

NEWS

OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN

SERIES CHEMISTRY AND TECHNOLOGY

ISSN 2224-5286

Volume 5, Number 425 (2017), 31 – 38

UDC 541.135

**G.K. Bishimbayeva¹, B.A. Trofimov², G.F. Prozorova², D.S. Zhumabayeva¹,
A.G. Malkina², S.A. Korzhova², A.M. Nalibayeva¹, U.O. Kydyrbayeva¹**¹D.V. Sokolskiy Institute of Fuel, Catalysis & Electrochemistry, Almaty, Kazakhstan;²A.E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, Irkutsk, Russia

E-mail: g.bishimbayeva@ifce.kz

**ORIGINAL TECHNOLOGY OF SYNTHESIS POLYMER SULFUR
COMPOSITES ON THE BASE OF BY-PRODUCT SULFUR
OF THE PETROLEUM DESULFURIZATION**

Abstract. Technological methods for obtaining of polymer sulfur composites by redox copolymerization on the basis of by-product sulfur with electrically conductive copolymers (pyrrole, aniline) have been developed. The conditions for carrying out the reaction are established, which allow varying the sulfur content of the obtained materials. The electrochemical activity and efficiency of the use of sulfurous polymeric compositions of aniline and pyrrole as active electrode materials of lithium-sulfur batteries have been studied. It was established by physical-chemical methods that the obtained high-sulfur polymers possess electroconductive properties, oxidation-reduction activity and are promising for the development of active cathode materials of modern rechargeable lithium current sources.

The developed technology of sol-gel synthesis of copolymers of aniline and pyrrole based on nanoscale sulfur by the method of redox copolymerization to produce electrically conductive high-sulfur polymers can be recommended for use in the creation of domestic production of cathode materials for lithium-sulfur batteries

Key words: polymer sulfur composites, polypyrrole, polyaniline, cathode materials, lithium-sulfur batteries.

Introduction. The annual growth in hydrocarbon production in Kazakhstan and the environmental requirements for the quality of petroleum products resulted in the accumulation of more than 10 million tons of sulfur at the sulfur storage site as it is a large-scale by-product of oil and gas processing. In this regard, there is an excess of world production of sulfur - the product of desulfurization of hydrocarbon raw materials over consumption. The inevitable consequence of this is the technogenic impact on the objects of the environment. The actual task is the development of modern utilization ways into new polymeric sulfur composites, possessing a number of valuable properties, which will increase the world demand for elemental sulfur.

In recent decades, special development has been given to a new direction in polymer sulfur technology: the development of electroconductive, electrochemically active polymeric sulfur composites for their use in modern lithium-sulfur batteries. Prospectivity of lithium-sulfur batteries is due to high values of their theoretical specific energy (2500 Wh / kg), low cost and environmental safety. In terms of their energy intensity, they outperform other chemical sources of current 2.5-5 times. Using rechargeable lithium cells allows to solve a purely economic problem, because their use is much cheaper than the use of relatively expensive elements of a one-time action. In this regard, particular interest is due to the peculiarities of the properties of polymeric sulfur [3-10]. Lithium-sulfur batteries were first shown to the world public by Sion Power in 2004. Even then, such batteries were much more efficient than current lithium-ion batteries. The main distinguishing features of these drives can be called a less expensive production, as well as more than double the capacity in comparison with analogues. This type of battery is called Li/S.

Despite intensive research in this field, up to the present there was practically no information on synthesis and properties high-sulfur polycondensed heterocyclic systems with oxidation-reduction

functions (S-S, S-H and C = S), which have redox activity and are promising as active cathode materials of rechargeable lithium current sources. In connection with this, the synthesis and study of new high-sulfur materials that combine in the molecule condensed aromatic heterocyclic fragments and redox-active functions are relevant.

There are various methods for obtaining polymeric sulfur [3-13], including the direct sulphuration of industrial polymers [4,7], the reverse vulcanization method [14]. Polymer sulfur with improved electrically conductive and redox activity properties for use as cathode materials of lithium-sulfur batteries is formed by using the initial nanostructured colloidal sulfur [15].

Conducting polymers such as polyaniline (PANI), polypyrrole (PPy), are very interesting materials for using in Li/S batteries. Polymer modification of the carbon surface facilitates a more complete reaction by providing a chemical gradient that retards diffusion of the polysulfides into the electrolyte. Reversible capacities up to 1320 mAh/g are attained with no shuttle phenomenon on the first cycle, indicating the shuttle mechanism is fully suppressed. This polymer modified composite clearly exhibits better morphological control than the unmodified composite during cycling [16]. Therefore, the development of new methods for the preparation of the sulfur-polypyrrole and sulfur-polyaniline composite by the method of redox copolymerization of elemental sulfur with aniline / pyrrole is actual.

Materials and methods. Used reagents: Petroleum-based sulfur was supported by TengizChevrOil LLP - S_{TCCO} (sulfur granulated), T_{melt} 122 °C, as well as the block sulfur of the Shymkent Petroleum Refinery (**PetroKazakhstan Oil Products** LLP) S_{SPR} , T_{melt} 113 °C. Other chemical ingredients, namely, aniline were purchased from Sigma-Aldrich Chemie GmbH, 99.5 (registration number is Beilstein 605631, density is 1,022 g / ml at 25 °C); pyrrole from Sigma - Aldrich GmbH, 98% (registration number is Beilstein 1159, density 0.967 g / ml at 25 °C); Iron trilog six water ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) - chemically pure, GOST (TU) 4147-74; Sodium sulfurous nine ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) - chemically pure for analysis, GOST (TU) 2053-77.

Method of redox copolymerization of sulfur with aniline or pyrrole. Colloidal cross-linked copolymers were synthesized by redox copolymerization of sulfur with monomer (aniline or pyrrole). The sulfur was introduced into the reaction mixture in a colloidal form. Colloidal activated sulfur was prepared by *in situ* from sodium polysulphides Na_2S_x ($x = 4.0-4.5$). Sodium polysulphide was synthesized from sodium sulfide $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (8.3 g, 34.7 mmol), preheated to 80-90 °C, to which 4.2 g (130 mmol) of powdered sulfur S_{TCCO} or S_{SPR} (for 30-40 minutes) was added in portions. The reaction mixture was stirred at 80-90 °C for 40 minutes, then diluted with 6.7 ml of hot water (80-90 °C), left over night at room temperature and then filtered from unreacted sulfur. The resulting sodium polysulfide Na_2S_x was used subsequently for the synthesis of new high-sulfur copolymers based on aniline/or pyrrole and sulfur. The synthesis was carried out in the presence of the oxidation system $\text{H}_2\text{O}_2 / \text{FeCl}_3 / \text{HCl}$, which is 7 ml of a 33% solution of H_2O_2 , 0.2 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 50 ml of 2 N HCl solution. In the second stage, a mixture of a water-alcohol solution of sodium polysulphide and monomer was prepared. This mixture was added with vigorous stirring to a $\text{H}_2\text{O}_2 / \text{FeCl}_3 / \text{HCl}$ oxidation system containing 1-5 wt % gelatin, and stirring was continued for 3 hours. As a result, the high sulfur copolymers on the base of aniline or pyrrole were obtained in the form of powders of dark brown color.

Results and discussion. Polyaniline is among the most studied conductive polymers, mainly due to the combination of high conductivity, various different oxidations and protonation states each one exhibiting different color and electronic properties, light weight, easy preparation and low cost. Its ability to form ultra-small nanostructures, including nanowires, nanoneedles and nanofibers has been proven particularly useful in the application of the polymer in sensors applications since their extremely high specific area enables the fast detection of small molecules that can cause immediate changes in the oxidation states and as it is expected to the conductivity values and the optical absorption spectrum, the latter can exhibit from one to three absorbance bands depending on the polymer form [8-11].

Colloidal activated sulfur was prepared by *in situ* from sodium polysulphides in the first stage. Synthesis of new sulfur and aniline copolymers was carried out in the presence of oxidation systems: $\text{H}_2\text{O}_2 / \text{FeCl}_3 / \text{HCl}$, and $\text{K}_2\text{Cr}_2\text{O}_7 (\text{H}_2\text{O}_2) / \text{HCl}$. In the second stage, the above oxidation system was prepared. The effect of surfactant and gelatin on the reaction process and the yield of the desired product were investigated. Gelatin (or surfactant, 0.25 g in 5 ml H_2O) was placed in the flask and stirred vigorously for 15 minutes, a solution of HCl (or H_2SO_4) was added to the emulsion and stirring was

continued for 0.4-2 hours. Next, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and the emulsion was stirred for 15 minutes before the formation of the oxidation system $\text{H}_2\text{O}_2 / \text{FeCl}_3 / \text{HCl}$ as a white foam. The product was filtered off, washed with water to $\text{pH} \sim 6$ and a negative reaction to chlorine ions, dried in vacuo at 40°C to constant weight (Table 1).

Table 1 - Conditions for the synthesis and yield of polymers based on aniline and elemental sulfur

Copolymer cipher	Reaction conditions			Yield, %
	Composition of the reaction mixture	Temperature, $^\circ\text{C}$	Time, h	
SPAN-1	polysulphide, aniline, HCl, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, H_2O_2 , surfactants	25-42 (self-heating)	4.0	61.2
SPAN-2	polysulphide, aniline, HCl, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, H_2O_2 , gelatin	25-45 (self-heating)	2.5	54.6

As a result of redox copolymerization of aniline with sulfur, sulfur-aniline polymers are synthesized in the form of powders from light brown to black. The composition of the obtained copolymers was determined by the methods of elemental analysis (Table 2).

Table 2 - Element composition and melting temperature of polymers based on aniline and elemental sulfur

Sample cipher	Elemental analysis					T_{melt} , $^\circ\text{C}$
	C	H	N	S	Cl	
SPAN-1	9.7	0.4	1.3	80.4	-	190-240
SPAN-2	8.5	0.4	1.4	89.2	0.8	165-260

Depending on the reaction conditions, the nature of the oxidation system, the addition of gelatin or surfactant to the reaction mixture, sulfur-aniline polymers with a high sulfur content were obtained: from 80.4 to 89.4 %.

The main synthesis conditions and properties of the copolymers obtained are shown in Table 3.

Table 3 - Composition of the obtained copolymers

Copolymer cipher	Composition of the reaction mixture	Yield, %	Sulfur content, %	T_{melt} , $^\circ\text{C}$	σ , S / cm
SPAN-1	polysulphide, aniline, HCl, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, H_2O_2 , surfactants	81.0	80.4	190-240 (partially)	$2.1 \cdot 10^{-5}$
SPAN-2	polysulphide, aniline, HCl, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, H_2O_2 , gelatin	73.4	80.2	165-260 (partially)	$1.2 \cdot 10^{-7}$

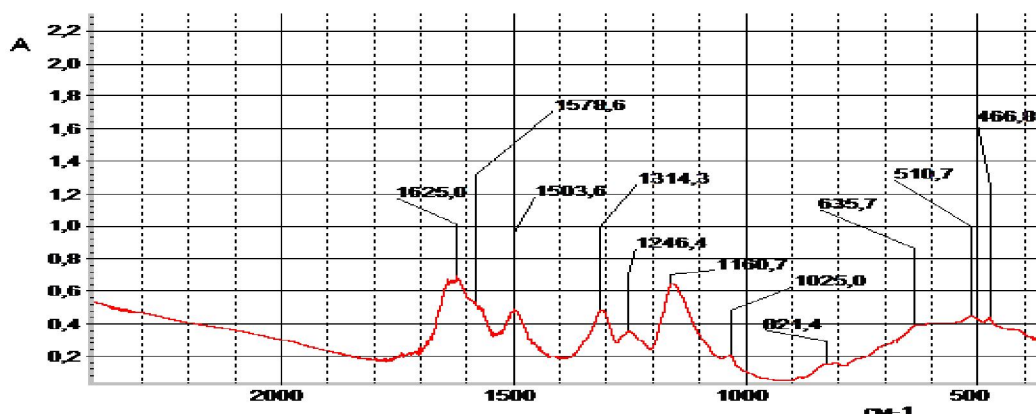


Figure 1 - IR spectra of a high-sulfur polymer based on Tengiz sulfur and aniline

Synthesized copolymers are characterized by a high sulfur content (80-89 %). In the IR spectra of copolymers there are characteristic absorption bands (cm^{-1}): 1625, 1503 (ν , C = C of the polyaniline chain); 1314 (ν , C = C-H); 1301 (ν , O = S = O); 1246 (ν , C = S, ν , C-N); 1160 (ν , O = S = O); 1025 (ν , O = S); 824 (ν , C = C-H); 635, 510 (ν , C-S); 467 (ν , S-S).

The composition of the obtained copolymers was determined by elemental analysis. IR spectra were recorded for all the samples, specific electrical conductivity (σ) was determined, and oxidative thermal destruction was studied by thermogravimetric analysis.

Copolymers have a high resistance to thermal oxidative degradation (up to 210-230 °C) and electrical conductivity of the order of 10^{-5} - 10^{-13} S / cm. Figure 1 shows the IR spectrum of a synthesized high-sulfur polymer based on Tengiz sulfur and aniline.

The redox copolymerization of elemental sulfur with pyrrole. In contrast with polyaniline that is a slightly hydrophilic polymer and can be solubilized in water upon high dilution, polypyrrole is a completely insoluble polymer in any solvent either organic or water. With respect to the above, the interfacial polymerization seems an excellent candidate for the synthesis of a thin film in the boundary of the two phases. This thin film can be easily extracted and purified. The poor solubility of polypyrrole in any solvent has been assigned to an extensive cross-linking 20 between the polymer chains. Oligomers however, tend to be easily dispersible. The polymerization of pyrrole involves oxidation of the monomer with metal cations.

For the synthesis of high-sulfur pyrrole-based polymers, the method of co-oxidation of pyrrole and polysulfone, previously generated *in situ* from an aqueous solution of sodium polysulphide in the presence of an oxidizing system and a colloidal stabilizer (gelatin), was used. The stabilizer was used as a pre-prepared aqueous solution. The oxidation system H_2O_2 / $FeCl_3$ / HCl includes 7 ml of a 33 % solution of H_2O_2 , 0.2 g of $FeCl_3 \cdot 6H_2O$ and 50 ml of a 2 N solution of HCl .

The resulting filtrate was used subsequently to prepare colloidal sulfur-pyrrole copolymers. In the same way, colloidal activated sulfur was obtained from the associated sulfur of Shymkent refinery S_{SPR} . As a result of the variation in the nature of the initial sulfur (S_{TSO} or S_{CPR}), sulfur-pyrrole copolymers are obtained in the form of powders of a dark brown color with a different sulfur content (Tables 4, 5).

Table 4 - Synthetic conditions and polymers yield based on pyrrole and the desulphurization product of TSP ($SPPy_{TSO}$) and ($SPPy_{SPR}$)

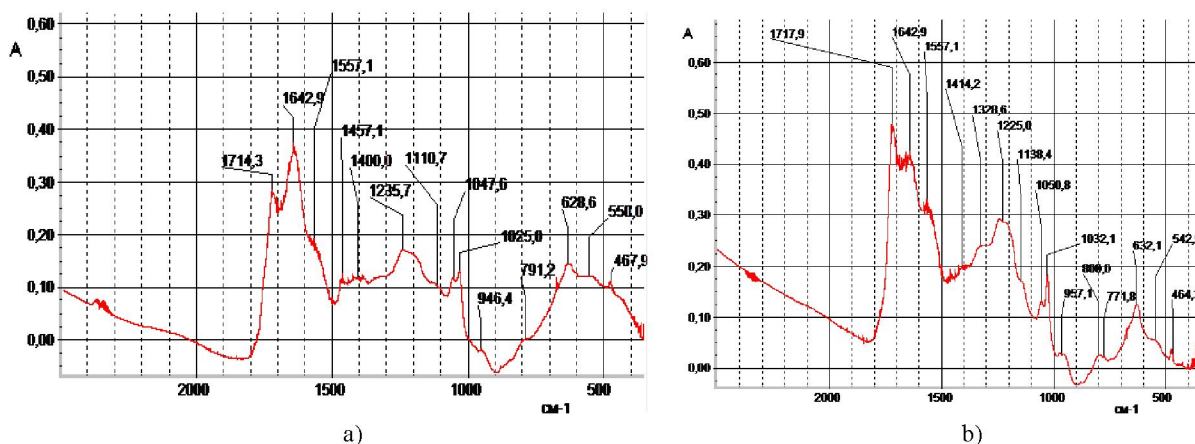
Copolymer cipher	Composition of the reaction mixture	Reaction temperature, °C	Reaction time, h	Yield, %
$SPPy_{TSO}$	polysulfide, pyrrole, HCl , $FeCl_3 \cdot 6H_2O$, H_2O_2 , gelatin	25-47 (self-heating)	4.0	80.3
$SPPy_{SPR}$	polysulfide, pyrrole, HCl , $FeCl_3 \cdot 6H_2O$, H_2O_2 , gelatin	25-53 (self-heating)	4.5	79.2

Table 5- Elemental composition and melting point of polymers based on pyrrole and sulfur

Sample cipher	Elemental analysis					T_{melt} , °C
	C	H	N	Cl	S	
$SPPy_{TSO}$	6.2	0.6	1.1	0.58	72.0	170-255
$SPPy_{SPR}$	10.6	1.5	1.8	0.38	80.0	167-210

Thus, as a result of redox synthesis of high-sulfur polypyrrole, sol-gel copolymerization of pyrrole with associated S_{TSO} or S_{SPR} sulfur, with other equal process conditions, depending on its origin, the sulfur content of sulfur - polipyrrole is higher than in case of succumbing associated Tengiz sulfur.

In the IR spectra of high-sulfur pyrrole-based polymers (Fig. 2 a, b), there are characteristic absorption bands (cm^{-1}): 1714, 1718 (ν , C-O); 1557, 1457, 1414, (ν , C=C a polypyrrole fragment); 1328, 1235 1225, 791 (δ , C=C-H); 1236, 1047, 1025 (12), 1225, 1138, 1051, 1032 (13) (ν , O=S); 791, 771, 800(δ , C=C-H); 628, 632(ν , C-S); 467, 464 (ν , S-S).



a) S_{TCO} and pyrrole; b) S_{SPR} and pyrrole
 Figure 2 - IR spectra of high-sulfur polymer based on:

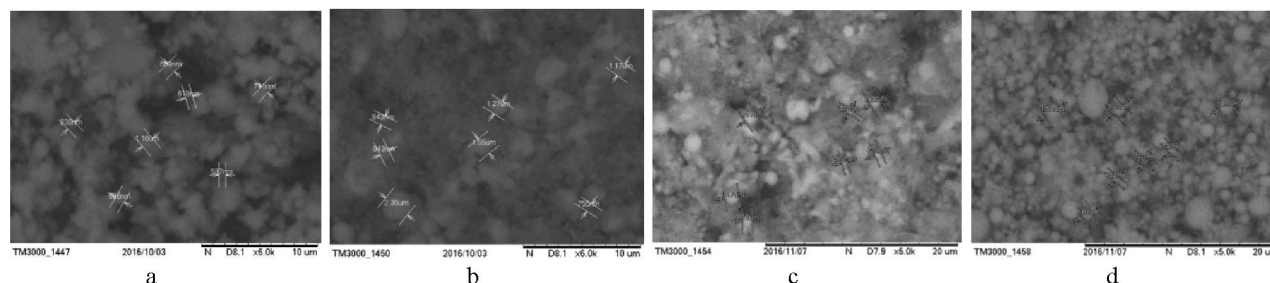
When studying the electrical conductivity of the obtained high-sulfur aniline-based polymers and also on the basis of pyrrole, they have a specific electric conductivity of the order of $10^{-5} - 10^{-7}$ S/cm, corresponding to high-resistance organic semiconductors (Table 6).

Table 6 - Specific electric conductivity (σ) and thermogravimetric analysis of high-sulfur polymers based on aniline SPAN (№ 1, № 2) and pyrrole SPPy (№ 3, № 4)

№ II/II	Sample cipher	Content S, %	The temperature of the onset of thermooxidative degradation, °C	σ , S/cm
1	SPAN-1	80.4	~210	$2.1 \cdot 10^{-5}$
2	SPAN-2	89.2	~210	$1.2 \cdot 10^{-7}$
3	SPPy -1	72.0	~220	$8.1 \cdot 10^{-7}$
4	SPPy -2	80.0	~210	$4.3 \cdot 10^{-7}$

According to the results of thermogravimetric analysis, the polymers obtained are highly resistant to thermal-oxidative degradation (up to 210 -220 °C).

Microstructure of synthesized polymers based on elemental sulfur and aniline. For the purpose of conducting comparative studies of the microstructure of synthesized high-sulfur polymers based on aniline, and also on the basis of pyrrole, X-ray dispersive spectral microanalysis was used. Typical micrographs of synthesized sulfonated copolymers SPAN (№ 1) and SPPy (№ 2) are presented in figure 3.



a) SPAN -1 (587 nm – 1.10 μ m); b) SPAN -2 (755 nm – 2.36 μ m); c) SPPy (474 nm – 1.47 μ m); d) SPPy (644 nm – 1.54 μ m)
 Figure 3 – Micrographs of synthesized sulfonated copolymers

The obtained results indicate that the synthesized copolymers have a developed microstructure, with sufficiently small microparticles of narrow polydispersity. The SPAN-1 copolymer has the smallest

particle sizes in the range of 587 nm to 1.10 μm , in the case of SPPy-1 in the range 474 nm - 1.54 μm . A somewhat larger particle (up to 755 nm - 2.36 μm) is formed in the synthesis of an aniline-sulfur copolymer SPAN-2, also slightly larger than the particle in the case of SPPy - 2 (up to 644 nm - 1.54 μm) using the $\text{H}_2\text{O}_2 / \text{FeCl}_3 / \text{HCl}$ oxidation system and adding gelatin to the reaction mixture.

The oxidation-reduction properties and the electrochemical activity of the synthesized products, as well as the possibility of their use as active cathode material in lithium batteries, were investigated by cyclic voltammetry and charge-discharge processes of cathodes.

Electrochemical properties of synthesized cathode samples № 1 SPAN-1 and № 2 SPPy-2 (Table 6) were studied in lithium batteries. Galvanostatic measurements were carried out on a multichannel tester (BT-2000, Arbin Instruments) in the range of potentials from 0.1 to 2 V. The values of current intensity and specific capacitance were calculated taking into account the weight content of sulfur in the SPAN-1 electrode composite (80.4 %) and SPPy - 2 (80 %) (Figure 4).

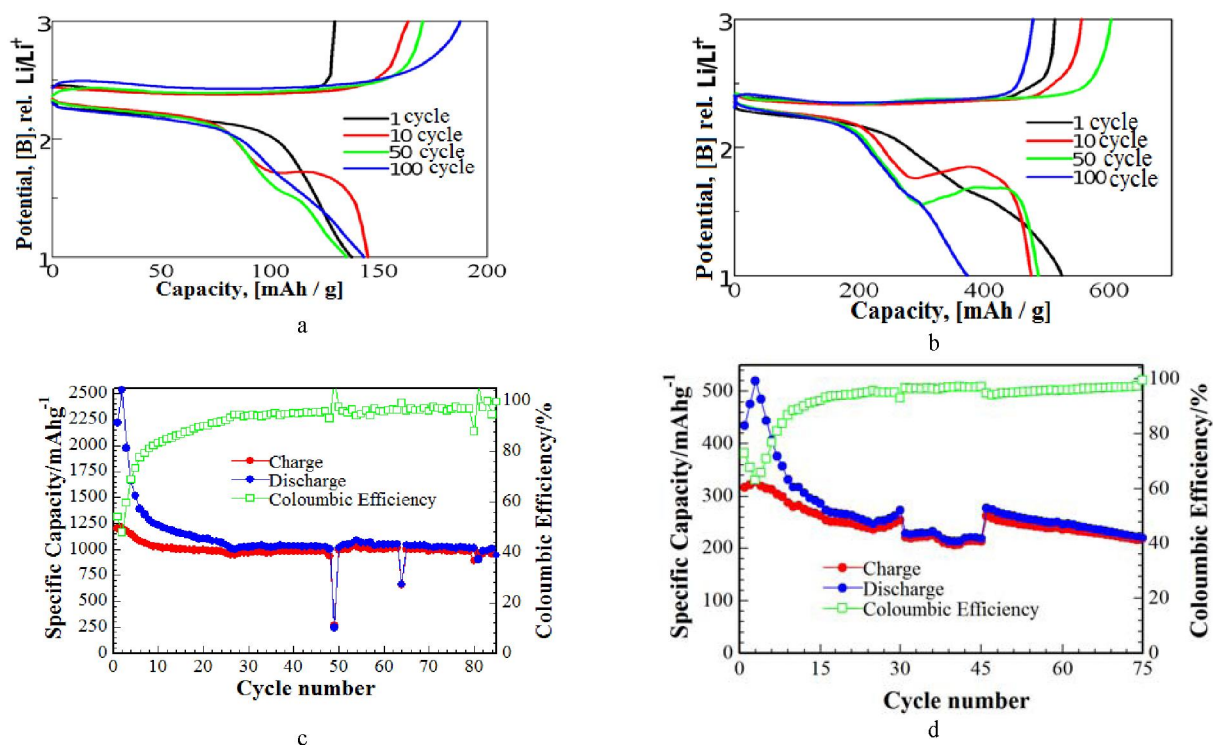


Figure 4 - Charging-discharge curves (a, c) and cycling curves (b, d) at a current density of 0.2 C of an aniline-based SPAN-1 (a, b) based aniline based polymer based on SPPy-2 (b, d)

The results of the electrochemical cycling of the SPAN-1 sample deposited on the aluminum current collector showed a low capacitance, but when deposited on carbon paper (TGP-H-030), showed a high capacitance (Fig. 4 a, b), the test samples of button batteries were high the initial discharge capacity is 2500 mAh^{-1} at a current density of 0.2 C, it can be seen that the battery gradually loses its original discharge capacitance to 50 % within 15 cycles. However, the charging capacity is more stable for 15 cycles (the battery continues to cycle).

The specimen of the SPPy-2 sample was also electrochemically tested, showed a smaller charge capacity within $430\text{-}320 \text{ mAh}^{-1}$ and a maximum discharge capacitance of 520 mAh^{-1} . Figure 4 c, d shows charge-discharge curves and cycling at a current density of 0.2 C.

On cyclic voltammograms one anode peak is observed at 2.5 V and two cathode at 2.4 and 1.9 B, which indicates the multistage nature of the reduction process in polymers. The electrochemical behavior of a polymer with polysulfide blocks is determined by two fundamentally different parts of it.

The first is polysulfide blocks, which give peaks of oxidation and reduction, in position close to the peaks of sulfur, and are not very dependent on the structure of the polymer. The second part is fragments

remaining on the cathode (organic or heteroorganic thiolates), which modify the cathode matrix in a certain way, accelerating or slowing down the intermediate stages of the redox process. It is possible to learn how to control this process in order to achieve its maximum reversibility and speed, by searching for the optimal structure and combination of the two specified parts of the electroactive sulfur-organic polymer.

Thus, technological methods for the synthesis of high-sulfur polymers have been developed, based on the redox copolymerization of elemental sulfur with aniline and pyrrole. Conditions for carrying out the reaction have been found, which make it possible to vary the sulfur content of the obtained materials. It has been established that synthesized high-sulfur polymers have thermal stability, semiconductor properties, developed surface morphology and are promising for the development of active cathode materials of modern rechargeable lithium current sources.

Conclusion. Technological methods for obtaining polymeric sulfur composites and an original sol-gel technology for the synthesis of nanoscale polymer sulfur and its composites with electrically conductive polymers (polypyrrole, polyaniline) have been developed. Conditions for carrying out the reaction have been found, allowing to vary the sulfur content in the obtained materials. The electrochemical activity and efficiency of the use of aniline and pyrrole-based gray polymer compositions as active electrode materials of lithium-sulfur batteries have been studied. It has been established by physico-chemical methods that the obtained high-sulfur polymers possess semiconductor properties, redox activity and are promising for the development of active cathode materials of modern rechargeable lithium current sources.

REFERENCES

- [1] Savin E. D., Frolova N. G., Nedelkin V. I. Polimernaya sera: nauchnyj i prakticheskij aspekty . Polymer sulfur: scientific and practical aspects. *Elektronnyy resurs*. Rezhim dostupa <http://www.chem.msu.ru/rus/journals/xr/sera.html>. (in Russ).
- [2] Chung W.J, Griebel, J.J. Kim, E.T. Yoon, H.S, Simmonds, A.G. Pyun. Utilization of Elemental Sulfur as an Alternative Feedstock for Polymeric Materials: Synthesis, Processing & Electrochemistry . *Nature Chemistry*, **2012** (in Eng).
- [3] Pat. US 2013 / 0040197 A1, Appl. No US 13 / 561,701. Polymer-sulfur composite materials for electrodes in Li-S energy storage. Jun Liu, Yuliang Cao, Lifan. (in Eng).
- [4] Trofimov B.A., Myachina (Prozorova) G.F., Rodionova I.V., Mal'kina A.G., Dorofeev I.A., Vakul'skaya T. I., Sinegovskaya L.M., Skotheim T.A. Ethynedithiol-based polyeneoligo sulfides as active cathode materials for lithium-sulfur batteries . *J. Applied Polymer Science*, **2008**, 2, 784 - 787. (in Eng).
- [5] Patent RF 2275392. 2006. B.I. **2006**. № 12. Hybrid three-dimensional copolymers of sulfur, including conductive and non-conductive polymer blocks and their compositions with sulfur, used as cathode materials. Trofimov B.A., Mihaleva A.I., Myachina (Prozorova) G.F., Malkina A.G. i dr. (in Russ).
- [6] Pat. US 2013 / 0040197 A1, Appl. No US 13 / 561,701. Polymer-sulfur composite materials for electrodes in Li-S energy storage. Jun Liu, Yuliang Cao, Lifan. (in Eng).
- [7] Bishimbayeva G.K., Zhumabaeva D.S. Tekhnologichnye metody polucheniya novyh komponentov katodnyh materialov pryamym oserneniem promyshlennykh polimerov. (Technological methods of obtaining new components of cathode materials by direct sulphuration of industrial polymers). *Izvestiya NAN RK. Ser. Him. i tehnologiya*, **2016**, 5, 28-38. (in Russ).
- [8] L. Xiao, Y. Cao, J. Xiao, B. Schwenzer, M.H. Engelhard, L.V. Saraf, Z. Nie, G.J. Exarhos, J. Liu. A Soft Approach to Encapsulate Sulfur: Polyaniline Nanotubes for Lithium-Sulfur Batteries with Long Cycle Life. *Adv. Mater*, **2012**, 24,1176-1181 (in Eng).
- [9] A Simple Preparation of Polyaniline-coated Sulfur Composites for use as Cathodes in Li-S Batteries. *Electrochemistry*, **2016**, 836–841 (in Eng).
- [10] Bishimbayeva G.K., Prozorova G.F., Zhumabayeva D.S., Korzhova S.A., Mazyar I.V., Nalibayeva A.M., Kydyrbayeva U.O. Synthesis of High-sulfur Polymers Based on the Tengiz Sulfur Copolymerization with Aniline. *Izvestiya NAN RK. Ser. Him. i tehnologiya*, **2017**, 4, 5-12 (in Eng).
- [11] W. Zhou, Y. Yu, H. Chen, F.J. DiSalvo, H. D. Abrun. A Yolk– Shell Structure of Polyaniline-Coated Sulfur for Lithium – Sulfur Batteries. *J. Am. Chem. Soc.* **2013**, 135, 16736–16743 (in Eng).
- [12] Victor Yavorsky New principles in the polymeric sulfur technology. *Chemistry & Chemical Technology*, **2008**, 2, 29-73 (in Eng).
- [13] A. Z. Rys, I. A. Abu-Yousef, D. N. Harpp. A powerful method to prepare sulfur-rich macrocycles . *Tetrahedron Letters*. Iss. 47, 6670–6673 (in Eng).
- [14] A.G. Simmonds, J. J. Griebel, J.Park, K. R. Kim, W. J. Chung, R. S. Glass, C. L. Soles, J.Pyun. Inverse Vulcanization of Elemental Sulfur to Prepare Polymeric Electrode Materials for Li–S Batteries. *ACS Macro Lett.*, **2014**, 3, 229–232 (in Eng).
- [15] R. G. Chaudhuri, S. Paria. Synthesis of sulfur nanoparticles in aqueous surfactant solutions. *Journal of Colloid and Interface Science*, **2010**, 343, 439–446 (in Eng).
- [16] X. Ji, K. T. Lee, L. F. Nazar. A highly ordered nanostructured carbon–sulphur cathode for lithium–sulphur batteries. *Nature Materials*, **2009**, 8, 500 – 506 (in Eng).

Г.Қ. Бишимбаева¹, Б.А. Трофимов², Г.Ф. Прозорова², Д.С. Жұмабаева¹,
А.Г. Малькина², С.А. Коржова², А.М. Налибаева¹, Ұ.О. Қыдырбаева

Д.В. Соколовский ат. Отын, катализ және электрохимия институты., Алматы, Қазақстан;
²А.Е. Фаворский ат. Иркутск химия институты. Ресей ғылым академиясының
Сібір бөлімшесі, Иркутск, Ресей

МҰНАЙДЫ КҮКІРТСІЗДЕНДІРУДЕ АЛЫНҒАН ІЛЕСПЕЛІ КҮКІРТ НЕГІЗІНДЕ КҮКІРТ- ПОЛИМЕРЛІ КОМПОЗИТТЕРДІҢ СИНТЕЗІНІҢ ӨЗІНДІК ТЕХНОЛОГИЯСЫ

Аннотация. Полимерлі күкірт композиттерін электрлік өткізгіш сополимерлермен (пиррол, анилин) ілеспелі күкірт негізінде тотығу-тотықсыздану сополимерлеу арқылы технологиялық әдістер жасалынды. Алынған материалдардағы күкірттің мөлшерін өзгертуге мүмкіндік беретін реакцияны жүргізу шарттары белгіленді. Литий-күкірт аккумуляторларының белсенді электродтық материалдары ретінде анилин мен пирролдың күкіртті полимерлі композицияларының электрохимиялық белсенділігі мен тиімділігі зерттелді. Физико-химиялық әдістер бойынша алынған жоғары күкірт полимерлерінің электр өткізгіш қасиеттерімен, тотығу-тотықсыздану белсенділігімен және қазіргі заманғы қайта зарядталатын литийлі ток көздерінің белсенді катодты материалдарын әзірлеу үшін перспективалы болып табылатыны анықталды.

Литий-күкірт аккумуляторлары үшін катодты материалдарды өндіретін отандық өндірісті құру кезінде электр өткізетін жоғары күкірт полимерлерін шығаруға арналған тотығу-тотықсыздану сополимеризация арқылы наномөлшерлі күкірт негізінде анилин мен пиррол сополимерлерін золь-гель синтезінің дамыған технологиясын ұсынуға болады.

Түйін сөздер: полимерлі күкірт композиттері, полипиррол, полианилин, катодты материалдар, литий-күкірт батареялары.

Г.К. Бишимбаева¹, Б.А. Трофимов², Г.Ф. Прозорова², Д.С. Жумабаева¹,
А.Г. Малькина², С.А. Коржова², А.М. Налибаева¹, У.О. Кыдырбаева

¹Институт топлива, катализа и электрохимии им. Д.В. Сокольского, Алматы, Казахстан;

²Иркутский химический институт им. А.Е. Фаворского, Сибирского отделения
Российской академии наук, Иркутск, Россия

ОРИГИНАЛЬНАЯ ТЕХНОЛОГИЯ СИНТЕЗА СЕРОПОЛИМЕРНЫХ КОМПОЗИТОВ НА ОСНОВЕ ПОПУТНОЙ СЕРЫ ОБЕССЕРИВАНИЯ НЕФТИ

Аннотация. Разработаны технологические методы получения полимерных серных композитов путем окислительно-восстановительной сополимеризации на основе попутной серы с электропроводящими сополимерами (пиррол, анилин). Установлены условия проведения реакции, которые позволяют варьировать содержание серы в полученных материалах. Изучена электрохимическая активность и эффективность использования сернистых полимерных композиций анилина и пиррола в качестве активных электродных материалов литий-серных батарей. Физико-химическими методами установлено, что полученные высокосернистые полимеры обладают электропроводящими свойствами, окислительно-восстановительной активностью и перспективны для разработки активных катодных материалов современных перезаряжаемых источников тока лития.

Разработанная технология золь-гель синтеза сополимеров анилина и пиррола на основе наноразмерной серы методом окислительно-восстановительной сополимеризации для получения электропроводящих высокосернистых полимеров может быть рекомендована для использования при создании отечественного производства катодных материалов для литий-серных аккумуляторов.

Ключевые слова: полимерные серные композиты, полипиррол, полианилин, катодные материалы, литий-серные батареи.