

# EFFECT OF WATER-SOLUBLE POLYMER NV-1A ON ELECTROCHEMICAL PARAMETERS OF SULFUR ELECTRODE

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Studies have shown the possibility of a long cycle of sulfur electrode with a high content of active material. The use of water-soluble binder material NV-1A leads to the realization of high current loads in the Li-S battery. Impedance spectroscopy has shown that the low coulombic efficiency in the cycling of the sulfur electrode is primarily due to the spontaneous dissolution of sulfur in the electrolyte, which requires high energy consumption when charging the Li-S battery. The reduction of the specific capacity during cycling is associated with the formation and accumulation of non-conductive films of short-chain polysulfides. On the basis of the conducted researches and the review of the literature sources ways of overcoming of this problem are offered. The ability of cycling the sulfur electrodes at the high current loads has been shown. The discharge capacity values of the sulfur electrodes at the current load  $790 \text{ mA}\cdot\text{cm}^{-2}$  are 500 i  $420 \text{ mAh}\cdot\text{g}^{-1}$  on the 5-th and 100-th cycles, accordingly. Using the method of impedance spectroscopy, it has been supposed that the formation and accumulation of uncondutive  $\text{Li}_2\text{S}_2$  /  $\text{Li}_2\text{S}$  phases is the main process, which induce the quick capacity reduction of Li - S batteries upon cycling.

**Key words:** sulfur electrode, discharge capacity, coulombic efficiency, cyclability.

**INTRODUCTION.** The growing interest in the Li-S system is due to its high energy density ( $2567 \text{ Wh}\cdot\text{kg}^{-1}$ ), low cost of sulfur and increased safety [1–3]. Li-S batteries are of particular interest for stationary and electric vehicles where high capacity and downsizing are important. However, the efficiency and service life of Li - S batteries need to be improved in order for them to be used in practice [4].

However, the practical application of Li-S battery technology is hindered by several factors:

- sulfur and its discharge product  $\text{Li}_2\text{S}$  are not electrically conductive ( $5 \cdot 10^{-30} \text{ S}\cdot\text{cm}^{-1}$  at  $25 \text{ }^\circ\text{C}$ ). This makes it necessary to combine sulfur with various electrically conductive substrates (activated carbon, nanotubes, graphene oxide, leading polymers, metal oxides, etc., in

which the maximum sulfur concentration is reached);

- the density of sulfur differs from the density of the product of its discharge  $\text{Li}_2\text{S}$ , and the volumetric expansion or contraction that occurs during the charging-discharging processes reaches (76%);

- dissolution and movement of long-chain lithium sulfides ( $\text{Li}_2\text{S}_x$ ,  $2 < x < 8$ ) in the electrolyte causes a loss of active sulfur, which leads to a decrease in the capacity and Coulomb efficiency of the battery [5–9].

One of the ways to improve the parameters of a sulfur electrode can be the use of a polymer binder with a large number of polar functional groups, which makes it possible to fix long-chain lithium sulfides and effectively suppress the shuttle effect in Li-S batteries.

When a Li-S battery is discharged, sulfur dissolves in the liquid electrolyte, which leaves numerous voids in the S / C cathode, while at the end of the discharge, dissolved polysulfides precipitate back onto the cathode in the form of  $\text{Li}_2\text{S}_2$  and  $\text{Li}_2\text{S}$  [10,11].

To ensure high electrochemical characteristics of the cathode during the cycling of the Li / S element, a union capable of maintaining a higher porous structure is needed. Conventional unions such as polyvinylidene fluoride and poly (ethylene oxide) cannot meet this requirement due to swelling and gelation under the action of electrolyte solvents [4]. In addition, the reduction of sulfur as an intermediate produces anionic polysulfide radicals that react with many organic polymers, the so-called vulcanization process [12]. Therefore, the union for the cathode of the Li / S element must be insoluble in the liquid electrolyte and chemically resistant to all types of sulfur.

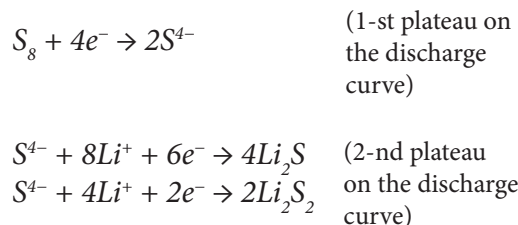
In our work, we study the electrochemical behavior of a Li-S battery with a new multi-functional water-soluble material NV-1A [13]. Despite a large number of studies [14,15] showing that the best results in the cycling of Li-S batteries are observed at a mass sulfur content of about 30%, from our point of view for effective practical application the content of inactive sulfur electrode components should not exceed 30–40 %.

*EXPERIMENT AND DISCUSSIONS OF THE RESULTS.* The positive electrode of the Li-S battery consisted of sulfur (99.9%, Ukraine), graphite (99.95%, GAK-1, Ukraine), carbon black (Super P, Alfa Aesar China Limited, China) and water-soluble binder NV-1A (Zhejiang Casnovo New Materials Co. Ltd, China) taken in a ratio of 70: 20: 5: 5, respectively.

1M  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  (Sigma Aldrich) in a solution of 1,2-dimethoxyethane (G1): dioxolane (DOL) (1:1) by volume (Aldrich) was used as the electrolyte. Celgard 2325 acted as a separator. Lithium metal was used as an auxiliary electrode in elements of dimensions of 2016.

Galvanostatic cycling (MTech G410-4, Ukraine) and impedance spectroscopy (Autolab PGSTAT302, Switzerland) were used to obtain electrochemical parameters of the electrode.

Galvanostatic curves of the sulfur electrode (Fig. 1) are characterized by the presence of 2 shelves of discharge / charge processes corresponding to the following reactions:



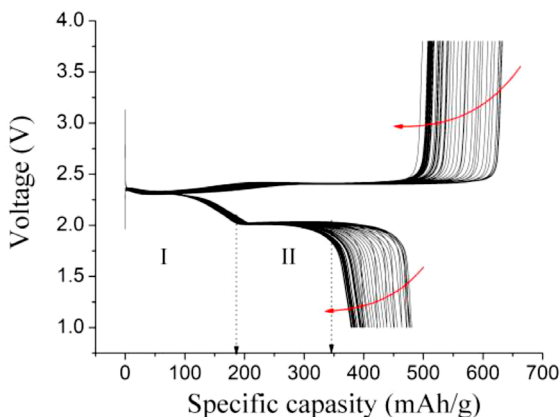
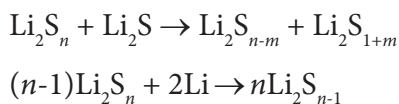


Fig. 1. Galvanostatic charge/discharge curves for the sulfur electrode at  $i = 790 \mu\text{A} \cdot \text{cm}^{-2}$ .

During the cycling of the Li-S battery there is a decrease in discharge / charging capacity, which indicates the degradation of the electrode due to partial loss of active substance due to migration of soluble polysulfides from the cathode material to the electrolyte, followed by their reduction on the carbon surface of the working electrode and lithium counter electrode as a result of the solubility of long-chain lithium polysulfides in DOL and glim solvents, this process can occur spontaneously (the so-called "polyshatl effect").



This in turn has a negative effect on the preservation of the Li-S battery and requires additional electricity when it is charged, which in turn leads to low coulombic efficiency (Fig. 2), which does not exceed 80% at specified modes of galvanostatic cycling ( $i = 790 \mu\text{A} \cdot \text{cm}^{-2}$ ). The reduction of the current load by 2 and 4 times practically does not change the specific capacity during discharge and is 420 and 450  $\text{mAh} \cdot \text{g}^{-1}$ , respectively.

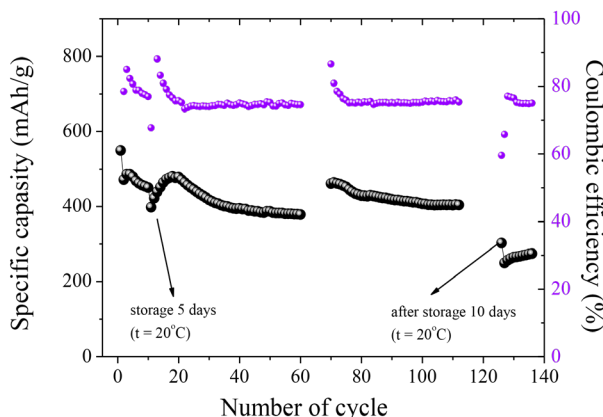


Fig. 2. Changes in the specific capacity and coulombic efficiency of the sulfur electrode upon cycling.

The main parameters of the cell were calculated by impedance spectroscopy, and it was proved that the greatest contribution to the total resistance of the Li - S battery is made by the resistance corresponding to the charge transfer process through the SEI film on the lithium anode (Fig. 3). Moreover, a sharp increase in this resistance is observed at the end of the discharge of the sulfur electrode, which is associated with the formation of poorly soluble  $\text{Li}_2\text{S}_2$  and  $\text{Li}_2\text{S}$  films on its surface. At a lower degree of discharge of the electrode, the increase in the resistance to charge transfer at the lithium anode is practically not observed, in contrast to the resistance of the electrolyte in the pores of the separator. This behavior of the Li-S element is due to the solubility of long-chain sulfides  $\text{S}_n^{2-}$  ( $n \geq 4$ ), the accumulation of which in the electrolyte leads to a change in its specific electrical conductivity. When the degree of discharge of the sulfur electrode is more than 50%, lithium sulfides  $\text{S}_n^{2-}$  ( $n \geq 4$ ) begin to be converted into  $\text{Li}_2\text{S}_2$  and  $\text{Li}_2\text{S}$ , which have low solubility, which leads to their crystallization from the electrolyte solution. Therefore, no further increase in electrolyte resistance is observed.

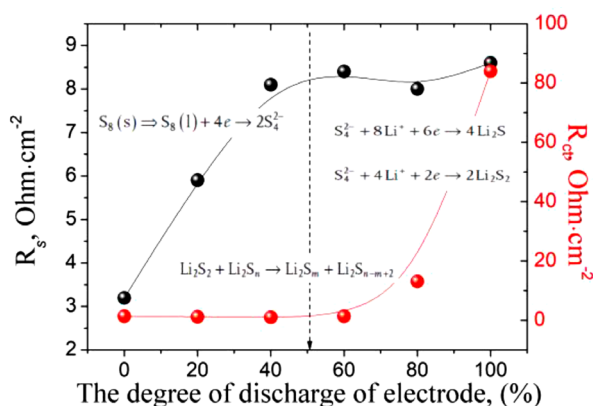


Fig. 3. Change in the resistance of the electrolyte and SEI depending on the degree of discharge of the electrode.

The presence of the above factors leads to the need to optimize the composition of the components of the sulfur electrode in order to create a porous surface that is able to hold lithium polysulfides (in liquid and solid state) in the structure of the electrode. As well as the use of electrolyte systems that inhibit the migration of soluble polysulfides in Li - S batteries.

**CONCLUSIONS.** Studies have shown the possibility of a long cycle of sulfur electrode with a high content of active material. The use of water-soluble binder material NV-1A leads to the realization of high current loads in the Li-S battery. Impedance spectroscopy has shown that the low coulombic efficiency in the cycling of the sulfur electrode is primarily due to the spontaneous dissolution of sulfur in the electrolyte, which requires high energy consumption when charging the Li-S battery. The reduction of the specific capacity during cycling is associated with the formation and accumulation of non-conductive films of short-chain polysulfides. On the basis of the conducted researches and the review of the literature sources ways of overcoming of this problem are offered.



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### ВПЛИВ ВОДОРІЗЧИННОГО ПОЛІМЕРУ NV-1A НА ЕЛЕКТРОХІМІЧНІ ПАРАМЕТРИ СІРЧАНОГО ЕЛЕКТРОДА

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Дослідження показали можливість тривалого циклування сірчаного електрода з високим вмістом активного матеріалу. Використання водорозчинного сполучного NV-1A призводить до реалізації високих струмових навантажень у Li-S батареї. Імпедансна спектроскопія показала, що низька кулонівська ефективність при циклуванні сірчаного електрода насамперед пов'язана зі спонтанним розчиненням сірки в електроліті, що вимагає високого споживання енергії при зарядженні Li-S акумулятора. Зниження питомої ємності під час циклування пов'язане з утворенням і накопиченням непровідних плівок на основі коротколанцюгових полісульфідів. На основі проведених досліджень та огляду літера-

турних джерел запропоновано шляхи подолання цієї проблеми. Показано здатність циклування сірчаних електродів при високих струмових навантаженнях. Значення розрядної ємності сірчаних електродів при струмовому навантаженні  $790 \text{ mA}\cdot\text{cm}^{-2}$  становлять  $500$  і  $420 \text{ mA}\cdot\text{g}^{-1}$  на 5-му і 100-му циклах відповідно. Використовуючи метод імпедансної спектроскопії, висунуто припущення, що утворення та накопичення непровідних фаз  $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$  є основним процесом, який спричиняє швидке зниження ємності Li-S акумуляторів при циклуванні.

**Ключові слова:** сірчаний електрод, розрядна ємність, кулонівська ефективність, циклічність.

#### REFERENCES

- Ji X., Nazar L.F. Advances in Li-S batteries. *J. Mater. Chem.* 2010. 20 (44): 9821–9826.
- Mikhaylik Y.V., Kovalev I., Schock R., Kumaresan K., Xu J., Affinito J. High energy rechargeable Li-S cells for EV application: Status, Remaining Problems and Solutions. *ECS Trans.* 2010. 25 (35): 23–25.
- Hagen M., Dörfler S., Fanz P., Berger T., Speck R., Tübke J., Althues H., Hoffmann M.J., Scherr C., Kaskel S. Development and costs calculation of lithium-sulfur cells with high sulfur load and binder free electrodes. *J. Power Sources.* 2013. 224 (1): 260–268.
- Zhang S.S. Liquid electrolyte lithium/sulfur battery: Fundamental chemistry, problems, and solutions. *J. Power Sources.* 2013. 231 (1): 153–162.
- Mikhaylik Y.V., Akridge J.R. Polysulfide shuttle study in the Li/S battery system. *J. Electrochem. Soc.* 2004. 151 (11): A1969–A1976.
- Yuan L., Qiu X., Chen L., Zhu W. New insight into the discharge process of sulfur cathode by electrochemical impedance spectroscopy. *J. Power Sources.* 2009. 189 (1): 127–132.
- Cui Y., Fu Y. Polysulfide transport through separators measured by a linear voltage sweep method. *J. Power Sources.* 2015. 286 (1) 557–560.
- Diao Y., Xie K., Xiong S., Hong X. Analysis of polysulfide dissolved in electrolyte in discharge-charge process of Li-S battery. *J. Electrochem. Soc.* 2012. 159 (4) A421.
- Diao Y., Xie K., Xiong S., Hong X. Shuttle phenomenon – The irreversible oxidation mechanism of sulfur active material in Li-S battery. *J. Power Sources* 2013. 235 (1) 181–186.
- Y. Yin, S. Xin, Y. Guo, L. Wan. Lithium-Sulfur Batteries: Electrochemistry, Materials, and Prospects. *Angew. Chem. Int. Ed.* 2013. 52 (50): 13186–13200.
- Canas N. A., Wolf S., Wagner N., Friedrich K.A. In-situ X-ray diffraction studies of lithium-sulfur batteries. *J. Power Sources* 2013. 226 (1): 313–319.
- Zhang S.S. Binder based on polyelectrolyte for high capacity density lithium/sulfur battery. *J. Electrochem. Soc.* 2012. 159 (8): A1226–A1229.
- Potapenko O., Potapenko A., Zhou C., Zhang L., Xu J., Gu Z. Improved effect of water-soluble binder NV-1A on the electrochemical properties LFP Electrodes. *Rus. J. Electrochem.* 2020. 56 (12): 1043–1050.
- Першина К. Д., Сірош В. А., Глоба Н. І. Спектри електрохімічного імпедансу системи літій – сірка – біс (трифторметан) сульфонімід літію: моделювання й аналіз температурної залежності. *Наукові вісті НТУУ «КПІ»*. 2016. 109 (5): 116–126.
- Globa N.I., Sirosh V.A., Shmatok Y.V., Kirillov S.A. Enhancing of electrochemical characteristics of Li-S system by means of optimization of sulfur electrode and electrolyte composition. *Advanced Batteries, Accumulators and fuel Cells*, 21<sup>st</sup> International Conference, Brno, Czech Republic, 2020: 104–106.

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