IRSTI 29.19.21 29.15.53 https://doi.org/10.26577/RCPh.2022.v81.i2.010

Zh.T. Bugybay[1,2*], M.T. Aitkulov[1], E.E. Beisenova[2], A.M. Akhanov[1]
[1]Institute of Nuclear Physics, Kazakhstan, Almaty
[2]Satbayev University, Kazakhstan, Almaty
*e-mail: zh.bugybay@inp.kz

APPLICATION OF THE NEUTRON RADIOGRAPHY METHOD TO STUDY THE MIGRATION OF LITHIUM IONS IN ELECTRIC BATTERIES DURING DISCHARGE

Li-ion batteries are widely used in modern technology as a reliable and stable power source. They are a pair of electrodes separated by a special material impregnated with electrolyte. The charge carriers in such devices are lithium ions. One of the factors affecting the performance of such batteries is the migration of lithium ions. Studies have shown that anisotropic migration of lithium ions on the electrode leads to local lattice dislocations. As a result, the structure of the anode ceases to be heterogeneous, which leads to inefficient movement of charges in it and, accordingly, to a decrease in battery efficiency [1]. Therefore, new types of lithium-ion batteries with increased efficiency are being developed and existing ones are being improved. To this end, research is being carried out, in particular to investigate the migration processes and behavior of lithium in batteries. One of the effective non-destructive methods for such studies is neutron radiography, as the total microscopic cross section of ^{6}Li interaction with neutrons is about 940 barns [2]. In addition, modern neutron radiography facilities allow us to *in situ* study the internal processes in lithium-ion batteries.

This article presents the results of a real-time study of the distribution of lithium in two commercial types of lithium-ion batteries during their discharge. The research was carried out by a non-destructive method at the TITAN neutron radiography facility. As a result of the research, experimental data were obtained on the migration and distribution of lithium in batteries in different states. It is shown that when the battery is discharged, lithium ions migrate to the cathode at a rate of 0.83×10^{-5} and 0.36×10^{-4} cm/s.

Key words: LIB, neutron radiography, WWR-K, migration of lithium ions.

Ж.Т. Бұғыбай[1,2*], М.Т. Айткулов[1], Е.Е. Бейсенова[2], А.М. Аханов[1]
[1]Ядролық физика институты, Қазақстан, Алматы қ.
[2]Satbayev University, Қазақстан, Алматы қ.
*e-mail: zh.bugybay@inp.kz

Электрлік аккумуляторлардағы литий иондарының разряд кезіндегі миграциясын зерттеу үшін нейтронды рентгенография әдісін қолдану

Литий-ионды батареялар сенімді және тұрақты қуат көзі ретінде заманауи технологияда кеңінен қолданылады. Олар электролитпен сіңдірілген арнайы материалмен бөлінген жұп электродтардан тұрады. Мұндай құрылғылардағы заряд тасымалдаушылар литий иондары болып табылады. Мұндай батареялардың жұмысына әсер ететін факторлардың бірі литий иондарының миграциясы болып табылады. Зерттеулер көрсеткендей, литий иондарының электродтағы анизотропты миграциясы кристалдық тордың жергілікті дислокациясының пайда болуына әкеледі. Нәтижесінде анодтың құрылымы біртексіз болуды тоқтатады, бұл ондағы зарядтардың тиімсіз қозғалуына және сәйкесінше батареяның тиімділігінің төмендеуіне әкеледі [1]. Сондықтан тиімділігі жоғары литий-иондық батареялардың жаңа және жетілдірілген түрлері әзірленуде. Ол үшін көптеген зерттеулер, атап айтқанда, батареялардағы литийдің миграция процесі мен литий иондарының қозғалыс жылдамдықтарын зерттеуге бағытталған. Мұндай зерттеулердің тиімді әдістерінің бірі нейтрондық радиография бұзбайтын әдісі болып табылады, өйткені ^{6}Li нейтрондармен әрекеттесуінің жалпы микроскопиялық қимасы шамамен 940 барн ды құрайды [2]. Сонымен қатар, қазіргі заманғы нейтронды радиография қондырғылары литий-иондық аккумуляторлардағы ішкі процестерді нақты уақыт режимінде зерттеуге мүмкіндік береді.

Бұл мақалада литий-ионды аккумуляторлардың екі коммерциялық түріне литийдің нақты уақыт режимінде зарядсыздану кезінде таралуын зерттеу нәтижелері берілген. Зерттеулер TITAN нейтронды радиографиялық қондырғыда бұзылмайтын әдіспен жүргізілді. Зерттеу нәтижесінде әртүрлі күйдегі аккумуляторлардағы литийдің миграциясы және таралуы туралы тәжірибелік деректер алынды. Батарея зарядсызданған кезде литий иондары катодқа 0,83·10^{-5} және 0,36·10^{-4} см/с жылдамдығымен көшетіні көрсетілген.

Түйін сөздер: ЛИБ, нейтрондық радиография, ССР-Қ, литий ионының миграциясы.

Ж.Т. Бугыбай[1,2*], М.Т. Айткулов[1], Е.Е. Бейсенова[2], А.М. Аханов [1]
[1]Институт ядерной физики, Казахстан, г. Алматы
[2]Satbayev University, Казахстан, г. Алматы
*e-mail: zh.bugybay@inp.kz

Применение метода нейтронной радиографии для исследования миграции ионов лития в электрических батареях в процессе разряда

Литий-ионные батареи широко используются в современной технике в качестве надежного и стабильного источника питания. Они представляют собой пару электродов, разделенных специальным материалом пропитанным электролитом. Носителями заряда в таких устройствах являются ионы лития. Одним из факторов, влияющим на работу таких батарей, является миграция ионов лития. Исследования показали, что анизотропная миграция ионов лития на электроде приводит к возникновению локальных дислокаций кристаллической решетки. В результате этого структура анода прекращает быть неоднородной, что приводит к неэффективному передвижению зарядов в нем и соответственно к снижению эффективности батареи [1]. Поэтому разрабатываются новые и улучшаются существующие типы литий-ионные батареи с повышенной эффективностью. Для чего проводятся исследования, в частности, направленные на изучение процессов миграции и поведения лития в батареях. Одним из эффективных неразрушающих методов таких исследований является нейтронная радиография, поскольку полное микроскопическое сечение взаимодействия ^{6}Li с нейтронами составляет около 940 барн [2]. Кроме того, современные установки нейтронной радиографии позволяют исследовать внутренние процессы в литий-ионных батареях в режиме реального времени.

В настоящей статье приведены результаты исследования распределения лития в двух коммерческих типах литий-ионных батареях в процессе их разрядки в режиме реального времени. Исследования проведены неразрушающим методом на установке нейтронной радиографии TITAN. В результате проведенных исследований были получены экспериментальные данные о миграции и распределении лития в батареях в разных состояниях. Показано, что при разрядке батареи происходит миграция ионов лития к катоду со скоростью 0,83·10^{-5} и 0,36·10^{-4} см/с.

Ключевые слова: ЛИБ, нейтронная радиография, ВВР-К, миграция ионов лития.

Introduction

Lithium-ion batteries (LIBs) have the best complex characteristics among currently existing secondary batteries, due to high energy density, long service life, non-toxicity, absence of environmental pollution, flexibility and lightness of design [3]. Currently, LIBs are widely used to power portable electronic devices. The LIB consists of three main components: electrode materials (cathode and anode), electrolyte and current collectors. During the electrochemical reaction in the electrodes, the distribution of lithium ions on the surface and inside the electrode is different, which manifests as a concentration gradient of lithium ions, which in turn leads to the migration of lithium ions. In most cases the migration of lithium ions plays an important role in the kinetic processes occurring in the electrode materials, as the migration determines the reaction rate in the electrode materials and as a result the speed characteristics of the electrode [4, 5]. Lithium ion migration also affects lattice deformation, which is crucial in limiting battery life. For this reason a great deal of attention has been paid to research into the materials and processes involved in lithium-ion batteries [6-10]. Methods such as X-ray powder diffraction, X-ray photoelectron spectroscopy and other methods are used to study the migration of lithium ions. [11]. One of the effective methods of studying the migration of lithium ions in LIBs is the non-destructive method of neutron radiography. As the following nuclear reaction takes place on lithium: $^{6}Li+n \rightarrow ^{3}H+^{4}He+4.78$ MeV. The total cross-section of the interaction of this nuclear reaction is about 940 barns. In this work, the method of neutron radiography and tomography was used to study the migration and distribution of lithium ions in commercial types of lithium-ion batteries during their discharge.

Materials and methods

In this paper, two types of commercial lithium-ion batteries were investigated: CR2016 and CR2032. The CR2016 battery has a diameter of 20 mm and a thickness of 1.6 mm. The electrical capacity of the battery is 90 mAh. The CR2032 battery has a diameter of 20 mm and is 3.2 mm thick. The electrical capacity of the battery is 230 mAh. The sample batteries are shown in figure 1.

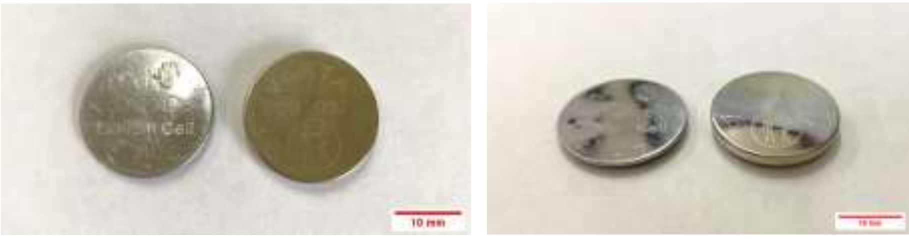


Figure 1 – Outside view of the tested batteries

The cathode in the two types of battery is manganese dioxide and the anode is lithium. The batteries also use an organic electrolyte and a polypropylene separator. The battery case is made of stainless steel.

Neutron radiography and tomography were used to study the migration process of lithium ions in these types of batteries. The essence of the neutron radiography method is that the object under study is irradiated with a collimated neutron flux, where the difference in neutron absorption cross sections for different elements of the object provides information about the internal distribution of inhomogeneities of the materials under study. The detector records the distribution of the neutron flux behind the object. The neutron radiography method is shown schematically in Figure 2.

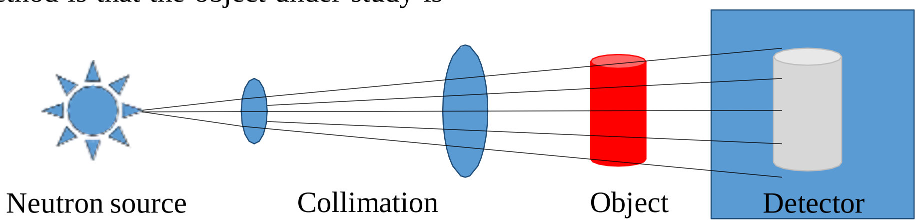


Figure 2 – Schematic diagram of the neutron radiography method

Neutron radiation passing through the material will weaken and is described by the formula (1) – the Beer–Lambert law [12].

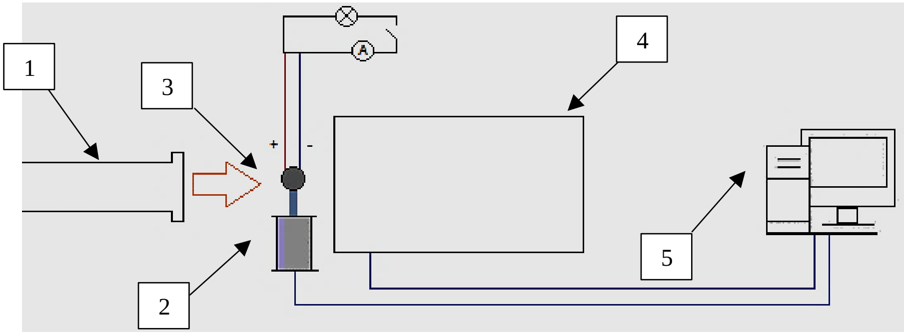
$$I = I_0 e^{-\int_0^t N(x)\sigma(x)dx}. \quad (1)$$

The degree of attenuation of radiation will depend on two processes - scattering and absorption. A radiation attenuation coefficient (μ) is introduced to quantify this value. Substituting this coefficient into the formula (1), the Beer–Lambert law is transformed into (2). This value describes the degree of penetration of the radiation into the material.

$$I = I_0 e^{-\mu x}. \quad (2)$$

During the experiments, the batteries were connected to a 0.068 W resistive load (see Fig. 3) and were irradiated with a polychromatic neutron beam. During the tomographic images, the batteries rotated around the central axis. All neutron images were processed and analyzed in the ImageJ program [13]. In addition, due to the irregularity of the neutron beam, each type of sample in each experiment, images of an open beam (Open Beam) with an open gate (protective shutter) and a dark background with a closed gate (Dark Field) were taken. The dark background is eliminated by pixel-wise subtraction of the average dark background image without the neutron beam. The image was corrected according to formula (3) [14, 15].

$$P_n = -log\left(\frac{I_{proj} - I_{dark\ field}}{I_{open\ beam} - I_{dark\ field}}\right). \quad (3)$$

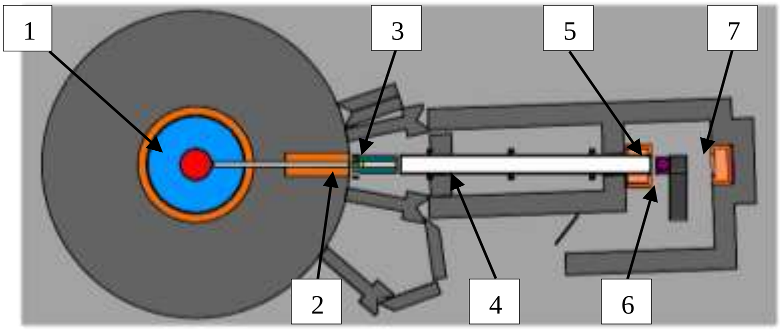


1 – neutron guide, 2 – goniometer, 3 – sample, 4 – detector system, 5 – PC.

Figure 3 – Electrical scheme of the experiment.

TITAN facility

Neutronographic experiments were carried out on the TITAN neutron radiography facility [16,20]. A schematic view of the facility is shown in Figure 4. The facility is located on the first horizontal channel of the WWR-K research reactor [17-19]. The parameters of the TITAN facility that were used during the experiments are shown in Table 1.



1 – WWR-K reactor core, 2 –shutter, 3 – collimator and neutron beam filter, 4 – neutron guide, 5 – goniometer, 6 –detector system, 7 –beam stop.

Figure 4 – The layout of the main elements of TITAN facility (top of view).

Table 1 – TITAN setup parameters during experiments

Energy spectrum of neutrons	Maxwell spectrum (thermal neutrons)
Distance from the moderator to diaphragm	3.5 m
Distance from diaphragm to sample L	7 m
Hole diameter D	20 mm
L/D	350
Field of view	9*9 cm^2
Scintillation screen	^{6}LiF/ZnS: Ag –thickness 0.1 mm
Camera CCD	HAMAMATSU-S12101 2048*2048 pixels, size 12*12 μm Full size 24x24 mm
Thermal neutron flux per sample	1.2*10^7 n/cm^2/sec at L/D=350
Neutron filter	Sapphire (thickness - 106 mm)
Standard exposure time	20 sec

The neutron beam of the facility is formed using a simple collimator system, which consists of several boron-contained polyethylene and cadmium disks with different collimator pinholes with variable aperture diameters D from 5 to 90 mm. To increase the characteristic parameter L/D, a neutron guide was installed behind the protective shutter. This allow to increase aperture-detector distance L and total distance is 7 m. The characteristic parameter L/D can be changed from 75 to 1400. To suppress background gamma and fast neutron radiation, a cylindrical single-crystal sapphire filter, with thickness 106 mm and diameter 110 mm, is mounted in the collimator system. Environment in neutron guide is vacuum which necessary to reduce neutron beam losses due to an air scattering. Maximum thermal neutron flux at the sample position is 10^8 $cm^{-2}s^{-1}$.

Results and discussion

The lithium ion dynamics were controlled until the batteries were completely discharged. Three-dimensional neutron images of the studied batteries in charged and discharged states are shown in Figures 5 and 6. The figures visually show the migration of lithium ions from the negatively charged electrode (anode) to the positively charged electrode (cathode) as the batteries are discharged. According to [5, 6], three pathways for the migration of lithium ions in batteries are possible: (1) pathway, along the direction; (2) pathway, a zigzag trajectory in the crystal plane; (3) pathway, in the crystal plane. Each path has its own migration barrier energy. The migration of lithium ions in a battery is a complex process and cannot be described by Fick's second law.

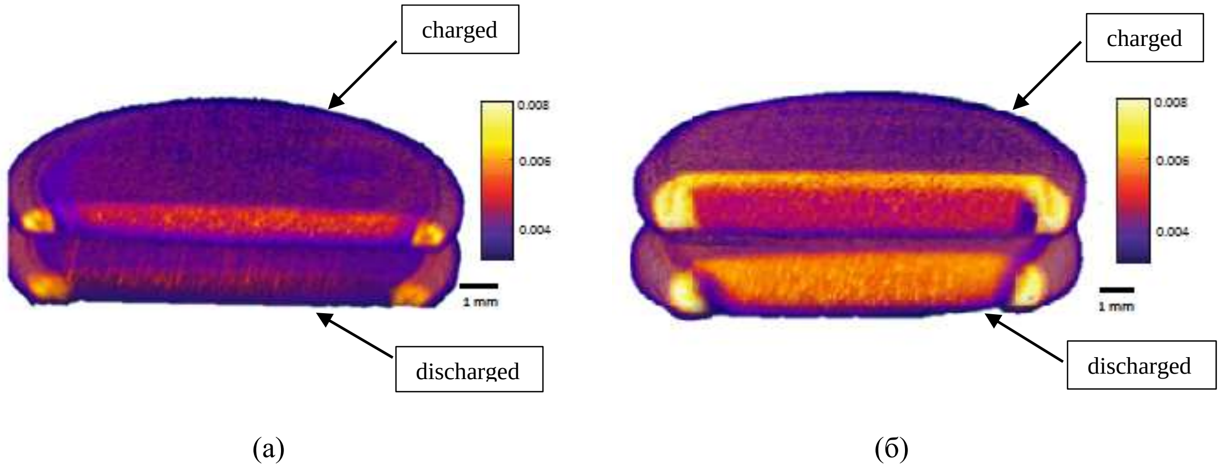


Figure 5 – Three-dimensional image of the battery: (a) CR2016; (b) CR2032

Figure 6 shows the distributions of the linear attenuation coefficient of neutron radiation over the thickness of the batteries during their discharge. The graphs show that in the CR2016 battery the peak of the neutron attenuation coefficient during discharge, and therefore the maximum concentration of lithium, has moved 0.3 mm closer to the cathode (Fig. 6(a)). In a CR2032 battery, the migration of lithium ions across the battery, from anode to cathode, and the saturation with lithium of the area close to the cathode is clearly demonstrated (Fig.6(b)).

The migration rate of lithium ions was: for CR2016 – 0.83×10^{-5} cm/s; for CR2032 - 0.36×10^{-4} cm/s.

It should be noted that the behavior of lithium ions in the studied batteries is different. In the CR2032 battery, lithium ions, during discharge, were distributed almost evenly over the entire thickness. Whereas in CR2016 batteries, lithium ions were moved to the area of the separator with the electrolyte.

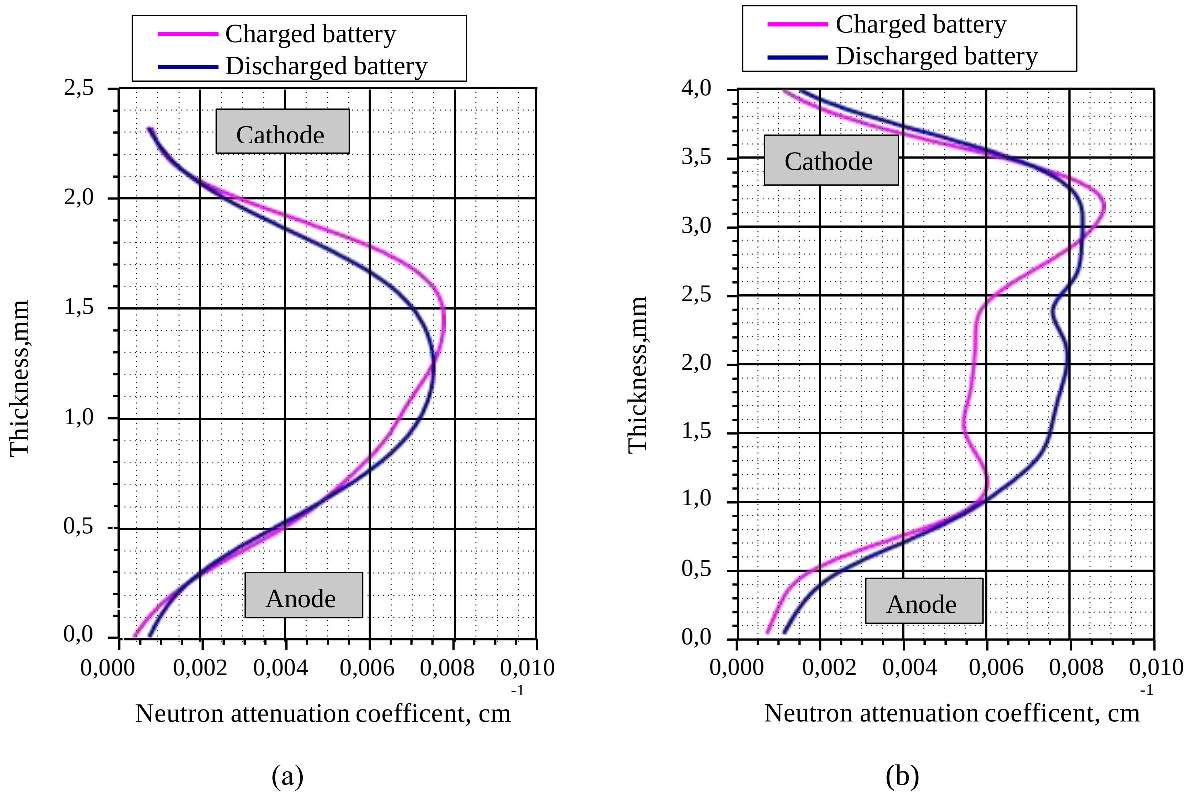


Figure 6 – Distribution of neutron attenuation coefficient by battery thickness: (a) CR2016; (b) CR2032

Conclusions

In this work, two types of commercial lithium-ion batteries CR2016 and CR2032 were investigated by neutron radiography. These batteries have different electrophysical characteristics. Experimental studies were carried out in real time with the connection of a resistive load to the batteries.

As a result of this research, the migration of lithium ions and their distribution in the battery during discharge was studied. It is shown that lithium ions migrate from the anode to the cathode. The lithium ion migration velocity was: for CR2016 $0.83{\cdot}10^{-5}$ cm/s, for CR2032 $0.36{\cdot}10^{-4}$ cm/s. The results obtained help to understand the migration of lithium ions in the batteries under consideration. Three-dimensional tomography of batteries also showed intuitive images of the migration of lithium ions in batteries during their discharge.

References

1 Yang Z., Gu L., Hu Y.S., & Li H. Atomic-scale structure-property relationships in lithium ion battery electrode materials //Annual Review of Materials Research. – 2017. – Vol.47. – P.175-198.
2 https://atom.kaeri.re.kr/ – Nuclear database.
3 Wu Musheng, Xu Bo, Ouyang Chuying. Physics of electron and lithium-ion transport in electrode materials for Li-ion batteries //Chinese Physics B. – 2016. – Vol. 25(1). – Art.No 018206.
4 Siegel J.B. et al. Neutron Imaging of Lithium Concentration in LFP Pouch Cell Battery //J. Electrochem. Soc. – 2011. – Vol.158. – P.A523-A528.
5 Butler L.G., Lehmann E.H., Schillinger B. Neutron radiography, tomography, and diffraction of commercial lithium-ion polymer batteries //Physics Procedia. – 2013. – Vol.43. – P.331 – 336.
6 Jia M., Wang H., Sun Z., Chen Y., Guo C. and Gan L. Exploring ion migration in Li2MnSiO4 for Li-ion batteries through strain effects //RSC Adv. – 2017. – Vol.7. – P.26089–26096.
7 Luo Y., Shui M., Shu J. Understanding the lithium transport mechanism in monoclinic Li3V2(PO4)3 cathode material by atomistic simulation //Results in Physics. – 2019. – Vol.14. – Art.No 102490.
8 Yang F. Field-Limited Migration of Li-Ions in Li-Ion Battery //ECS Electrochemistry Letters. – 2015. – Vol.4 (1). – P.A7-A9.
9 Kordatos A., Kuganathan N., Kelaidis N., Iyngaran P., Chroneos A. Defects and lithium migration in Li2CuO2 //Scientific reports. – 2018. – Vol.8. – P.6754.

10 Choo Y., Halat D.M., Villaluenga I., Timachova K., Balsara N.P. Diffusion and migration in polymer electrolytes //Progress in Polymer Science. – 2020. – Vol.103. – P.101220.
11 Lee Y.S., Ryu K.S. Study of the lithium diffusion properties and high rate performance of $TiNb_6O_{17}$ as an anode in lithium secondary battery //Sci Rep. – 2017. – Vol.7. – P.16617.
12 Raventosa M., Hartia R.P, Lehmann E. and Grünzwei C. A method for neutron scattering quantification and correction applied to neutron imaging //Physics Procedia. – 2017. – Vol.88. P.275-281.
13 Collins TJ. ImageJ for microscopy // Biotechniques. – 2007. – Vol.43. – P.25-30.
14 Carminati C., Boillat P., Schmid F., Vontobel P., Hovind J., Morgano M., Raventos M., Siegwart M., Mannes D., Gruenzweig C., Trtik P., Lehmann E., Strobl M., Kaestner A. Implementation and assessment of the black body bias correction in quantitative neutron imaging. //PLoS ONE. – 2019. – Vol. 14(1). – e0210300.
15 Abd el Bar W., Imbaby I. Mahmoud, Hussein A. Konber, T. Mongy Image reconstruction technique using projection data from neutron tomography system // Alexandria Engineering Journal. – 2015. – Vol.54. – P.1057-1066.
16 Nazarov K.M., Muhametuly B., Kenzhin E.A., Kichanov S.E., Kozlenko D.P., Lukin E.V., Shaimerdenov A.A. New neutron radiography and tomography facility TITAN at the WWR-K reactor //Nuclear Inst. and Methods in Physics Research A. – 2020. – Vol.982. – P.164572.
17 Аринкин Ф.М., Шаймерденов А.А., Гизатулин Ш.Х., Дюсамбаев Д.С., Колточник С.Н., Чакров П.В., Чекушина Л.В. Конверсия активной зоны исследовательского реактора ВВР-К // Атомная энергия. – 2017. – 1 (123). – С. 15-20.
18 Shaimerdenov A.A., Nakipov D.A., Arinkin F.M., Gizatulin Sh.Kh., Chakrov P.V., and Kenzhin Ye.A. The 50th Anniversary of the WWR-K Research Reactor // Physics of Atomic Nuclei. – 2018. – Vol. 81, No. 10. – P.1408–1411.
19 Bauyrzhan A.B., Koltochnik S.N., Aitkulov M.T., Dyussambayev D.S., Shaimerdenov A.A., Mukhametuly B., Burtebaev N.T. Neutron-physical parameters at the outlet of the WWR-K reactor beam tube. //Eurasian Journal of Physics and Functional Materials. – 2019. – Vol.3(3). – P.219-225.
20 Nazarov K.M., Kichanov S.E., Lukin E.V., Zel I.Yu., Kozlenko D.P., Zholdybayev T.K., Muhametuly B., Kenessarin M., Rutkauskas A.V., Yskakov A., Belova M.O. A comparative study of promising filter materials for neutron imaging facilities //Eurasian Journal of Physics and Functional Materials. – 2021. – Vol.5(4). – P.169-180.

References

1 Z. Yang, L. Gu, Y.S. Hu, & H. Li Annual, Review of Materials Research, 47, 175-198 (2017).
2 https://atom.kaeri.re.kr/ link to Nuclear database
3 Wu Musheng, Xu Bo, Ouyang Chuying, Chinese Physics B, 25(1), 018206 (2016).
4 J.B. Siegel et al., J. Electrochem. Soc. 158, A523-A528 (2011).
5 L.G. Butler, E.H. Lehmann, B. Schillinger, Physics Procedia, 43, 331–336 (2013).
6 M. Jia, H. Wang, Z. Sun, Y. Chen, C. Guo and L. Gan, RSC Adv.,7, 26089-26096 (2017).
7 Y. Luo, M. Shui, J. Shu, Results in Physics 14, 102490 (2019).
8 F. Yang, ECS Electrochemistry Letters, 4 (1), A7-A9 (2015).
9 A. Kordatos, N. Kuganathan, N. Kelaidis, et al., Scientific reports, 8, 6754 (2018).
10 Y. Choo, D.M. Halat, et.al., Progress in Polymer Science, 103, 101220 (2020).
11 Y.S. Lee, K.S. Ryu, Scientific reports, 7, 16617 (2017).
12 M. Raventosa, R.P. Hartia, E. Lehmann and C. Grünzwei, Physics Procedia, 88, 275-281, (2017).
13 T.J.Collins, Biotechniques, 43, 25-30 (2007).
14 C. Carminati, P. Boillat, F. Schmid, P. Vontobel, J. Hovind, M. Morgano, et al, PLoS ONE 14(1). e0210300 (2019).
15 Waleed Abd el Bar, Imbaby I. Mahmoud, Hussein A. Konber, T. Mongy, Alexandria Engineering Journal, 54, 1057-1066 (2015).
16 K.M. Nazarov, B. Muhametuly, E.A. Kenzhin, S.E. Kichanov, D.P. Kozlenko, E.V. Lukin, A.A. Shaimerdenov, Nuclear Inst. and Methods in Physics Research, 982, 164572 (2020).
17 Arinkin F.M., Shaimerdenov A.A., Gizatulin Sh.Kh., Dyusambaev D.S., Koltochnik S.N., Chakrov P.V., Chekushina L.V., Atomnaya energiya, 1 (123), 5-20 (2017). (in Russ)
18 A.B. Bauyrzhan, S.N. Koltochnik, M.T. Aitkulov, D.S. Dyussambayev, A.A. Shaimerdenov, B. Mukhametuly, N.T. Burtebaev, Eurasian Journal of Physics and Functional Materials, 3(3), 219-225 (2019).
19 K.M. Nazarov, S.E. Kichanov, et.al., Eurasian Journal of Physics and Functional Materials, 5(4), 169-180 (2021).
20 K.M. Nazarov, S.E. Kichanov, et.al., Eurasian Journal of Physics and Functional Materials, 5(4), 169-180 (2021).