C/100 mbar for 140 h to afford 8.25 g (yield 69%) of orange powder, completely insoluble in dichloromethane, ethyl acetate, or methanol. The unified filtrates were evaporated under reduced pressure until constant weight to give 3.87 g of an orange resin, consisting according to GPC (PSt calibration) of a small amount (~5%) of **1** and a polymer with $M_n = 7094$, $M_w = 29023$. Nitroxide concentration, [NO*] = 94.3%, in the insoluble polymer was calculated from the mass balance under the assumption that all ethylene glycol dimethacrylate was incorporated into the insoluble polymer.

Electrode Preparation and Electrochemical Measurements. Electrodes were prepared by coating a slurry of the powdered nitroxide polymer, graphite (Timrex KS6, Timcal Ltd.), carbon black (Ensaco 250, Timcal Ltd.), and a binder (PVdF 6020, Solvay SA) dissolved in NMP. The slurry was cast on an Al current collector foil by a doctor-blading method. The electrodes were dried for 12 h at 120 °C in vacuo and then transferred into an argon-filled glove box (H_2O, O_2, N_2 < 5 ppm) for cell assembly without exposure to air. In the dry electrodes the ratio of nitroxide polymer:graphite:carbon black:binder was 27:46:8:19 by weight. Their geometric surface area was 1.33 cm^2. Laboratory test cells with a coin-cell-type design[26] comprising a lithium metal counter and reference electrode and a glass fiber separator soaked with the electrolyte were assembled and closed tightly under argon. $LiPF_6$ (1 M) in EC/DMC 1:1 was used as the electrolyte. Electrochemical tests were performed at 25.0(±0.1) °C on a Batsmal battery measurement system (Astrol Electronic AG). Cyclic voltammetry (CV) was carried out at a sweep rate of 0.1 mV s^{-1}. Galvanostatic cycling experiments were performed between 3.0 and 4.0 V vs Li/Li$^+$.

Scheme 2. GTP Polymerization of 1



Results and Discussion

GTP Polymerization of 1 and Polymer Characterization. The nitroxide monomer 4-methacryloyloxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl (**1**) was prepared in 70% yield via acylation of a commercially available 4-hydroxy-TEMPO with methacryloyl chloride following the slightly modified reported procedure.[22] The GTP polymerization of **1** proceeded rapidly at room temperature in THF, giving an exotherm of about 25 °C (Scheme 2). The GTP-PTMA polymer was obtained in almost quantitative (99.6%) yield. The commercial initiator methoxy-2-methyl-1-trimethylsilyloxy-propene (MTS) was used in conjunction with tetrabutylammonium fluoride (TBFA) catalyst. This system was demonstrated[27] to work excellently for GTP of benzyl methacrylate (BM), affording low-polydispersity (PD = M_w/M_n < 1.1) poly(benzyl methacrylate) up to [BM]/[MTS] ratio as high as 477. In our case polymerization of **1** was performed at [**1**]/[MTS] = 50. This seems to be the upper limit as the trial [**1**]/[MTS] = 100 did not produce any polymer. In principle, GTP of **1** at [**1**]/[MTS] = 50 should afford PTMA with a number-average degree of polymerization of 50, number-average degree molecular weight M_n ≈ 12 000, and low polydispersity PD (PD = M_n/M_w < 1.5). However, gel permeation chromatography using polystyrene standards indicated $M_n = 13\,881$, $M_w = 41\,221$, and PD = 2.97. GTP-PTMA differs quite a lot from polystyrene routinely used for GPC calibration; therefore, the molecular weight distribution measurement was repeated using the universal calibration GPC method. Slightly higher numbers were obtained: $M_n = 17\,972$, $M_w = 56\,583$, PD = 3.15. Clearly, the higher than expected molecular weights M_n and the high polydispersities indicate that GTP of **1** is not truly a living process. This may also explain why the polymerization failed at [**1**]/[MTS] = 100. The GTP-PTMA is completely insoluble in hexane (in contrast to **1**) and can thus be purified by precipitation from it but is soluble in THF or dichloromethane and also in the common Li-ion battery electrolytes such as ethylene carbonate. Our inde-

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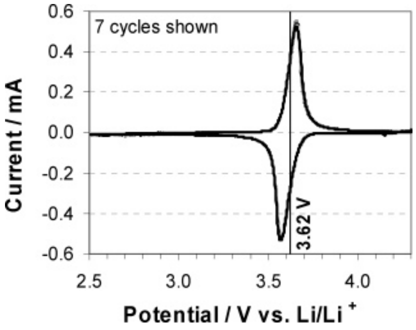

Figure 1. CV of an X-GTP-PTMA composite electrode vs metallic Li at 0.1 mV s^{-1} in EC/DMC 1:1, 1 M $LiPF_6$ electrolyte.

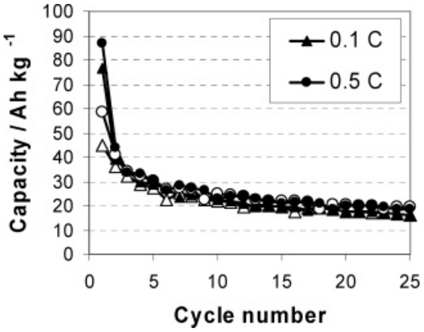

Figure 2. Changes in charge (solid symbols) and discharge (empty symbols) capacities of GPT-PTMA with cycling in half-cells vs metallic Li at 0.1 and 0.5 C rate. Electrolyte: EC/DMC 1:1, 1 M $LiPF_6$.

pendent trials indicated that the PTMA evaluated by others[11] in ORB is also significantly soluble in these solvents despite its higher molecular weight ($M_n = 26\,970$, $M_w = 89\,000$, PD = 3.3). Different methods, e.g., ESR,[18,23] SQUID,[11] iodometry,[28] or UV spectroscopy,[18] were used to determine nitroxide concentration in polymers. We used UV spectroscopy for its simplicity and good accuracy. The long-wavelength (∼460 nm) absorption of dichloromethane solutions of GTP-PTMA at two concentrations (ca. 5 and 10 g L^{-1}) and the molar extinction coefficient of highly pure 4-acetoxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl, determined under same conditions, were used. The result (100.26%) indicates that the theoretical amount of nitroxide groups is present in GTP-PTMA.

The solubility of GTP-PTMA prompted us to try the synthesis of cross-linked polymer. This was achieved by admixture of ∼4 mol % of a bifunctional co-monomer ethylene glycol dimethacrylate (EGM) while leaving the other parameters the same. Smooth and rapid polymerization occurred, and cross-linked polymer was obtained in ∼69% yield. However, polymerization was not complete at this time and a trace amount of **1** and some low molecular weight, non-cross-linked PTMA was obtained. The reason for this is probably rapid solidification of the reaction mixture after catalyst injection. The nitroxide concentration in the cross-linked polymer calculated from the mass balance under the assumption that all EGM was incorporated into it is 94.3%. This nitroxide concentration is still higher than the one achievable by the polymer analogous oxidations (vide supra). The cross-linked polymer (X-GTP-PTMA) is completely insoluble and swells only slightly in THF, dichloromethane, or ethylene carbonate.

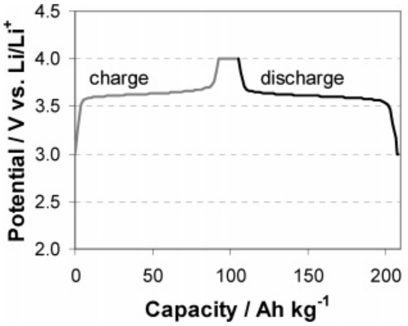

Figure 3. Charge−discharge of X-GTP-PTMA in half-cells vs metallic Li. Electrolyte: EC/DMC 1:1, 1 M $LiPF_6$. The current rate, 1 C, was applied during charging until 4 V; then there was a constant voltage until a current rate of C/20. Discharging at 1 C.

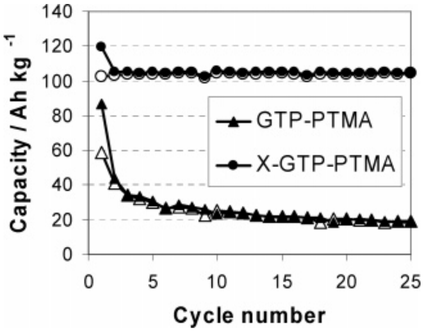

Figure 4. Changes in charge (solid symbols) and discharge (empty symbols) capacities of non-cross-linked and cross-linked PTMA with cycling in half-cells vs metallic Li. Electrolyte: EC/DMC 1:1, 1 M $LiPF_6$.

Organic Radical Battery with the New GTP-PTMA. The suitability of the new GTP-PTMA for application as active material in the positive electrode of organic radical batteries[10,11,14−16] was tested in half-cells vs metallic lithium. Electrodes were prepared from PTMA, conductive carbon, and PVdF binder with an aluminum foil current collector. In cyclic voltammetry (CV) vs metallic Li, a single, sharp, highly reversible redox couple at a potential of ca. 3.6 V (vs Li/Li^+) was identified (Figure 1). This redox potential is very similar to the potential of commonly used oxide materials (e.g., $LiCoO_2$) for the positive electrode in lithium-ion batteries. The traces of seven consecutive CV cycles of an X-GTP-PTMA composite electrode shown in Figure 1 are almost indistinguishable, showing that the redox reaction is very reversible with little or no side reactions and/or deactivating processes. In galvanostatic cycling experiments on composite electrodes with the non-cross-linked GTP-PTMA the initial specific charge was significantly lower than that theoretically calculated (111.5 Ah kg^{-1}) from the nitroxide content. Thus, 45.1 (76.7 Ah kg^{-1}) and 58.7 (86.9 Ah kg^{-1}) Ah kg^{-1} were obtained during discharge (charge) at current rates of 0.1 and 0.5 C, respectively. In the technical literature the nominal charge capacity of a battery or an electrode is called C. Thus, in our case, the current rates of 0.1 and 0.5 C mean that the full theoretical charge capacity of 111.5 Ah kg^{-1} is reached in 10 and 2 h, respectively. We attribute this low capacity and the fact that higher capacities are obtained at higher currents to dissolution of GTP-PTMA in the electrolyte. Dissolution may occur in both the

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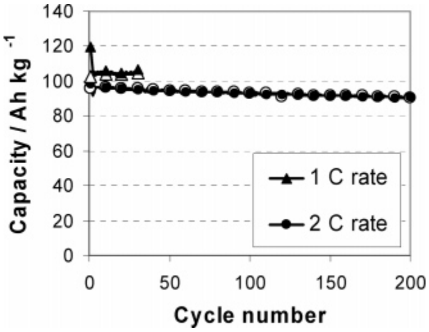

Figure 5. Changes in charge (solid symbols) and discharge (empty symbols) capacities of X-GTP-PTMA with cycling in half-cells vs metallic Li. Electrolyte: EC/DMC 1:1, 1 M $LiPF_6$.

discharged (nitroxide) and/or the charged (oxoammonium) state. Upon cycling between 3.0 and 4.0 V, a rapid fading of the capacity is observed (Figure 2). With the cross-linked X-GTP-PTMA a reversible specific charge of ca. 103 Ah kg^{-1} at current rates up to 1 C could be obtained in galvanostatic cycling experiments between 3.0 and 4.0 V (Figure 3). This value is very close to the value of 105.2 Ah kg^{-1} theoretically calculated for a radical content of 93.4%, indicating very good utilization of the nitroxide. The comparison of the cycling behavior of the two polymers demonstrates the severe impact of solubility on the performance of the ORB (Figure 4). While most of the charge capacity is lost after only a few cycles with the non-cross-linked material, the fading is very low with X-GTP-PTMA and after 25 cycles the initial reversible specific charge is preserved. At a 2 C rate, a slightly lower reversible specific charge of 96.6 Ah kg^{-1} was observed (most probably due to nonoptimized electrode fabrication). Nonetheless, capacity retention with cycling was excellent—after 200 cycles, 95% of the initial reversible charge capacity was achieved (Figure 5).

Conclusions

Group-transfer polymerization has been successfully applied for the synthesis of new GTP-PTMA nitroxide polymer containing the theoretical amount of nitroxide groups. The new GTP-PTMA can be utilized as an active material in the positive electrode of ORB. The solubility of the polymer in the electrolyte plays a crucial role. Soluble materials result in rapid capacity fading of the battery. With the insoluble, cross-linked X-GTP-PTMA, utilization of the NO* groups close to 100% and high cycling stability can be achieved.

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