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APPLICATION OF MODIFIED CONDUCTIVE ADDITIVES AND AQUEOUS BINDERS IN POSITIVE ELECTRODES BASED ON LITHIUM IRON PHOSPHATE FOR LITHIUM ION BATTERIES

Abdrakhmanova A.B.*[1], Kuderina B.T.[2], Omarova N.M.[3], Sabitova A.N.[1]

[1]NCJSC Shakarim University, Semey, Kazakhstan
[2]Sh. UalikhanovKokshetau University, Kokshetau, Kazakhstan
[3]Eurasian National University named after L.N. Gumilev, Nur-Sultan, Kazakhstan
E-mail: zzzk2014@mail.ru

Abstract. *Introduction.* Positive electrodes play a significant role in operation of lithium-ion batteries. The inactive constituents of the electrode coating, electrically conductive additive and binder, are key components for efficient operation of active material. Therefore, minimizing the toxicity of some and the synthesis or modification of others remain an urgent topic for increasing the energy intensity of lithium-ion batteries, which is the main goal of this work. *The purpose:* Synthesis and modification of nanostructured carbon electrically conductive additives and the study of their influence on the specific characteristics of the electrode in combination with water-soluble polymers. *Results.* During the research, the optimal compositions of the positive electrode were found: 1) using aqueous polymers, 2) with the addition of synthesized graphene oxide obtained by the Hummers method; 3) with the addition of modified carbon nanotubes obtained by the Hummers method. *Conclusion*. Graphene oxide synthesized by the Hummers method and carbon nanotubes reduced by the same method give a discharge specific capacity of more than 150 mAh/g and 140 mAh/g, respectively, with an active material theoretical capacity of 160-170 mAh/g, those using them instead of commercial conductive additives can significantly improve the specific characteristics of positive electrodes. This is due to an increase in the kinetics of lithium ion transfer inside the active material due to many structural defects due to synthesis, in addition, they are better dispersed in water, and it is also possible to obtain thick coating layers.

Keywords: lithium-ion batteries, graphene oxide, carboxymethylcellulose, styrene-butadiene rubbers, reduced carbon nanotubes, lithium iron phosphate, cathode, Hummers method.

Abdrakhmanova Azhar Bauyrzhanovna	*Master of chemistry, chemistry teacher, NCJSC Shakarim University, Semey, Kazakhstan, e-mail: zzzk2014@mail.ru*
Kuderina Balken Talgatbekovna	*Master of chemistry, chemistry teacher, Sh. UalikhanovKokshetau University, Kokshetau, Kazakhstan. e-mail:balkenkaparova@mail.ru*
Omarova Nuriya Moldagalievna	*candidate of biological sciences, chemistry teacher L.N. Gumilyov Eurasian National University, e-mail: omarovanm@enu.kz*
Sabitova Alfira Nurzhanovna	*PhD, chemistry teacher, NCJSC Shakarim University, Semey, Kazakhstan, e-mail:alfa-1983@mail.ru*

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1. Introduction

Lithium-ion batteries are one of the high energy storage devices. They are widely used in portable devices such as smartphones, laptops due to their high energy efficiency, cycling ability, no memory effect and environmental friendship. Moreover, this particular type of battery is used in electric vehicles and plug in hybrids [1,].For example, the global manufacturer of electric vehicles, the American company Tesla [2], uses complete lithium-ion batteries as an energy source in its cars. And despite the development of other types of batteries such as solid state, sodium-ion, lithium-sulphur, lithium-air and multivalent batteries, lithium-ion batteries are still likely to dominate the market for the next 10 years [3].

Like all typical batteries, lithium-ion batteries consist of a positive and a negative electrode, and an electrolyte and a separator between them to prevent short circuits. The electrodes, in turn, are obtained by applying an electrode suspension to the current collector: aluminum foil in the case of a positive electrode and copper foil in the case of a negative electrode [4]. The electrically conductive additive and polymer binder are inactive components of the electrode coating, but they play an equally important role in the electrode coating.The electrically conductive additive contributes to the electronic and ionic conductivity of the active material, while the polymer binder ensures the adhesion of the electrode coating to the current collector and the particles of the active material and the electrically conductive additive to each other [5,6].

Reducing energy costs with the environmental safety of the resulting electrodes are key tasks in the technology of lithium-ion batteries. Therefore, numerous studies in the field of modification of cathode materials remain topical [7].

The purpose of this work is the synthesis and modification of nanostructured carbon conductive additives and the study of their effect on the specific characteristics of electrode in combination with water-soluble polymers.To achieve this goal, the following tasks were defined:

- synthesis of graphene oxide by the Hummers method;
- modification of carbon nanotubes by the Hummers method;
- developmentof water technology in obtaining positive electrodes.
- manufacturing of positive electrodes based on commercial cathode materials and synthesized conductive additives;

The objects of study are positive electrodes based on lithium iron phosphate $LiFePO_4$.

The subjects of research are 1) polymers – carboxymethylcellulose(CMC) and styrene-butadiene rubber (SBR); 2) graphene oxide (GO) and carbon nanotubes (CNTs).

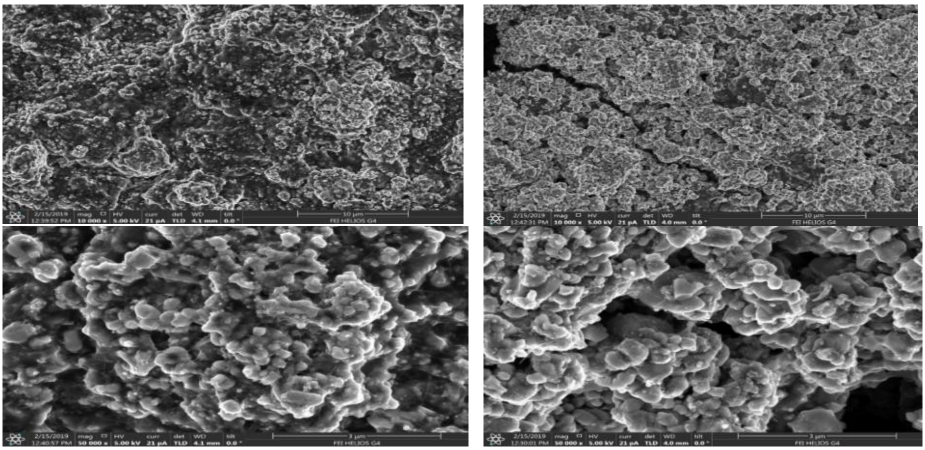
2. Results and discussion

Obtaining electrodes using aqueous polymer binders

In order to understand the behavior of aqueous polymers, SBR and CMC electrodes were obtained on their basis separately. The electrode coatings based on the polymers used are inhomogeneous, crack and have poor adhesion to aluminum foil. Application thickness 400 μm.

Since, SBR has good elasticity, viscosity, and CMC - strength. To solve this problem, it was decided to use these polymers together in a 1:1 ratio, but it was not possible to obtain satisfactory results.

Figure 1 shows SEM micrographs of positive electrodes marked CC001 and CC002. These images show that the particles of the electrodes are not completely connected with each other, there are voids and, therefore, the kinetics of the transfer of lithium ions is not satisfactory, this is confirmed by electrochemical studies of the cells. Galvanostatic cycling of the cells was carried out on an 8-channel MTI-BST8-MA power source analyzer in the voltage range of 2–4 V. The cell charge/discharge current was set at the rate of 10 mA per gram of cathode coating. Figure 6 shows the discharge curves of cells with a positive electrode based on $LiFePO_4$ and various polymer binders (4% wt.): SBR, CMC and SBR:CMC. Discharge current - 10 mA/g.



a b

Figure 1– SEM micrographs of electrodes using as a polymer binder a) SBR, b) CMC.

From this graph, shown in Figure 2, it can be seen that the sample using SBR polymer binder showed the lowest capacity. The CMC sample showed the highest capacity.

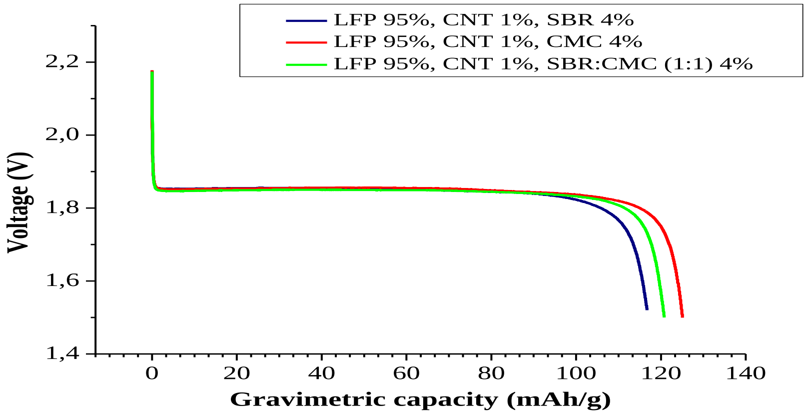


Figure 2 – Galvanostatic discharge curves of cells with a positive electrode based on $LiFePO_4$ and various polymer binders (4% wt.): SBR, CMC and SBR:CMC. Current - 10 mA/g.

Despite the fact that the sample using CMC has a higher capacity, it cannot be used only when creating a composite electrode, because electrodes at large thicknesses will crack badly and have poor adhesion to aluminum foil. Since, SBR has good elasticity, viscosity, and CMC - strength. To solve this problem, it was decided to use these polymers together in a ratio of 1:1, however, it was not possible to obtain satisfactory results, the capacity was 120 mAh/g.

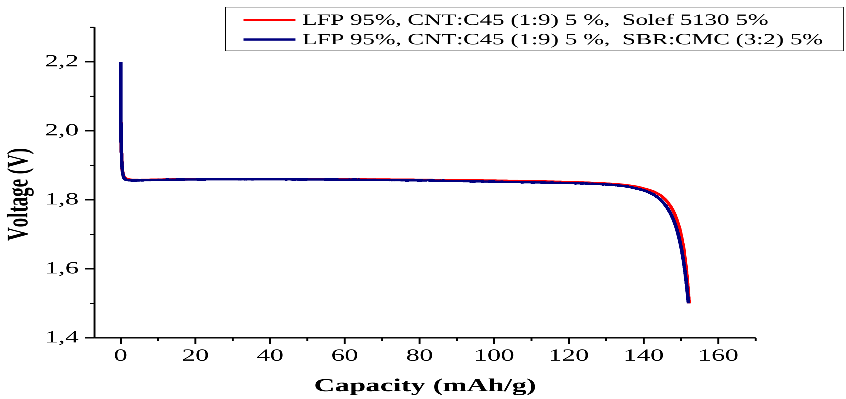


Figure 3 – Galvanostatic discharge curves of cells with a positive electrode based on $LiFePO_4$ and various polymer binders (4% by weight): Solef5130 andSBR:CMC. Current – 10 mA/g.

A comparison of the best obtained test result of an electrochemical cell with a cathode mixed with water with the results of testing an electrochemical cell with a cathode of the same composition, but already with a polymer binder PVDF is shown in figure 3, showed that the replacement with a water-soluble polymer did not affect the performance of the electrochemical cell. From this it can be concluded that the replacement of traditional polymers with water-soluble ones is carried out without loss of capacity.

Application of synthesized and modified conductive additives

Figure 4 shows galvanostatic discharge curves of cells with a positive electrode based on $LiFePO_4$ and a different composition of the conductive additive: roCNT:C45 (1:9), roCNT, CNT. It can be seen that cells with a cathode based on carbon black and modified nanotubes demonstrate the greatest capacity. The use of these conductive additives in a ratio of 1:9 improves the transport of ions inside the active material, as a result of which the results obtained show. The graph also shows curves with modified and commercial CNTs in the amount of 1%. Modified roCNTs by the Hammers method demonstrate similar results, due to many structural defects, they are better dispersed in water and also make it possible to obtain thick layers of electrode coatings.

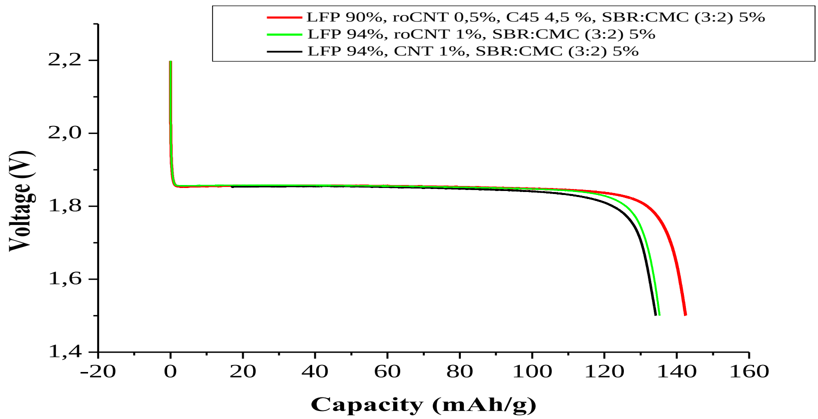


Figure 4 – Galvanostatic discharge curves of cells with a positive electrode based on $LiFePO_4$ and a different composition of the conductive additive: roCNT:C45 (1:9), roCNT, CNT.

Figure 5 shows a graph of galvanostatic discharge/charge curves of a cell with a positive electrode based on $LiFePO_4$, synthesized graphene oxide was used as a conductive additive by the Hammers method, its mass fraction in the composite electrode is 1%.

Studies show that only 1% of the synthesized conductive additive provides excellent kinetics of lithium ions, the discharge capacity of this sample is 151 mAh/g. Micrographs of the SEM of the positive electrode, shown in figure 6, indicate that due to the lamellar structure, the rGO envelops all particles of the active material, thereby increasing the electrical conductivity of the electrode.

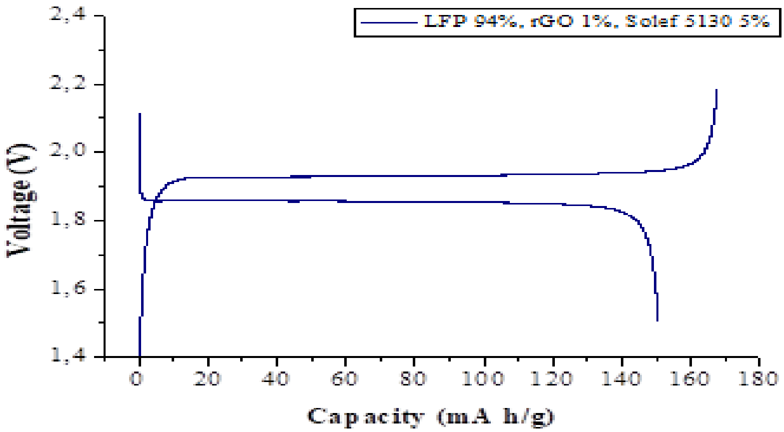


Figure 5 – Galvanostatic discharge/charge curves of an electrochemical cell with a positive electrode based on $LiFePO_4$.

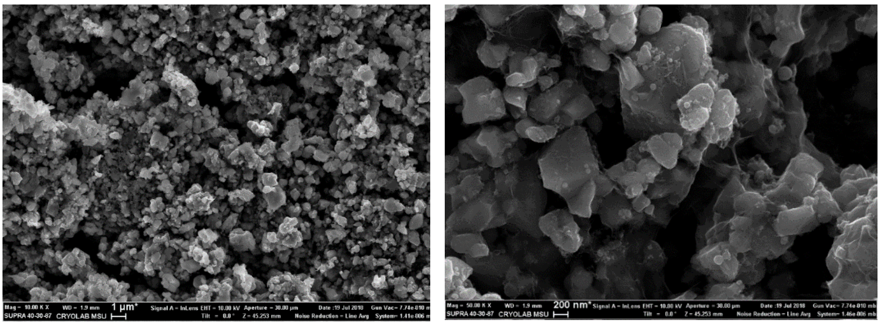


Figure 6 – SEM micrographs of a positive electrode based on $LiFePO_4$ and a conductive additive.

3. Experimental part

Synthesis of conductive additives

The chemical synthesis of graphene was carried out by the modified Hummers method. This method makes it possible to obtain a higher quality graphene oxide due to a long exposure of the reagent in an oxidized medium and thorough washing to remove by products of chemical synthesis.

The scheme of graphene oxide synthesis:

1. Intercalation of acids into graphite: graphite $+H_2SO_4$ + H_3PO_4
2. Oxidation of intercalated graphite: addition of $KMnO_4$
3. Lamination of oxidized graphite: addition of $H_2C_2O_4$
4. Dissolution of MnO_2
5. Reduction by hydrothermal method

Synthesis was carried out on the chemical reactor IKA, LR-2ST. 5.6 g of thermally expanded graphite, 1000 ml of concentrated sulfuric acid (96%) and 100 ml of phosphoric acid were added to the reactor with constant stirring (40 turn/min) and cooling for 1.5 h until a homogeneous mixture was obtained. As a result of this interaction, there is an increase in interlayer distances in graphite, that is, the intercalation of acids into the graphite structure. At the second stage, 33.6 g of potassium permanganate was added to the mixture for 30 minutes, controlling the temperature, it should not exceed 35 ° C, the mixture becomes dark green in color. This indicates the oxidation of intercalated graphite. Then turn on the heating to 50˚C and the resulting mixture is subjected to prolonged exposure with stirring for 21 h, after 21 h of stirring without heating and 17 h with heating to 50˚C. As a result, the stratification of oxidized graphite occurs, that is, the formation of particles of graphene oxide. During the synthesis, a precipitate of manganese oxide was formed, in order to dissolve it, 50 g of oxalic acid was added to the mixture. To remove by-products of the synthesis, the suspension was subjected to dialysis for 20 days, as well as centrifugation. The obtained suspension of graphene oxide was reduced by the hydrothermal method in order to obtain electrical conductivity.

The modification of carbon nanotubes was similar to the synthesis of graphene oxide, except for the amount of reagents. As a result, modified carbon nanotubes of various structures were obtained.

The process of obtaining electrodes

Obtaining a positive electrode coating begun with the kneading of the paste. To begin with, the binder polymer is dissolved in a solvent until completely dissolved on a magnetic stirrer at a temperature of 60℃. Then, the addition of a carbon conductive additive with constant stirring with an overhead stirrer at a speed of ~800 turn/min, and the final step in the preparation of the electrode paste is the gradual addition of the active material. Stirring with an overhead agitator takes ~15 h. at 1500 turn/min resulting in a homogeneous paste.

The next step was to apply a paste of the required thickness to a carbon-coated copper foil 20 μm thick using an MTI-AFA-II-V doctor blade and dry them on a thermal table at a temperature of 60℃ for at least 12 h.

The following materials were used for electrode coatings: the active material was lithium iron phosphate $LiFePO_4$ (LFP), the content of which varied in the range of 89–90%; conductive additives - carbon nanotubes TUBALL Coat_E H_2O 0.4% (Oksial, Russian Federation), reduced graphene oxide and carbon black (C45) with a content of 1 - 5%; binders - a suspension of SBR, CMC and Solef 5130 with a content of 4 - 7%, solvents - N-methylpyrrolidone (99.83%) and distilled water, as well as natural graphite in the amount of 90 - 95% and the above were used to make the negative electrode binders. The carbon conductive additives were dispersed in solution with a Bandelin ultrasonic homogenizer three to four times for 3 minutes.

Development of water technology in the preparation of positive electrodes

The peculiarity of the preparation of electrodes based on water is a significant time saving, low cost and environmental friendliness, everyone knows the fact that the vapors of the organic solvent N-methyl-2-pyrrolidone are toxic to the body. In this regard, the study of electrode coatings, synthesized carbon materials was carried out in samples prepared using aqueous polymers.

$LiFePO_4$ was used as the active material. In order to obtain the optimal composition, the amount of the conductive additive and the binder polymer were varied.

Paste mixing process with composition: LFP 90%, roCNT 0.5%, C45 (carbon black) 4.5%, SBR:CMC (3:2) 5%. CMC was dissolved in distilled water at a temperature of 80°C for ~ 30 minutes on a magnetic stirrer. Further, CNTs were dispersed in the resulting suspension with ultrasound for 10-15 minutes, after which SBR, carbon black and active material were added in turn while stirring with an overhead stirrer.

Soot was previously ground in a mortar. Stirring lasted ~ 1 hour, at a speed of 2500 turn/min. As a result, a viscous-fluid homogeneous paste was obtained.

Drying of the electrodes was carried out on a thermal table at a temperature of 60°C for at least 6 h.

Conducted electrochemical studies of electrode coatings, presented in Table 1.

Table 1– Sample data

№	Electrodes	Compound		
		Activematerial, %	Conductiveadditive, %	Polymerbinder, %
1	CC001	LFP 94%	CNT 1%	SBR 5%
2	CC002	LFP 94%	CNT 1%	CMC 5%
3	CC003	LFP 94%	CNT 1%	SBR:CMC (1:1) 5%
4	CC004	LFP 90%	CNT0.5%, C45(soot) 4.5%	SBR:CMC (3:2) 5%
5	CC005	LFP 90%	redCNT 0.5%, C45 (soot) 4.5%	SBR:CMC (3:2) 5%
6	CC006	LFP 90%	CNT 0.5%, C45 (soot) 4.5%	Solef 5130 5%

At the same time, if to pay attention to masses, then the electrode using SBR as a polymeric binder has the largest mass, and the electrode using CMC is much lighter. Based on these two parameters, it can be concluded that when using SBR, the electrode has a large mass load per cm^2.

To compare the samples obtained by the above technology with the generally accepted one, using NMP, an electrode coating CC006 was obtained. Obtaining the electrode coating was carried out similarly to the above process.

4. Conclusion

Replacing polymers that dissolve in organic solvents with water-soluble ones is a solution to the problem of environmental safety in lithium-ion battery technology. A composite in which the polymer binder is a water-soluble polymer carboxymethylcellulose (CMC) has the best discharge specific capacity, but further attempts to increase the thickness of the cathode coating are limited by the loss of its adhesion to the foil. Therefore, it is necessary to combine two water-soluble polymers - carboxymethylcellulose and styrene-butadiene rubber, the electrode with the use of which has a discharge specific capacity of 120 mAh/ g.

As a result of the research, the water technology was mastered: the optimal composition of the electrodes was found and homogeneous electrode coatings were obtained.

In the course of research, it was revealed that the use of modified carbon nanotubes by the Hammers method as conductive additives instead of commercial carbon nanotubes can significantly increase the specific characteristics of positive electrodes. This is due to an increase in the kinetics of lithium ion transfer inside the active material due to many structural defects of the conductive additive, moreover, they are better dispersed in water and also make it possible to obtain thick layers of coatings.

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Conflict of interest: there were no conflicts of interest during the study.

ПРИМЕНЕНИЕ МОДИФИЦИРОВАННЫХ ЭЛЕКТРОПРОВОДЯЩИХ ДОБАВОК И ВОДНЫХ ПОЛИМЕРНЫХ СВЯЗУЮЩИХ ВЕЩЕСТВ В ПОЛОЖИТЕЛЬНЫХ ЭЛЕКТРОДОВ НА ОСНОВЕ ФОСФАТА ЖЕЛЕЗА ЛИТИЯ ДЛЯ ЛИТИЙ ИОННЫХ АККУМУЛЯТОРАХ

Абдрахманова А.Б.[1*], Кудерина Б.Т.[2], Омарова Н.М.[3], СабитоваА.Н.[1]

[1]НАО Университет им. Шакарима, Семей, Казахстан
[2]Кокшетауский университет им. Ш.Уалиханова, Кокшетау, Казахстан
[3]Евразийский национальный университет имени Л.Н. Гумилева, Нур-Султан, Казахстан
E-mail: zzzk2014@mail.ru

Резюме. ***Введение*****.** Положительные электроды имеют значительную роль в работе литий ионных аккумуляторов. Неактивные составляющие электродного покрытия – электропроводящая добавка и полимер связующее вещество являются ключевыми компонентами для эффективной работы активного материала. Поэтому минимизация токсичности одних и синтез или модификация других остаются актуальной темой повышения энергоемкости литий ионных аккумуляторов, что является главной задачей данной работы. *Цель*. Синтез и модификация наноструктурированных углеродных электропроводящих добавок и исследование их влияния на удельные характеристики электрода в сочетании с водорастворимыми полимерами. *Результаты*. В ходе исследований были найдены оптимальные составы положительного электрода:1) с применением водных полимеров, 2) с добавлением синтезированного оксида графена, полученного методом Хаммерса; 3) с добавлением модифицированных углеродных нанотрубок, полученных методом Хаммерса. *Заключение*. Синтезированный методом Хаммерса оксид графена и восстановленные этим же методом углеродные нанотрубки выдают разрядную удельную емкость больше 150 мАч/г и 140 мАч/г соответственно, при теоретической емкости данного активного материала 160-170 мАч/г, т.е. использование их вместо коммерческих проводящих добавок позволяет значительно повысить удельные характеристики положительных электродов. Это связано с увеличением кинетики переноса ионов лития внутри активного материала из-за множества структурных дефектов вследствии синтеза, кроме того, они лучше диспергируются в воде, а также возможно получения толстых слоев покрытий.

Ключевые слова: литий-ионные аккумуляторы, оксид графена, карбоксиметилцеллюлоза, бутадиен-стирольные каучуки, восстановленные углеродные нанотрубки, метод Хаммерса

Абдрахманова Ажар Бауыржановна	*Магистр химии*
Кудерина Балкен	*Магистр химии*
Омарова Нурия Молдагалиевна	*Кандидат биологических наук*
Сабитова Альфира Нуржановна	*PhD*

ЛИТИЙ-ИОНДЫ АККУМУЛЯТОРЛАР ҮШІН ЛИТИЙ ТЕМІР ФОСФАТЫ НЕГІЗДЕГІ ОҢ ЭЛЕКТРОДТАРДА МОДИФИКАЦИЯЛАНҒАН ЭЛЕКТР ӨТКІЗГІШ ҚОСПАЛАР МЕН СУДА ЕРИТІН ПОЛИМЕР БАЙЛАНЫСТЫРҒЫШТАРДЫ ҚОЛДАНУ

Абдрахманова А.Б.[1*], Кудерина Б.Т.[2], Омарова Н.М.[3], Сабитова А.Н.[1]

[1] КеАҚ Шәкәрім атындағы университеті, Семей, Қазақстан
[2]Ш.Уалиханов атындағы Кокшетау университеті, Кокшетау, Қазақстан
[3]Л.Н.Гумилев атындағы Еуразиялық ұлттықуниверситеті, Нұр-Сұлтан, Қазақстан
E-mail: zzzk2014@mail.ru

Түйіндеме. *Кіріспе***.** Оң электродтар литий ионды аккумуляторлардың жұмысында маңызды рөл атқарады. Электродты жабындының белсенді емес компоненттері-өткізгіш қоспа және полимер байланыстырғыш белсенді материалдың тиімді жұмысының негізгі компоненттері болып табылады. Сондықтан кейбіреулердің уыттылығын азайту және басқаларын синтездеу немесе модификациялау литий-ионды аккумуляторлардың энергия сыйымдылығын арттыру осы жұмыстың негізгі міндеті болып табылады. *Мақсаты*. Наноқұрылымды көміртекті электр өткізгіш қоспаларды синтездеу және модификациялау, сонымен қатар олардың суда еритін полимерлермен үйлесімде электродтың спецификалық сипаттамаларына әсерін зерттеу. Зерттеу жұмыстарында қолданылатын карбоксиметилцеллюлоза және бутадиен-стирол каучуктары улы органикалық еріткіштерде ерітуді қажет ететін винил полимерлеріне балама алмастырғыш болып табылады. Көміртектің аллотропты модификациясы-графен және көміртекті нанотүтікшелер-электродтардың электрохимиялық қасиеттерін бірнеше рет жақсартуға қабілетті ерекше өткізгіш қасиеттерге ие. *Нәтижелер*. Зерттеу барысында оң электродтың оңтайлы құрамы анықталды: 1) су полимерлерін қолдана отырып, 2) Хаммерс әдісімен алынған синтезделген графен оксидін қосу арқылы; 3) Хаммерс әдісімен алынған модификацияланған көміртекті нанотүтікшелерді қосу арқылы. *Қорытынды*. Хаммерс әдісімен синтезделген графен оксиді мен көміртекті нанотүтікшелер осы белсенді материалдың теориялық сыйымдылығымен 160-170 мАч/г сәйкесінше 150 м Асағ/г-нан және 140 мАсағ/г-нан асатын нақты сыйымдылықты береді, яғни оларды коммерциялық өткізгіш қоспалардың орнына пайдалану оң электродтардың сипаттамаларын айтарлықтай жақсартуға мүмкіндік береді.

Түйінді сөздер: литий-ионды аккумуляторлар, графен оксиді, карбоксиметилцеллюлоза, бутадиен-стироль каучуктері, қалпына келтірілген көміртекті нанотүтікшелер, литий темір фосфаты, Хаммерс әдісі

Абдрахманова Ажар Бауыржановна	*Химия магистрі*
Кудерина Балкен	*Химия магистрі*
Омарова Нурия Молдагалиевна	*Биология ғылымдарының кандидаты*
Сабитова Альфира Нуржановна	*PhD*

References

1. Geon-Hyoung A., Do-Young L., Hyo-Jin A. Carbon-Encapsulated Hollow Porous Vanadium-Oxide Nanofibers for Improved Lithium Storage Properties. *Appl. Mater. Interfaces*,**2016**, 8, No. 30, 19466–19474. DOI: 10.1021/acsami.6b05307

2. Yangtao L., Ruihan Z., Jun W., Yan W. Current and future lithium-ion battery manufacturing. *Iscience***, 2021**, 24, No 4, 102332. DOI: 10.1016/j.isci.2021.102332

3. Tran H.-Y., Greco G., Täubert C., Wohlfahrt-Mehrens M., Haselrieder W., Kwade A. Influence of electrode preparation on the electrochemical performance of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ composite electrodes for lithium-ion batteries. *J. of Power Sources*, **2012**, 210, 276-285. DOI: org/10.1016/j.jpowsour.2012.03.017

4. Mostafa V., Mahmoud A., Seyed F., Chavoshian N. Experimental investigation of effect of PP/SBR polymer blends on the moisture resistance and rutting performance of asphalt mixtures. *Con. and Build.Mater.*,**2020**, 253, 119197. DOI: org/10.1016/j.conbuildmat.2020.119197

5. Sushma J., Vaishali B., Deepti T. Dielectric properties of MWCNT dispersed conducting polymer nanocomposites films of PVA-CMC-PPy. *Mater.today:proceedings*, **2021**, 45, No 2, 4824-4829. DOI:10.1016/j.matpr.2021.01.294

6. Aravamudhan A., Ramos D.M., Nada A.A., Kumbar S.G. Natural Polymers: Polysaccharides and Their Derivatives for Biomedical Applications. Chapter 4 in: *Natural and Synthetic Biomedical Polymers*, **2014**, 67-89, DOI: org/10.1016/B978-0-12-396983-5.00004-1

7. Atif R., Inam F. Reasons and remedies for the agglomeration of multilayered graphene and carbon nanotubes in polymers. *Beilstein J. Nanotechnol.*, **2016**, 11734-1196, DOI:10.3762/bjnano.7.109.