Novel preparation and electrochemical study of the dithiocarbamate polymer/thiuram disulfide redox system

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Abstract

Four dithiocarbamic polymers have been prepared by reacting a linear poly(ethylenimine) polymer (MW 50 000) with CS_2. Depending on the reaction conditions the resulting polymeric products contained, up to two sulfur atoms per one nitrogen atom ($\sim$40% w/w). These polymers are soluble in dimethylsulfoxide and insoluble in acetonitrile solutions. In both solvents they are electrochemically active, in the latter case as cast film on glassy carbon or platinum electrodes. Specifically, upon oxidation the polymers turn into highly crosslinked (S–S bonds) form. The crosslinked polymer preserves partial electroactivity, although lower than expected due to its rigid structure but, more importantly, it is permeable to solvents and can act as an active matrix for electroactive species from the bulk solution. The switch between anionic and non-ionic (crosslinked) forms of the dithiocarbamic polymer results in transport of the solvent and lithium counterions between the film and the bulk solution.

1. Introduction

Carbamates are the half-amides of carbonic acid. Their sulfur analogs, the dithiocarbamates, are the half-amides of dithiocarbonic acid, and were discovered as a class of chemical compounds early in the history of organo-sulfur chemistry. The most notable property of the dithiocarbamates is their strong metal-binding ability, which is due to the insolubility of the metal salts, with the exception of those of sodium and other alkali and the alkaline earth metals, and to the capacity of the molecules to form chelate complexes stemming from the presence of two donor sulfur atoms. Various dithiocarbamates, notably sodium diethyldithiocarbamate, have found practical application in the field of trace metal analysis because of this characteristic [1–8]. The unique physicochemical and electrochemical properties of dithiocarbamates has prompted investigations into finding other areas of applications, which include: monolayers in chemical recognition [9, 10], molecular wires [11] photoanodes [12], flotation agents [13], electrocatalysts [14–16], homogeneous catalysts [17] engine wear inhibitors [18], corrosion inhibitors [19–21], metal recovery from sea water [22] or wastes [23, 24], ion-selective electrodes [25], biosensors [26], and photochromic materials [27]. Last, but not least, the organosulfur positive electrodes, based on the chemically reversible oxidation of alkali metal thio salts to the corresponding disulfides, offer unique properties in advanced batteries [28–31].

We present in this paper a new dithiocarbamate/thiuram disulfide system based on linear poly(ethylenimine). The equivalent weight of the new material and its theoretical gravimetric capacity density (Table 1), make it attractive as a cathodic material in lithium batteries.
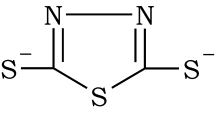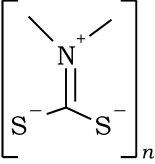
2. Experimental details

2.1. *Materials*

Reagent-grade poly(2-ethyl-2-oxazoline) (Aldrich), N,N'-dimethylethylenediamine (Aldrich), HCl, LiOH, NaOH, CS_2, $LiClO_4$ and solvents methanol, ethanol, anhydrous dimethylsulfoxide (DMSO)(Aldrich), anhydrous acetonitrile (AN) (Merck), Ni phthalocyanine (NiPh) (Aldrich) were used without further purification.

2.2. *Synthesis of linear poly(ethylenimine) (LPEI)*

20 g of poly(2-ethyl-2-oxazoline), MW 50 000 was dissolved in 200 cm^3 of water and then 200 cm^3 of 37% HCl was added. This 5% polymer in 6 M HCl solution was heated at 120 °C for five days under continuous stream of nitrogen. During hydrolysis white LPEI hydrochloride precipitated. The hydrochloride

Table 1. Equivalent weights and theoretical energy densities of representatives $(SRS)_n$ compounds

Monomer	Equivalent weight	Gravimetric capacity density/Ah kg^{-1}	Energy density/ (Wh kg^{-1}) Li/$(SRS)_n$ *
DMcT	74	360	990
TiS$_2$	112	240	600
	118	230	620†

* Gravimetric energy densities calculated by multiplying the corresponding capacity densities by the estimated OCV *vs* a lithium negative electrode, 2.5–2.7 V.

† Reduction potential of thiuram disulfide/dithiocarbamate couple, calculated for a monomeric dithiocarbamate compound, is −0.56 V vs SCE. This corresponds to open-circuit voltage of about 2.7 V for Li/ organosulfur electrochemical couple.

acid was subsequently decanted, the polymer dissolved in 1000 cm^3 of water and again precipitated by adding 2000 cm^3 of acetone. The polymer was dissolved again in water and made alkaline by adding aqueous NaOH portion wise with continuous stirring. The white precipitate was then filtered off and washed with water till neutral. Subsequently it was reprecipitated from ethanol and dried. Semitransparent solid of anhydrous LPEI was obtained in 90% yield: mp 60–61 °C; ^{1}H NMR (CD$_3$OD) shows CH$_2$ peak at $d = 4.28$ ppm and NH peak at $d = 6.4$ ppm. Anal. Calcd. for C$_2$H$_5$N: C, 55.8; H, 11.6; N, 32.6. Found: C, 54.8; H, 11.6; N, 31.3 [32].

2.3. Synthesis of lithium polydithiocarbamate salts

The lithium salts of polymeric dithiocarbamates were prepared by reaction between lithium hydroxide, carbon disulfide and the LPEI [33], they were purified by precipitation from ethanol solution with acetone.

Four various dithiocarbamic polymers, **P**, were prepared by changing LPEI : CS$_2$ ratio in the mixture. Each product contained a different fraction of sulfur, characterized by the following ratios S:N 2; 1.5; 1; 0.5, which correspond to every nitrogen substituted with CS$_2$, every second (on average), every fourth, and every eight, respectively.

The elemental analysis was as follows:

P1 Anal. Calcd. for C$_3$H$_4$NS$_2$: C, 30.5; H, 3.4; N, 11.9; S, 54.2.

Found : C, 25.7; H, 4.8; N, 9.1; S, 40.0.
$S : N = 1.92$

P2 Anal. Calcd. for C$_5$H$_8$N$_2$S$_2$: C, 37.5; H, 5.0; N, 17.5; S, 40.0.

Found : C, 33.9; H, 6.5; N, 9.2; S, 34.4.
$S : N = 1.64$

P3 Anal. Calcd. for C$_9$H$_{16}$N$_4$S$_2$: C, 44.3; H, 6.6; N, 23.0; S, 26.2

Found : C, 34.6; H, 6.3; N, 12.9; S, 31.0.
$S : N = 1.06$

P4 Anal. Calcd. for C$_{17}$H$_{32}$N$_8$S$_2$: C, 50.0; H, 7.8; N, 27.2; S, 15.5.

Found : C, 37.8; H, 6.5; N, 18.0; S, 23.3
$S : N = 0.57$

2.4. Apparatus and procedures

Glassy carbon (GC) or Pt discs (0.08 cm^2), set in a Teflon tube were used as working electrodes. Fresh electrode surfaces were produced by polishing them with a diamond paste. Cast films were produced by applying a drop of a stock solution of the polymer in DMSO and allowing the solvent to evaporate. A one-compartment electrochemical cell containing the working electrode, a Pt mesh as auxiliary electrode, and an Ag/AgCl reference electrode was assembled and used in an argon atmosphere at ambient temperature. The dithiocarbamates are quite unstable in acidic aqueous solutions where they undergo protonation with subsequent decomposition into carbon disulfide and protonated amine. In non-aqueous solutions they are much more stable [34], therefore the electrochemical characterization of the polymeric dithiocarbamates was carried out in contact with 0.1 M LiClO$_4$ solutions in DMSO and AN. All polymers are insoluble in the latter solvent, therefore they were used for the experiments with the cast films. Cyclic voltammograms curves were obtained with a PAR 170/270 system. All potentials are presented with respect to an aqueous, saturated calomel electrode (SCE).

The electrochemical quartz crystal microbalance (EQCM) setup consisted of a quartz crystal 5 MHz 'AT-cut' (13 mm dia.) covered with a gold film (100 nm thick) with an area of 0.22 cm^2. A detailed description of the setup was reported earlier [35].

3. Results

3.1. Polymers in solution

Cyclic voltammograms of the polymers dissolved in a 0.1 M LiClO$_4$/DMSO solution are shown in Figure 1. Initially the potential was driven in the direction of the positive potentials where a prewave can be seen at
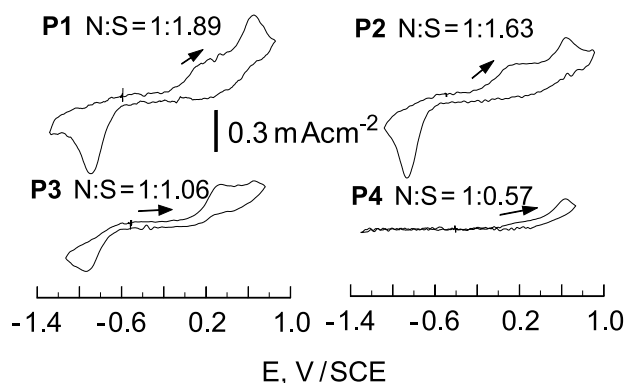
Fig. 1. Cyclic voltammograms of the dithiocarbamic polymers (50 mM) in 0.1 M LiClO$_4$/DMSO solution at scan rate 0.1 V s^{-1} at the glassy carbon electrode.

potentials ranging from 0.1 to 0.3 V followed by a peak at about 0.7 V. The position of these waves does not vary with the sulfur content, whereas their heights decrease when the sulfur content is lower. The process suggested by this experiment is the oxidation of the dithiocarbamate ions to free radicals (Equation 1) followed by their rapid coupling (Equation 2) to thiuram disulfide according to an overall scheme: [36–40].

$$R(S)S^- \rightarrow R(S)S^{\cdot} + e^- \tag{1}$$

$$2\,R(S)S^{\cdot} \rightarrow R(S)S - S(S)R \tag{2}$$
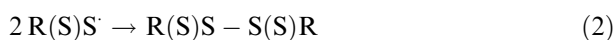
This process should result in the formation of inter- and/or intramolecular crosslinking similar to that occurring in nature during protein folding. The rate of the electrodic reaction is not directly related to the concentration of the active groups in the polymeric chain, because entangling of these chains makes some of the sulfur groups unavailable for the oxidation [41]. Moreover, crosslinking reduces the polymer flexibility and mobility. As a result some of the free radical groups may not find a partner for coupling, instead they can make covalent bonding with the electrode surface or oxidize the incoming dithiocarbamate anions from the bulk solution. These processes should lower the activation energy of the process, thus account for the observed prewave. The dependence of the oxidation rate on the distance between the active groups in the reacting compound was reported earlier for thiols [42–44].

Upon cathodic polarization the sulfur–sulfur or the GC–S bonds are cleaved at relatively high negative potentials ranging from −0.6 to −1.2 V. The most striking observation (i.e., the large peak separation from the anodic peak) implies slow electrode reaction rates. According to several authors the electroreduction of RS–SR proceeds at reasonable rates if both sulfur atoms interact with the electrode surface, as observed with mercury [45–48]. For steric reasons this is unlikely, because the most stable configuration of disulfides is that in which the non-bonding orbitals are at 90° to each other, thus minimizing electron repulsion. It is most

likely that interaction with the electrode surface takes place via one sulfur atom at a time, inhibiting the electron transfer. Although the oxidized polymer can be reduced to its initial form, some of the S–S bonds do not break and the charge consumed during oxidation (Q_a) is greater compared to the reduction charge (Q_c). In the case of the polymer containing approximately 1 sulfur per 2 nitrogen atoms (P4) there are no redox peaks in the voltammogram. This indicates that below a certain limit of the sulfur content the polymer becomes inactive.

The crosslinking of the reacting polymer and ensuing loss of the anionic character inevitably leads to decrease in its solubility and subsequent deposition at the electrode. An important question arises if the resulting film conducts charge (does not passivate the surface) or/and is permeable to the solvent. On prolonged anodic polarization or multiple cycling a yellow film, also insoluble in water, deposits at the electrode. Chemical oxidation of the dithiocarbamic polymers also leads to products, which are insoluble in these solvents. We have carried out X-ray Photoelectron Spectroscopy (XPS) analysis of the P polymers and the anodic deposits to obtain better insight into the chemical changes in the polymers owing to their oxidation. From the intensity ratio I_{s2p}/I_{N1s} and according to XPS relative intensities [49] it was possible to calculate the ratio between the number of sulfur atoms and nitrogen atoms present on the surface. The XPS analysis performed before the electrochemical treatment showed, that the I_{s2p}/I_{N1s} ratio, related to c_S to c_N ratio, agrees with results obtained by the elemental analysis. After anodic deposition in dry DMSO these ratios remained unchanged. However, when the studied system contained traces of water then the ratio c_S/c_N in the film was always lower. For example, in the case of P1 instead of ∼2 it ranged from 1.25 to 1.32. Similar depletion in sulfur content for the oxidation of methionine and cysteine was observed by Reynaud and coworkers [50]. The depletion in sulfur atoms with respect to nitrogen atoms (as indicated by the ratio c_S/c_N), observed in our experiments, strongly suggests a break in the molecule at a C–S bond during oxidation. Moreover, the XPS results reveal the presence of highly oxidized sulfur, presumably owing to reaction with water [50–52]

$$RS^{\cdot} + 3\,H_2O \rightarrow RSO_3H + 5\,e^- + 5\,H^+ \tag{3}$$
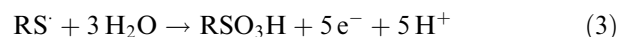
The electrode covered with the crosslinked polymer (obtained from dry DMSO) showed no electrochemical activity in aqueous or DMSO solutions containing only supporting electrolyte (0.1 M LiClO$_4$). However, the film does not passivate the electrode as shows Figure 2. Upon prolonged cycling the anodic current, notably the prewave at 0.1–0.3 V, and the cathodic peak at about −0.9 V tend to increase significantly at each scan. Moreover, the experiment in which the scan was stopped at 0.9 V for 2 h showed three large cathodic peaks −0.9, −1.3 and −1.6 V.

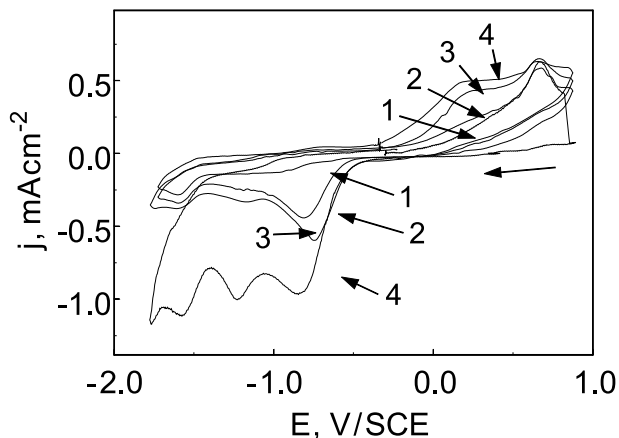It is well known that the electrode material may influence the kinetics (or mechanism) of the S–S bond

Fig. 2. Cyclic voltammograms of 50 mM of **P1** in 0.1 M LiClO₄/ DMSO solution at scan rate 0.3 V s⁻¹ at the glassy carbon electrode. Key: (1) 1st scan; (2) 50th scan; (3) 200th scan; (4) stop at 0.9 V for 2 h.

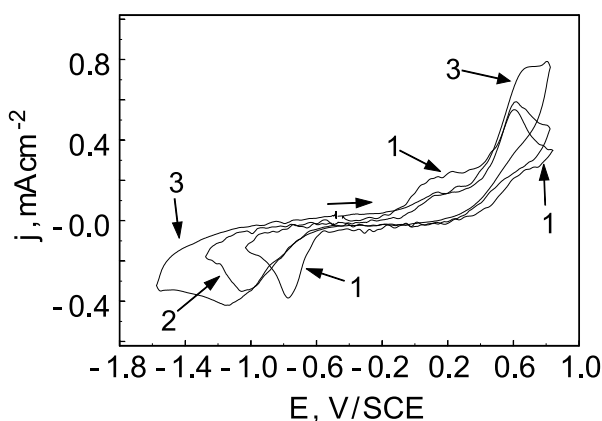Fig. 3. Cyclic voltammograms of 50 mM of **P1** in 0.1 M LiClO₄/ DMSO solution at scan rate 0.3 V s⁻¹ at: (1) glassy carbon; (2) platinum; (3) acetylene black pellet containing 1% w/w Ni phthalocyanine.

reduction in aliphatic or aromatic disulfides [29, 53, 54]. This effect, observed in various solvents, was attributed to the interaction (adsorption) of the reagents with the electrode surface [29]. Cyclic voltammograms of the polymer dithiocarbamates at different electrode materials are shown in Figure 3. The observation of the strong positive displacement of the cathodic peak potentials (about 250 mV), as opposed to the slight shift of the anodic peak potentials (about −10 mV), implies the variation of the desorption energy due to the change of the molecule-substrate interaction. The third curve in this figure depicts the redox processes at the acetylene black pellet containing Ni phthalocyanine. This catalyst accelerates the oxidation reaction; however, in the case of the reduction processes we see an inhibition effect. The observed negative shift of the reduction peak indicates the same reaction mechanism as that at Pt, but the heterogeneous rate constant is lower. It seems that the inhibiting effect is due to interaction of only one sulfur atom at a time with a metal center in the phthalocyanine.

3.2. Cast films

An important question of the counterion transport through an electrode/solution interface was addressed by the slow cyclic voltammetry experiments with simultaneous recording of the frequency change of the quartz crystal electrode. The gold surface of this electrode was covered with the cast film and immersed in a 0.1 M LiClO₄/An solution, in which the polymers and their oxidized forms (crosslinked) are insoluble. The obtained voltammograms show a very broad anodic peak at ∼0.6 V and relatively narrow, asymmetric reduction peak at about −0.6 V (Figure 4). In opposition to the results with the polymers in solution, the electroactivity of the cast polymer steadily dies out during consecutive sweeps. Our studies show that 50 to 80% of the theoretical number of the active centers in the film are oxidized during the first few sweeps. These active sites cannot be recovered during reversal sweep, and therefore the current steadily drops (curve 2).

The plots of frequency against charge are shown in Figures 5 and 6 for the first and tenth sweep, respectively. During the first sweep the frequency increase was observed in the potential range corresponding to the oxidation current. Initial decrease in frequency is attributed to the film soaking. The slope of the linear part of the curve, between 4 and 6 mC cm⁻², allows calculating the apparent molecular weight (MW) of
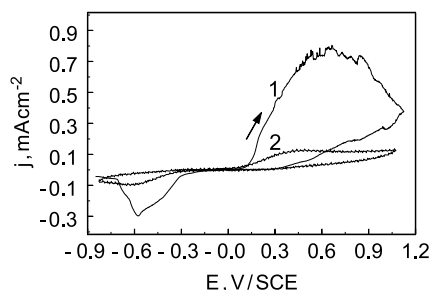

Fig. 4. Cyclic voltammograms of the cast film of **P1** in 0.1 M LiClO₄/ AN solution at scan rate 0.05 V s⁻¹: (1) 1st run; (2) 10th run.
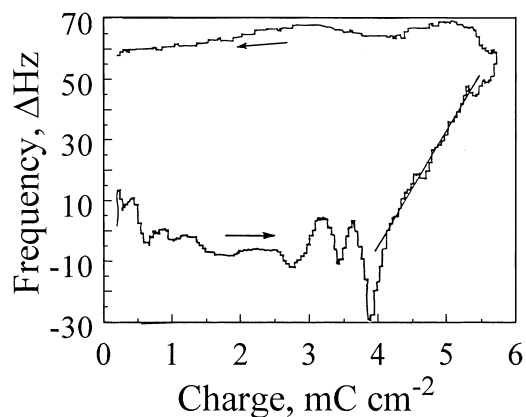

Fig. 5. EQCM frequency plot recorded simultaneously with the voltammogram 1 in Figure 4.
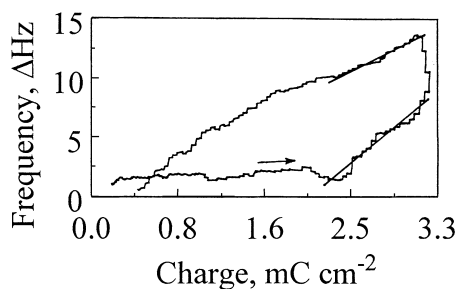
Fig. 6. EQCM frequency plot recorded simultaneously with the voltammogram 2 in Figure 4.

species, which leave the film during oxidation. The calculation yield MW = 73 g mol^{-1}. On backward polarization the frequency practically does not change, even at the potential corresponding to the reduction current. In other words, the final mass of the electrode does not return to the initial value. As the voltammograms show, the activity of the cast film dramatically decreases on consecutive sweeps. Accordingly, the charge and the frequency changes are much lower on reverse polarization. In this case, for the potential range of the reduction process, the frequency linearly decreases until it reaches the starting value. The calculated MW is 17 and 9 g mol^{-1} for the oxidation and reduction processes, respectively. The MW values can be interpreted as being caused by Li ions and the solvent egress from the film. During oxidation S–S bonds are formed and the charge of the polymer mer changes from −1 to 0. Therefore Li ions have to leave the film to preserve its electroneutrality. Accordingly, MW = 73 g mol^{-1} could correspond to egress of 1 Li$^+$ + 1.5 AN. These acetonitrile molecules slowly leave the film during consecutive sweeps, and do not reenter it. Therefore, we observe the lower MWs corresponding to egress of 1 Li$^+$ + 0.2 AN and ingress of Li$^+$ on reduction (MW = 9 g mol^{-1}).

4. Conclusions

(i) The linear poly(ethylenimine) polymer has been substituted with dithiocarbamic groups. The resulting polymeric products contained up to two sulfur atoms per one nitrogen atom (approx. 40% w/w), depending on the reaction conditions.

(ii) The dithiocarbamic polymers are soluble in aqueous and DMSO solutions, although in the former solvent they are unstable.

(iii) The polymers can be oxidized electrochemically in DMSO and AN solutions. During this process the –S—S– crosslinking bonds are formed. The resulting non-ionic polymers are insoluble in DMSO and accumulate on the electrode surface. The film preserves only partial electroactivity upon reduction, probably due to rigidity of the polymer structure. However, the film is permeable to solvent and behaves as a conductive matrix towards the

electroactive species incoming from the bulk solution.

(iv) The switch between anionic and non-ionic (crosslinked) forms of the dithiocarbamic polymers results in transport of the solvent and lithium counterions between the film and the bulk solution.

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