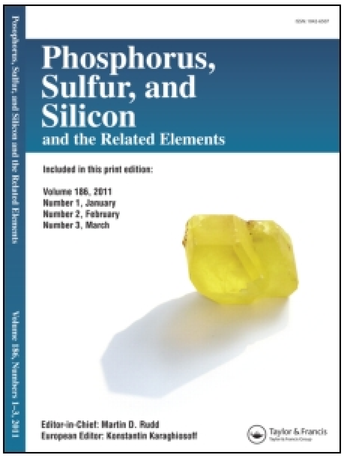

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A Polysulfide Based on Bis(thien-2-yl)sulfide: Synthesis and Testing as an Active Cathode Material

Galina F. Myachina[a]; Svetlana A. Korzhova[a]; Lyubov K. Papernaya[a]; Eleonora N. Deryagina[a]; Terje A. Skotheim[b]; Boris A. Trofimov[a]
[a] A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, Irkutsk, Russia [b] Moltech Corporation, Tucson, USA

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Galina F. Myachina
Svetlana A. Korzhova
Lyubov K. Papernaya
Eleonora N. Deryagina
A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch
of the Russian Academy of Sciences, Irkutsk, Russia

Terje A. Skotheim
Moltech Corporation, Tucson, USA

Boris A. Trofimov
A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch
of the Russian Academy of Sciences, Irkutsk, Russia

A reaction of the polycondensation product of bis(thien-2-yl)sulfide and formaldehyde with elemental sulfur affords a polymer containing polysulfide moieties (S-content = 67.2%). When used as active cathode material for model lithium rechargeable cells, the polymer shows the discharge capacity of 620 mA·h·g^{-1} *at the first cycle.*

Keywords Bis(thien-2-yl)sulfide; cathode materials; elemental sulfur; lithium battery; polycondensation

INTRODUCTION

Elemental sulfur is known to possess a high electrochemical activity (theoretical capacity 1676 mA·h·g^{-1}) and is widely studied as the active cathode material for lithium rechargeable batteries.[1–4] In practice, there still exists a number of so-far unsolved problems that worsen the properties of lithium-sulfur batteries, such as an incomplete involvement of sulfur in redox processes, their insufficient reversibility, etc. Therefore, a series of investigations on the synthesis of new high sulfur

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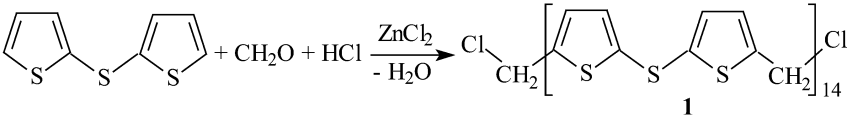
Address correspondence to Boris A. Trofimov, A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, 1 Favorsky Street, Irkutsk 664033, Russia. E-mail: myachina@irioch.irk.ru

content polymers containing redox-active S—S bonds based on polyethylene, polyacetylene, polystyrene, and poly(5-vinyl-2-methylpyridine), which proved to be promising active cathode materials for lithium batteries, has been carried out.[5–11]

This work deals with the synthesis and investigations of electrochemical properties of new high sulfur content polymers prepared from bis(thien-2-yl)sulfide and elemental sulfur. The choice of the reagents is based on the high electrochemical activity of thiophene series compounds.[12]

RESULTS AND DISCUSSION

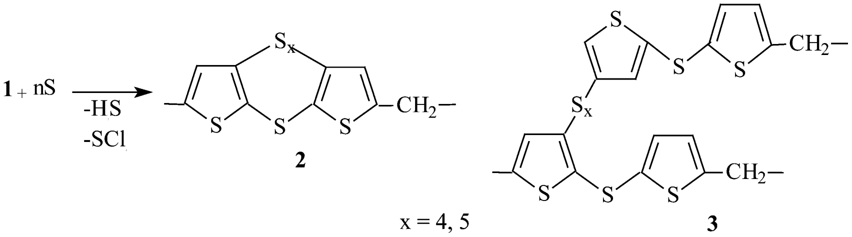
Chloromethylation of bis(thien-2-yl)sulfide with formaldehyde in hydrochloric acid in the presence of $ZnCl_2$ at −10°C results in rapid polycondensation to form poly(2-thienylthio-2-thienyl-2-methylene) **1** (Scheme 1).



SCHEME 1

The structure of the polymer **1** follows from its elemental analysis and IR spectrum. The latter shows the following absorption bands, cm^{-1}: 3080 (νCH, thiophene), 2916, 2855 (νCH_2), 1421, 1206, 1208, 1056 (δCH, CH_2), 977 (δCH, thiophene), 796, 699 (C-S), and 419 (C-Cl). The molecular mass of the polymer estimated from the terminal chlorine atom content is around 3100, while the sulfur content is 42.1%.[13]

Further sulfurization of polymer **1** was performed by melting it together with elemental sulfur at 135–140°C and washing the reaction product from unreacted sulfur with carbon disulfide to give a new higher sulfur content polymer (S-content = 67.2%) (Scheme 2). According to



SCHEME 2

the elemental analysis and the IR spectrum, the polymer may consist of macrocyclic units **2** and cross-lineal structures **3**.

Polymers **1** and (**2** + **3**) possess electroconductivity of $1.4 \cdot 10^{-11}$ and $6.4 \cdot 10^{-12}$ S·cm^{-1}, respectively. In the IR spectrum of the polymer (**2** + **3**), stretching of the S—S bonds are observed at 489 and 466 cm^{-1}, while the stretching of the C—Cl bond at 419 cm^{-1} disappears. The presence of polysulfide chains in the polymer (**2** + **3**) is also confirmed by cyclic voltammetry. Cyclic voltammograms of the initial polymer **1** contain no distinct cathode and anode maxima (Figure 1). Analogous cycling of the polymer (**2** + **3**)-based cathodes shows two intense cathode maxima at 2.3 and 2.0 V and one anode maximum at 2.6 V (Figure 2). Such location of the maxima as well as the two-stage character of the polymer reduction and subsequent single-stage oxidation of the reaction products at 2.6 V are characteristic features of both elemental sulfur and polysulfide chains.[4,6–10] Charge and discharge capacities of the polymer (**2** + **3**) are approximately 50 times higher than those of the polymer **1**.

Taking into account high redox activity of polymer (**2** + **3**), we have studied the cycling of cathodes based therein in model button lithium cells in the potential range of 1.25–2.80 V (Figure 3). The cathodes show

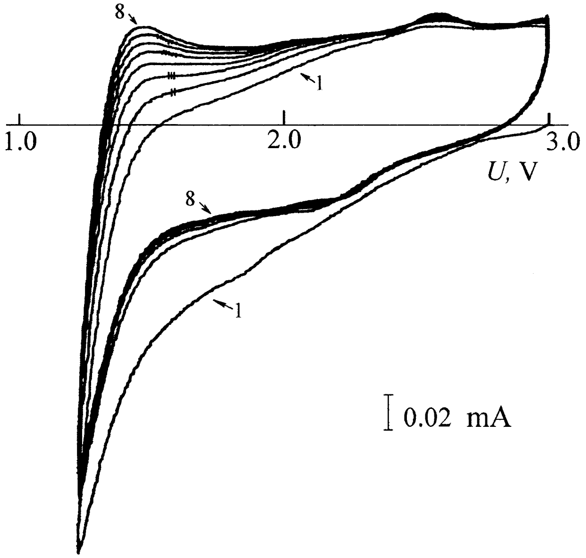


FIGURE 1 Cyclic voltammogram of the polymer **1** for the first to the eighth cycles (*vs*. Li/Li$^+$). Potential scan rate is 1 mV/s. Cycle numbers are indicated as numerals.

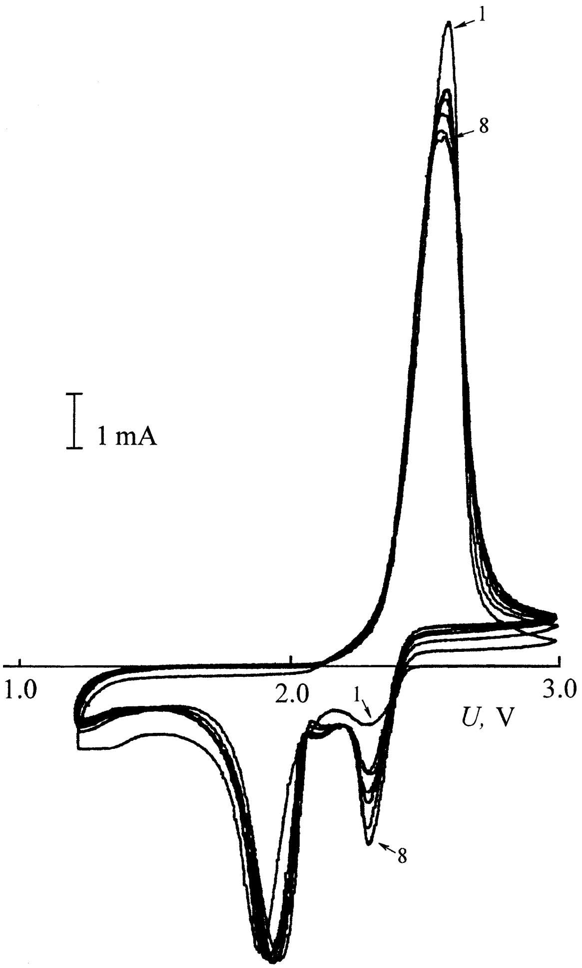


FIGURE 2 Cyclic voltammogram of the polymer (**2** + **3**) for the first to the eighth cycles (*vs.* Li/Li$^+$). Potential scan rate is 1 mV/s. Cycle numbers are indicated as numerals.

a high discharge capacity for the first cycle (622 mA·h·g^{-1}). A drastic drop of the capacity on the second and third cycles is explained by the worsening of the redox kinetics due to the formation of lithium mono- and disulfides in the second stage of the polymer reduction. These sulfides are insoluble or poorly soluble in the electrolyte and thus are difficult to oxidize. Moreover, they partly remain as suspensions in the electrolyte and partly precipitate on the surface of electrodes, thus

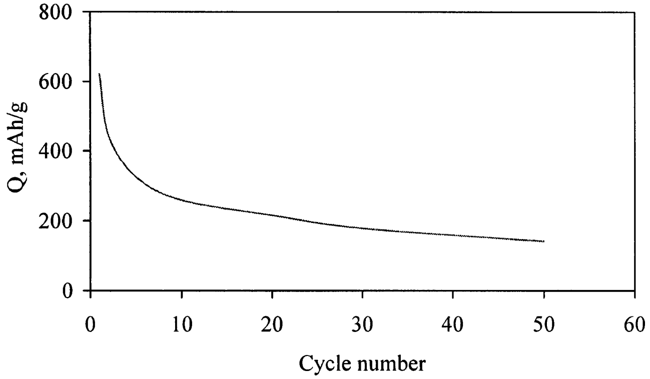


FIGURE 3 Discharge capacity (Q) *vs* cycle number for cathode based on the polymer (**2** + **3**) (a model lithium cell). Current density −0.25 mA/cm^2.

blocking their activity. The capacity stabilizes after the tenth cycle (Figure 3). The cathode capacity on the fiftieth cycle is 32% of the capacity on the second one.

Chronopotentiometric curves of the polymeric cathode (Figure 4) illustrate stable cycling in the potential range of 1.25–2.8 V. The discharge curves of the polymeric cathode (Figure 5) show two plateaus indicating that the process of electrochemical reduction of the polymer is a two-stage one. The plateaus' potentials (2.3 and 2.0 V) correspond to the location of cathode maxima on the polymer cyclic voltammograms. Specific discharge capacity on the second plateau is significantly higher than that on the first one for both the first and subsequent cycles, in particular, for the tenth cycle (Figure 5).

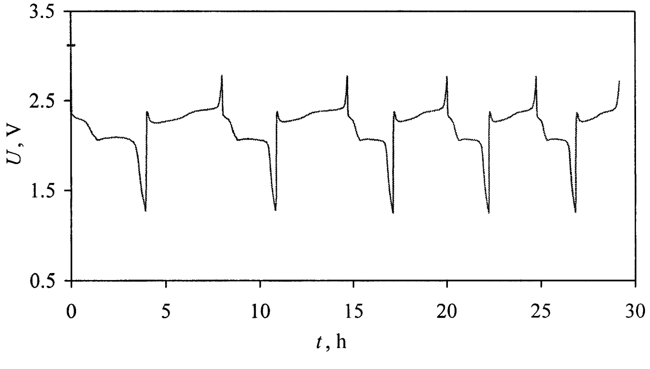


FIGURE 4 Cyclic chronopotentiogram of a cathode based on the polymer (**2** + **3**) for the first to the fifth cycles. Current density −0.25 mA/cm^2.

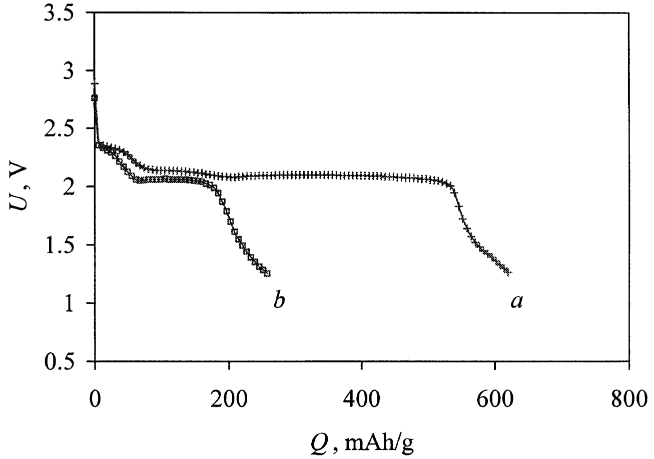


FIGURE 5 Chronopotentiometric discharge curves of the first (*a*) and tenth (*b*) cycles for cathodes based on the polymer (**2** + **3**) (model lithium cells). Current density −0.25 mA/cm^2.

Thus, we have shown a straightforward and simple route for the synthesis of new high sulfur content polymers by the sulfurization of bis(thien-2-yl)sulfide-based polymer with elemental sulfur. These polymers are prospective for the application as active components of the cathode for rechargeable lithium batteries.

EXPERIMENTAL

In electrochemical experiments, we used thin-layer two-electrode cells of a button type with an aluminum cathode (1.5 cm^2) covered with carbon and a composite of the polymer (**2** + **3**) and activated coal and polyethylene oxide in 65:30:5 wt% ratio. Porous polypropylene was used as a separator. The electrolyte used was 2 M solution of $(CF_3SO_2)_2NLi$ in a 1:1 mixture of 1,2-dimethoxyethane and 1,3-dioxolane. Cyclic voltammograms were taken at the potential scan rate of 1 mV·s^{-1} in the potential range of 1.25–3.00 V on Potentiostat PI-50-1. The cycling of cells was carried out on a bench testing unit for chemical power sources in a potential range of 1.25–2.8 V using a current density of 0.25 mA·cm^{-2}.

IR spectra were recorded on a IFS25, Sample Scant: 250 instrument (KBr or film).

Chloromethylation of Bis(2-thienyl)sulfide

A mixture of bis(thien-2-yl)sulfide (9.8 g, 0.05 mol), formaldehyde 40% solution (3.5 mL), concentrated HCl (5.3 mL), and $ZnCl_2$ (0.3 g) was cooled to -10°C, and hydrogen chloride was bubbled for 5 h upon stirring. The resultant solid mass of green color was filtered and washed with hot methanol and water (until a neutral reaction). Filtering and drying gave a grayish-pink powder polymer (9.7 g). Found, %: C, 50.00; H, 3.70; Cl, 2.28; S, 42.13. Ash was not found.

The Synthesis of the Polymer (2 + 3)

Powdered polymer **1** (1 g) was added to the melt of elemental sulfur (3 g) in small portions at 135–140°C upon vigorous stirring. The melt thickened and transformed to a black solid (3.83 g). Found, %: C, 9.43, H, 0.50, S, 86.28.

The product (1.3 g) was washed with carbon disulfide to remove unreacted sulfur (up to constant weight) to give 0.56 g of the polymer (**2** + **3**). Found, %: C, 26.95; H, 2.15; S, 67.24; Cl, 0.60.

REFERENCES

[1] E. Peled, A. Gorenshtein, M. Segal, and Y. Sternberg, *J. Power Sources*, **26,** 269 (1989).
[2] D. Marmorstein, T. H. Yu, K. A. Striebel, F. R. McLarnon, J. Hou, and E. J. Cairns, *J. Power Sources*, **89,** 219 (2000).
[3] V. S. Kolosnitsin, E. V. Karaseva, N. A. Amineva, and G. A. Batyrshina, *Electrochemistry*, **38,** 371 (2002).
[4] B. H. Jeon, J. H. Yeon, K. M. Kim, and I. J. Chung, *J. Power Sources*, **109,** 89 (2002).
[5] B. A. Trofimov, T. A. Skotheim, L. V. Andriyankova, A. G. Mal'kina, G. F. Myachina, S. A. Korzhova, T. I. Vakul'skaya, I. P. Kovalev, and Yu. V. Mikhailik, *Izv. Akad. Nauk, Ser. Khim.*, 462 (1999).
[6] B. A. Trofimov, T. A. Skotheim, A. G. Mal'kina, L. V. Sokolyanskaya, G. F. Myachina, S. A. Korzhova, T. I. Vakul'skaya, I. P. Kovalev, Yu. V. Mikhailik, and L. I. Boguslavsky, *Izv. Akad. Nauk, Ser. Khim.*, 872 (1999).
[7] B. A. Trofimov, T. A. Skotheim, A. G. Mal'kina, L. V. Sokolyanskaya, G. F. Myachina, S. A. Korzhova, E. S. Stoyanov, and I. P. Kovalev, *Izv. Akad. Nauk, Ser. Khim.*, 865 (2000).
[8] B. A. Trofimov, T. A. Skotheim, A. G. Mal'kina, L. V. Sokolyanskaya, G. F. Myachina, S. A. Korzhova, T. I. Vakul'skaya, L. V. Klyba, E. S. Stoyanov, I. P. Kovalev, and Yu. V. Mikhailik, *Izv. Akad. Nauk, Ser. Khim.*, 245 (2001).
[9] B. A. Trofimov, A. G. Mal'kina, L. V. Sokolyanskaya, V. V. Nosyreva, G. F. Myachina, S. A. Korzhova, I. V. Rodionova, T. I. Vakul'skaya, L. V. Klyba, E. S. Stoyanov, T. A. Skotheim, and Yu. V. Mikhailik, *Izv. Akad. Nauk, Ser. Khim.*, 269 (2002).
[10] B. A. Trofimov, A. G. Mal'kina, L. V. Sokolyanskaya, V. V. Nosyreva, G. F. Myachina, S. A. Korzhova, I. V. Rodionova, T. I. Vakul'skaya, T. A. Skotheim, and Yu. V. Mikhailik, *Elektrokhimicheskaya Energetika*, **1,** 26 (2001).
[11] B. A. Trofimov, *Sulfur Reports,* **24,** 283 (2003).
[12] J. Roncaly, *Chem. Rev.,* **92,** 711 (1992).
[13] L. K. Papernaya, E. N. Sukhomazova, E. P. Levanova, G. F. Myachina, and E. N. Deryagina, *Zh. Org. Khim.,* **38,** 1548 (2002).