



Pendant thioether polymer for redox capacitor cathodes

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ABSTRACT

While numerous organic molecules have promising oxidation potentials and theoretical energy densities for use as redox capacitor cathode materials, practical application requires that the molecules remain in contact with the electrode during cycling. In this report, a hybrid molecule was synthesized and electrochemically polymerized to prepare a conducting polymer backbone of poly(3,4-ethylenedioxythiophene) with pendant thioether functionalities as redox (and charge-storing) sites. The choice of an electron deficient aromatic solvent was critical to form a conducting polymer film from the hybrid monomer, as well as to achieve stable charge/discharge cycling of the pendant-type polymer. In nitrobenzene, 86% of the charge was retained after 100 charge/discharge cycles.

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1. Introduction

Inexpensive, light-weight, and abundant organic materials provide a compelling argument for the investigation of molecular-based charge storage. Additionally, organic synthesis enables facile tuning of capacity and oxidation potential in ways that are difficult to match for inorganic systems. Organic-based charge storage can be used in redox capacitor applications if the rate of charge transfer is sufficiently rapid or, alternatively, incorporated into a traditional “rocking-chair” type lithium-ion battery configuration by taking advantage of lithium association with anionic species [1]. While several promising organic systems have been proposed for lithium battery cathodes [2,3] and anodes, [4] and there have been interesting reports of alkylthioether-containing polymers for lithium batteries, [5,6] comparatively few reports discuss cation-forming molecules for redox capacitors.

Previously, our research group has thoroughly investigated a series of thioether-based redox active molecules [7] as potential cathode materials for supercapacitors. We found that 5,5-bis(methylthio)-2,2-bithiophene (BMTbT) provides two chemically and electrochemically reversible one-electron redox processes, and that it does so at sufficiently positive potentials (3.8 and 4.0 V vs. Li/Li⁺, respectively) to achieve an impressive theoretical energy density (~830 Wh kg⁻¹) [7].

While this molecule has a high theoretical capacity, its high solubility in organic solvents necessitates its confinement to the electrode surface for application in redox capacitor cathodes. This

report details an approach to attach BMTbT to a conducting polymer backbone. Poly(3,4-ethylenedioxythiophene) (PEDOT) was used as the polymer due to its chemical stability, high electronic conductivity in the *p*-doped state, and wide window of conductivity, all of which compare favorably to other conducting polymers [8]. Furthermore, PEDOT possesses redox reactions (and thus, additional capacity approaching 0.6 electrons per EDOT monomer [8]) that make it suitable as an electroactive material as well [9]. In the charging process, both BMTbT and PEDOT segments are oxidized and counter anions (e.g., PF₆⁻) transfer into the film from the electrolyte solution to maintain charge neutrality. During discharge, the oxidized film is reduced back to the neutral form and the counter anions return to solution.

In this study, BMTbT-attached EDOT (BMTbT-EDOT) was synthesized, and the electrochemical properties of the polymer film investigated after electrochemical polymerization at a glassy carbon electrode (GCE) in various organic electrolyte solutions. Although preliminary, this work validates the concept of a conducting polymer with pendant, chemically-tunable thioether groups for future applications in electrochemical energy storage.

2. Experimental

3,4-Ethylenedioxythiophene (EDOT) was obtained from Bayer Co. and used as received. High-purity HPLC-grade acetonitrile (MeCN), purchased from Burdick and Jackson, and anhydrous diethyl ether, purchased from Fischer Chemicals, were both stored over 3 Å molecular sieves and purged thoroughly with nitrogen prior to use. Additional chemicals (Aldrich Chemical Co.) were used as received.

BMTbT was synthesized as described previously, [7] then brominated using an equimolar ratio of *N*-bromosuccinimide (NBS) in

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dichloromethane at 0 °C. The extract was dried over MgSO₄ and the solvent removed *in vacuo* to obtain 4-bromo-5,5-bis(methylthio)-2,2-bithiophene. Heteronuclear bond coupling NMR of the crude mixture confirmed that the bromine was at the 3 position interior to the two rings. A tosylated EDOT (Ts-EDOT) was synthesized as described in an accompanying publication [10]. 2.1 g of 4-bromo-5,5-bis(methylthio)-2,2-bithiophene was lithiated with 4.1 mL of 1.6 M butyllithium, converted to the Grignard with 0.7 equivalents of MgBr₂, and added to 1.6 g Ts-EDOT with 0.11 g CuBr·DMS. The pure compound was isolated after flash chromatography on silica using a dichloromethane:hexanes solution (1:2) as eluent ($R_f = 0.4$) to give a colorless oil (1.45 g, 67%). IR (KBr) 2917.8, 2364.3, 2339.2, 1484.9, 1425.1, 1371.1, 1186.0, 1062.6, 1016.3, 759.8 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 6.98 (d, J = 3.7, 1H), 6.93 (s, 1H), 6.91 (d, J = 3.7, 1H), 6.31 (s, 2H), 4.33 (dddd [8] or appqd, J = 7.3, 7.1, 6.5, 2.1, 1H), 4.11 (dd, J = 11.6, 2.1, 1H), 3.88 (dd, J = 11.6, 7.3, 1H), 3.09 (dd, J = 14.7, 7.1, 1H), 2.97 (dd, J = 14.7, 6.5, 1H), 2.50 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 141.67, 141.63, 138.4, 137.0, 136.8, 134.4, 133.5, 133.2, 131.4, 127.1, 100.0, 99.8, 73.6, 67.8, 30.5, 22.1, and 21.7.

Cyclic voltammetric (CV) studies were carried out at room temperature using a potentiostat (Hokuto Denko Co., model HSV-100) in a three-electrode cell configuration with a 3 mm GCE, a Pt coil counter electrode, and a Ag/Ag⁺ reference electrode. The inner solutions employed for the Ag/Ag⁺ reference electrodes were prepared with the same organic solvents as the electrochemical solutions, and calibrated against metallic lithium in the same solution. The working electrode was polished with 0.3 and 0.05 μm alumina slurries, rinsed with distilled water (18 MΩ cm) and acetone, and dried prior to use. All electrolyte solutions were thoroughly pre-purged using purified nitrogen gas before use.

3. Results and discussion

After synthesis, the hybrid monomer was electrochemically polymerized to form electroactive films. The nature of the resulting polymers was strongly solvent-dependent due to reactions with the electrogenerated cations as well as complications arising from the multiple electroactive sites within each monomer.

Fig. 1a presents CVs taken during electrochemical polymerization of BMTbT-EDOT in an acetonitrile (MeCN) solution containing 0.1 M LiClO₄. In the first oxidative potential scan, anodic current peaks were observed at +0.49 V and +0.87 V vs. Ag/Ag⁺, ascribed to the oxidation of the BMTbT moieties. In the reverse scan, corresponding reduction current responses were observed, although with smaller peak currents. Subsequent cycles exhibited an increasing current response over the potential region from -0.1 V to +0.4 V, indicating

that a conducting film was formed. However, the BMTbT redox peaks were missing from the electropolymerized film, and the window of conductivity for the conducting film was narrower than typical for electropolymerized PEDOT films. Thus, oxidation of the hybrid monomer in MeCN resulted in degradation of the BMTbT sites as well as in a decrease in the effective π-conjugation length of the PEDOT backbone, possibly due to reactions of the oxidized BMTbT with MeCN or EDOT radical cations. In order to make functional materials from these monomers, it is imperative to preclude competing reactions and stabilize the cation radical species of the energy-storage unit.

Roncali and coworkers have reported that a polythiophene derivative incorporating tetrathiafulvalene (TTF) can be electropolymerized in nitrobenzene (NB), but not in acetonitrile [11,12]. The effect was proposed to arise from the formation of a donor-acceptor complex of TTF with NB molecules [11], stabilizing the TTF cation radical and thus preventing unfavorable reactions with thiophene radicals during formation of the polythiophene backbone. Electron paramagnetic resonance and time-resolved magnetic resonance measurements have also demonstrated that aromatic solvents prevent dimerization of thioether radical cations [13]. Therefore, it was anticipated that BMTbT-EDOT could also be cleanly electropolymerized in NB, owing to the stabilizing effect of the electron-poor aromatic solvent.

Fig. 1b presents CVs taken during electrochemical polymerization of BMTbT-EDOT in a NB solution containing 0.1 M tetrabutylammonium perchlorate (TBAP) (LiClO₄ is insufficiently soluble in NB). A set of well-defined oxidation and reduction waves, due to the BMTbT moieties, was clearly observed with formal potentials of +0.55 and +0.81 V vs. Ag/Ag⁺ (estimated from the second cycle). The current responses increased with increasing number of potential cycles, indicating that the PEDOT-based conducting polymer film was continuously deposited on the GCE surface. The importance of aromatic solvents was supported by the successful electropolymerization of BMTbT-EDOT in a TBAP/benzonitrile solution. Due to the positive reduction potential of NB, benzonitrile is a more promising solvent for devices.

The electrochemical response of BMTbT-PEDOT film-coated GCEs (prepared in NB) in propylene carbonate (PC) and NB monomer-free electrolyte solutions can be seen in Fig. 2b and d, respectively. For comparison, Fig. 2a and c presents the cyclic voltammetric responses of PEDOT films on the GCE in PC and NB. In both solvents, the polymer exhibited a broad oxidation peak from the PEDOT backbone and two well-defined and distinct sets of peaks corresponding to the surface-confined BMTbT species. Note that the onset of oxidation for the PEDOT backbone is still shifted positive of unsubstituted PEDOT, indicating that the steric bulk of the BMTbT groups shorten the

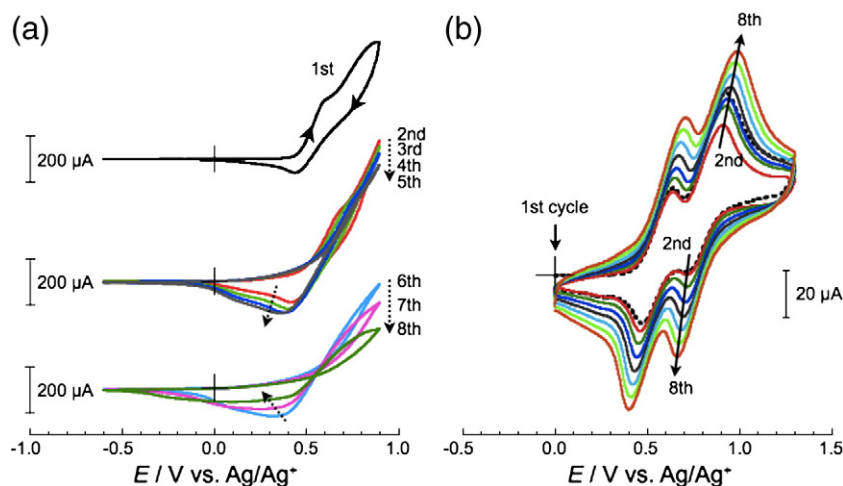


Fig. 1. Electropolymerization of BMTbT-EDOT at 20 mV/s in 10 mM BMTbT-EDOT in (a) 0.1 M LiClO₄/MeCN and (b) 0.1 M TBAP/NB.

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