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Application of ion modification for alteration of anode materials based on ZnO/CoZn nanostructures

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ABSTRACT

During the conducted studies, it was established that the use of ion modification by irradiation with O^+ and Ar^+ ions makes it possible to elevate the degradation resistance of anode materials due to the effect of vacancy defect creation, the density of which varies with the irradiation fluence. At the same time, the analysis of changes in the band gap and the optical density value, expressing changes in structural distortions, revealed that ion irradiation leads to a rise in the stability of the preservation of electronic properties during long-term resource tests, which are inextricably linked with the degradation of ZnO/CoZn nanostructures due to oxidation processes as a result of lithiation. During assessment of changes in the parameters of the band gap and optical density of the samples after resource tests, it was found that the observed growth in these indicators is due to oxidation processes and partial amorphization due to the formation of oxide inclusions in the structure of nanowires, the presence of which is due to the interaction of nanostructures with the electrolyte over a long period of time during charging/discharging, which results in near-surface layer degradation due to the introduction of oxygen, and in the case of a long service life, to the formation of oxide inclusions that elevate the density of defects and vacancies in the structure. According to tests of synthesized ZnO/CoZn nanostructures as anode materials, it was found that the use of O^+ and Ar^+ ions not only leads to a growth in the degradation resistance of capacitive characteristics during long-term tests, but also to the stability maintenance of indicators with a reversible decrease in the charging rate at charging rate variation.

1. Introduction

Ionic modification of nanostructured materials used as a basis for anode materials of lithium-ion batteries is one of the most promising methods for elevation of the operation efficiency and stability maintenance of the capacitive characteristics of anode materials during long-term operation of the battery [1–4]. This method is based on the mechanisms of creation of radiation-induced point and vacancy defects, the presence of which affects both conductive and structural properties. In this case, as a rule, the creation of radiation defects is caused by the interaction of incident particles (heavy ions, electrons, in some cases neutron radiation is used) with the crystalline structure, as a result of which processes of dissipation of the energy transferred by incident particles into the irradiated material arise, which are accompanied by ionization and athermal processes [5,6]. Ionization processes, as a rule, cause a redistribution of electron density associated with the detachment of electrons and the formation of holes, the appearance of which can be accompanied by cascade effects if a large amount of energy is transferred to the electrons as a result of collisions with an incident particle [7,8]. Athermal processes caused by irradiation can lead to the occurrence of thermal annealing effects of structural distortions in the case of low irradiation fluences, when the metastable regions formed as a result of athermal processes are isolated from each other (as a rule, such effects are observed at irradiation fluences of the order of 10^{10}–10^{11} ion/cm^2). In this case, the emergence of metastable (thermally overheated regions) in very short periods of time (on the order of

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10^{-11-13} s) can be accompanied by processes of structural rearrangement or relaxation, which in the case of synthesized nanostructured materials (which, regardless of the method of production, contain a large number of structural defects associated with the processes of formation and nucleation) can have a positive effect on the overall structural ordering degree, as well as reduce the defective or metastable inclusion concentration [9–11]. Also, exposure to ionizing radiation, in the case of small doses, can lead to the creation of barrier effects, the presence of which can have a positive effect on enhancement of resistance to oxidation and destruction processes that are initiated during long-term use of batteries and are associated with charging/discharging processes [12–14]. During long-term use of anode materials, during charging/discharging, lithium and oxygen are introduced into the near-surface layer of the anode material, which in turn can result in accelerated destruction and a decrease in the capacity characteristics of batteries due to the formation of oxide inclusions that can lead to amorphization or destructive partial destruction [15,16]. In some cases, such degradation effects can result in sharp reduction in capacitive characteristics (more than 30–50 % of the initial values), which significantly limits the service life of the anode material and the battery as a whole [17,18]. The use of the ion modification method in this case can contribute to an elevation in the stability of the material not only due to the partial relaxation of structural distortions (associated with growth processes), but also to a rise in the service life due to the creation of barrier effects resulting in degradation rate reduction [19–21]. In this case, the resulting effects of anisotropy of the electron density distribution associated with ionization processes of irradiation can have a significant impact on the charge transfer mechanisms, which will contribute to a magnification in capacitive characteristics, alongside the operation stability growth during long-term charging/discharging, and in the case of an alteration in the charging/discharging rate, contribute to the capacitive parameter stability maintenance.

The aim of this study is to determine the prospects of using the ion modification method to enhance the efficiency of using ZnO/CoZn nanostructures as a basis for anode materials and to improve their capacitive characteristics. The choice of these structures as objects of study is due to the possibilities of creating new highly efficient materials capable of replacing traditional silicon and sulfur-containing or nickel anode materials used in modern batteries with more efficient and degradation-resistant materials, the enhancement in efficiency of which is explained by the nanosized grains of which the structures consist, alonside the combination of their structural, optical and electronic properties. These nanostructures, in addition to their use as a basis for anode materials of lithium-ion batteries, also have quite large potential for application in photocatalysis, when used for the decomposition of organic dyes, as well as the capture of heavy metals from aqueous media [22–27]. The use of the ion modification method by exposing structures to heavy ions with fluences characteristic of creating single defective areas will make it possible to make changes to the charge distribution, as well as create additional vacancy defects, the concentration of which will facilitate charge transfer, and will also enhance degradation resistance during long-term resource testing.

2. Materials and methods

The synthesized cylindrical ZnO/CoZn nanostructures were subjected to heavy ion irradiation in order to conduct studies aimed at study of the prospects of using ionizing radiation in order to elevate the productivity of anode materials for lithium-ion batteries, in particular, to magnify the capacitive characteristic maintenance stability for a longer time. To synthesize ZnO/CoZn nanostructures of a given geometry (400 nm in diameter and 10 μm in height), a template synthesis method was used, in which polymer films based on polyethylene terephthalate with a pore density of 4×10^7 pores/cm^2 were used as template matrices. For the synthesis of nanostructures, a sulfuric acid solution was used – an electrolyte prepared using the following chemical reagents: $CoSO_4 \cdot 7H_2O$ (167 g/l), $ZnSO_4$ $7H_2O$ (58 g/l), H_3BO_3 (45 g/l), ascorbic acid C_8H_8O (1.5 g/l) [22]. Electrochemical deposition was carried out at an applied potential difference of 2.5 V, which made it possible to obtain structures with a phase composition of the ZnO/CoZn type, in which the cubic phase Co_2Zn_{11} dominates. The deposition process was monitored using the chronoamperometry method, the use of which made it possible to control the change in the geometry of the resulting nanostructures filling the pores of the polymer template during the synthesis process.

Ionic modification associated with irradiation of the obtained nanostructures with O^+, Ar^+ and Kr^+ ions with energies of 28, 31.5 and 147 MeV was carried out at the heavy ion accelerator DC-60, located in the Astana branch of the Institute of Nuclear Physics (Astana, Kazakhstan). The samples were placed on a special holder that allowed the sample geometry to be maintained parallel to the ion penetration depth in the material, which allowed simulating the ion impact processes with maximum efficiency (see Fig. 1).

Irradiation was implemented by placing ZnO/CoZn nanostructure samples synthesized in polymer templates on a target holder in such a way that passing ions could interact with maximum efficiency. For this purpose, samples of ZnO/CoZn nanostructures were placed on a target holder parallel to the ion beam. Irradiation fluences (10^{10}-10^{11} ion/cm^2) were chosen to achieve maximum ion modification efficiency without the destructive effect that occurs during high-dose irradiation. The choice of the ion type for modification was determined by the calculated data on the values of ionization losses of heavy O^+, Ar^+ and Kr^+ ions with energies of 28, 31.5 and 147 MeV, respectively. The calculations were performed using the SRIM Pro software code, according to which the maximum path length of O^+ and Ar^+ ions with the selected energies is about 7–8 μm, and in the case of using Kr^+ ions, the path length is close to 10 μm, which corresponds to the length of the ZnO/CoZn nanostructures used. Calculations of ion path lengths in nanostructures were performed using the SRIM Pro 2013 software code, which took into account the sample density values determined experimentally from X-ray phase analysis data. The ionization loss values were calculated taking into account the effects of cascade interactions, alongside the possibility of ion deflection during collisions. The choice was based on the conditions for creating structural changes in nanostructures associated with the emergence of point and vacancy defects along the trajectory of ion movement, caused by ionization effects arising as a result of the interaction of incident ions with the electronic and nuclear structure of ZnO/CoZn nanostructures. At the same time, the variation of the type of ions for irradiation causes more pronounced ionization effects that occur along the trajectory of the ions in the material, while the path length of the selected ions itself, due to their differences in radius and mass, does not have large differences. The rejection of lighter ions is due to the small ion range in CoZn nanostructures, which is less than 6 μm, which does not allow modification along the entire length of the nanostructures. The impossibility of changing the properties of nanostructures along the entire length excludes an objective assessment of the effect of ionizing radiation on the properties of the structures.

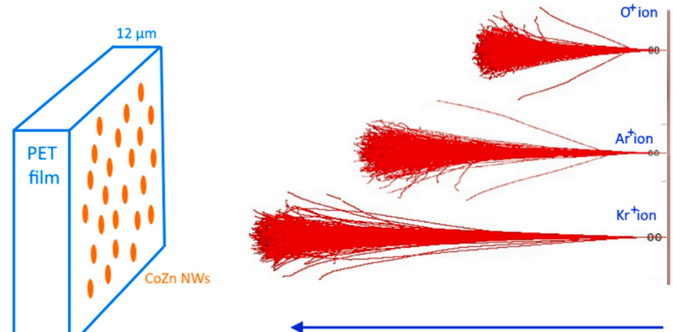

Fig. 1. Scheme of conducting experiments on irradiation.

The density of structural defects in the composition of the studied nanostructures was determined based on changes in optical spectra, as well as calculations of values such as band gap, refractive index and optical density, the change of which characterizes the effects of external influences on defective distortions and related changes. The change in the band gap (E_g) was estimated by constructing Tauc' plots, on the basis of which the values of the fundamental absorption edge were determined, and as a consequence, for samples subjected to ionic modification, changes in the electron density caused by charge redistribution due to ionization effects, as well as the introduction of new charges during ion implantation.

The refractive index ($n^{optical}$) was determined based on the changes in the fundamental absorption edge values and was estimated using the expression (1) [28]:

$$\frac{\left[\left(n^{optical}\right)^2-1\right]}{\left[\left(n^{optical}\right)^2+2\right]}=1-\sqrt{\frac{E_g}{20}}, \tag{1}$$

The optical density value was calculated using the Lorentz–Lorenz formula, which reflects the change in the concentration of defective inclusions in the material, leading to a change in the optical properties of nanostructures (2) [28]:

$$P=1-\frac{\left(n^2_{nanowires}-1\right)\left(n^2_{bulk}+2\right)}{\left(n^2_{nanowires}+2\right)\left(n^2_{bulk}-1\right)}, \tag{2}$$

The effect of the ion modification type on maintenance of the stability of the efficiency of using the selected nanostructures as anode materials was assessed by determining the capacitive characteristic degradation kinetics during long-term cycling in the charge/discharge mode. The applicability of the synthesized nanostructures as anode materials was assessed using two-electrode CR20 32 cells on a CT-3008 W–5V charge/discharge test bench (Neware). Cycling of the anode materials was carried out in a galvanostatic mode in the voltage range from 10 mV to 2 V, in the mode of limiting the charging capacity of 1000 mA h/g. In the anode cycle, the limitation was reaching a voltage of −2 V.

3. Results and discussion

Fig. 2a reveals the assessment results of changes in the band gap (E_g) for the studied ZnO/CoZn nanostructures depending on the irradiation fluence and the type of ions used for irradiation. In this case, the data are presented considering the observed alterations, expressed in the band gap reduction for modified ZnO/CoZn nanostructures (in this case, the differences in the E_g values for samples irradiated with ions with different fluences, as indicated by dotted lines, are meant in comparison with the initial E_g value for unirradiated ZnO/CoZn nanostructures). According to the data obtained, the observed alteration in the band gap in the case of ZnO/CoZn nanostructures, in the case of irradiation, can be explained by the formation in the structure of an exchange sp-d interaction between localized electrons in d-orbitals and band electrons arising as a result of ionization processes of interaction of incident ions with the crystal structure. Moreover, the presence of zinc oxide in the composition of nanowires makes it possible to generate free charge carriers due to weak chemical bonds, which leads to the formation of vacancy defects, an increase in the density of which reduces the width of the forbidden zone. It should be noted that this effect of the E_g value reduction in the case of the irradiation fluence change is most pronounced for Ar^+ ions, for which the decrease in the E_g value with a variation in fluence from 10^{10} to 10^{11} ion/cm^2 is about 10 % compared to the initial E_g value for unirradiated nanostructures, while when irradiated with O^+ ions, the maximum decrease is no more than 6 % compared to the initial value. It should be noted that when modified with Kr^+ ions, the observed decrease in the trend of the band gap reduction with an elevation in the irradiation fluence from 10^{10} to 10^{11} ion/cm^2 may be due to the probability of the formation of effects of partial overlapping of defective regions, which results in the formation of non-isolated structural changes, as in the case of modification with O^+, Ar^+ ions, and to the formation of more complex structural changes, the presence of which has a restraining effect and causes anisotropic changes in the electron density, as well as heterogeneity in the charge distribution in nanostructures. In this case, for Kr^+ ions, the energy of which significantly exceeds the energy of other ions selected for modification, and also taking into account the size of the ions, the number of collisions during interaction with the crystal structure will be significantly greater, which in turn causes an increase in the values of ionization losses, and as a consequence, the transferred kinetic energy to the electronic subsystem, which leads to its large changes. Also, for Kr^+ ions, it is necessary to consider the possible effect of kinetic energy transformation into thermal energy, which, in the case of the occurrence of the overlapping effect due to large diameters of damaged areas (these dimensions are associated with the values of ionization losses), can lead to the formation of complex defects [29–32], alongside a rise in the concentration of structural distortions, which in turn results in destabilization of the crystal structure.

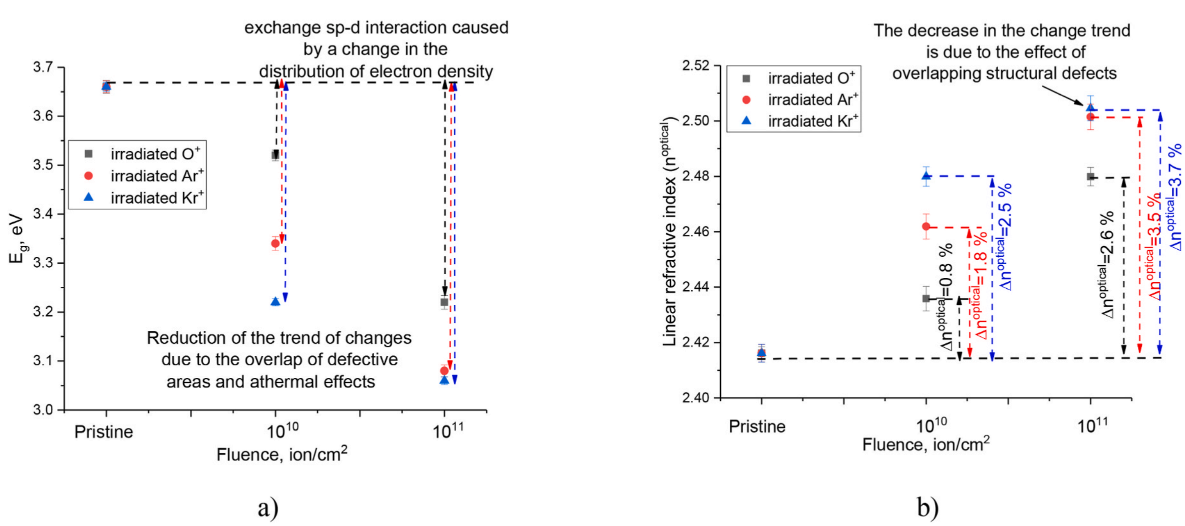

Fig. 2. Results of evaluation of optical and electronic properties of ZnO/CoZn nanostructures: a) Results of changes in the E_g value of the studied ZnO/CoZn nanostructures before and after ion modification; b) Results of comparative analysis of changes in the linear refractive index for ZnO/CoZn nanostructures depending on the type of ions and irradiation fluence.

Fig. 2b demonstrates the results of the linear refractive index evaluation, reflecting the changes in the absorption capacity of ZnO/CoZn nanostructures depending on the degree of structural distortions caused by irradiation. The change in the value of the linear refractive index is associated with the accumulation of structural changes caused by irradiation, as well as the formation of absorbing centers in the structure, the concentration of which can be due to the presence of oxygen vacancies, as well as structurally deformed inclusions. In this case, the most pronounced changes are observed for cases of irradiation with Ar^+ and Kr^+ ions, for which in the first case the formation of oxygen vacancies is caused by structural changes, alongside the redistribution of charges as a result of the interaction of ions with the crystal structure, and in the second case the formation of the effect of overlapping of structurally isolated damage, which leads to the growth of deformed inclusions in nanostructures. Moreover, the irradiation fluence variation during irradiation with Kr^+ ions results in less significant trend in changes in the linear refractive index value in comparison with ion irradiation with O^+ and Ar^+ ions.

Fig. 3 illustrates the assessment results of the connection between the optical density determined using equation (2) and the concentration of structural defects in ZnO/CoZn nanostructures caused by the interaction of incident ions with the crystal lattice, as well as transformation processes caused by the conversion of transferred kinetic energy into thermal energy as a result of collisions along the ion trajectory. The data were calculated based on changes in structural parameters, in particular, the volume of the crystal lattice of the dominant cubic phase Co_2Zn_{11}, the changes of which are due to structural changes caused by irradiation. The concentration of structural defects (CSD) was calculated using the expression $CSD = 1 - V_{irr}/V_0$, V_{irr} and V_0 are the values of the crystal lattice volume of the cubic phase of Co_2Zn_{11} in the irradiated and initial state. The comparative analysis results indicate a direct correlation between the concentration of structural defects and optical density, the change of which in this case is due to the formation of absorption centers, the presence of which is associated with defective inclusions and oxygen vacancies. It should be noted that a more pronounced trend in changes in the concentration of defective inclusions, and as a consequence, optical density, in the case of samples irradiated with Kr^+ ions indicates a growth in deformation distortions caused by more intense ionization processes arising as a result of the interaction of ions with the crystal structure. In this case, higher radiation doses can result in destabilization of the crystal structure, which in the case of resource

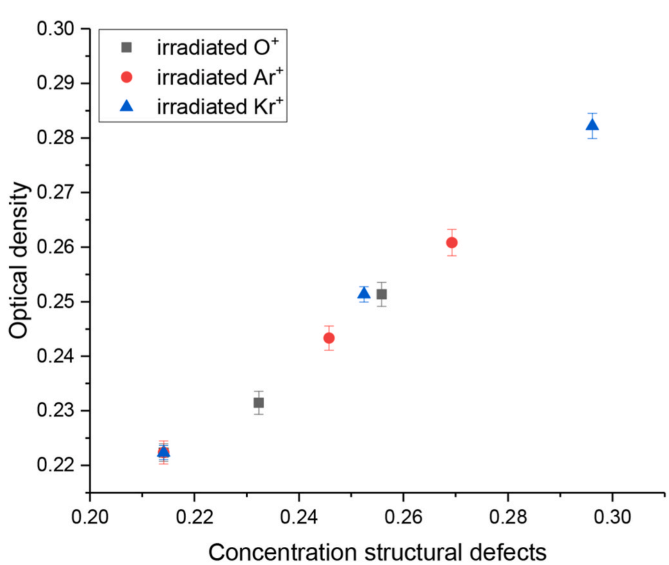

Fig. 3. Results of comparative analysis of the connection between the change in optical density and the concentration of structural defects in ZnO/CoZn nanostructures caused by heavy ion irradiation at irradiation fluence variation.

tests can negatively affect the resistance of materials to charge transfer processes during charging/discharging.

Fig. 4a–c shows the construction of the volt-ampere characteristics curves in the form of Z'' (Z') diagrams, reflecting changes in the resistance of nanostructures with variations in irradiation conditions (elevation of the irradiation fluence, alongside alteration in the type of ions during irradiation), the values of which indicate a positive effect of ionic modification on reducing the electrical resistance of nanostructures, which is expressed in a decrease in the circumference of the curves.

Fig. 5a–c reveals the results of resource cyclic tests of the synthesized ZnO/CoZn nanostructures when testing them as anode materials in order to establish the potential for the applicability of ion irradiation to enhance resistance to degradation resulting from lithiation processes, as well as the associated corrosion oxidation processes, which were clearly demonstrated in the work [32]. The established effects of changes in the electrical parameters of nanostructures associated with the impact of ion irradiation on materials are in good agreement with a number of literary data [33–37], in which the use of various types of ionizing radiation was considered as one of the promising methods for elevation of the conductivity of nanostructures, and magnification of their degradation resistance by creating a hardening defect layer in nanomaterials that prevents corrosion processes. In this case, a rise in the conductivity of the studied nanostructures subjected to ionic modification can be explained by the fact that when ionizing radiation affects the material, an anisotropic distortion of the electron density occurs, which in turn can reduce the resistance due to such effects. It should also be noted that the main changes in the structure of nanowires associated with the transformation of kinetic energy into thermal energy and the resulting athermal effects as a result of such transformations occur in a fairly small volume limited by the diameter of the nanowires, which results in more intense structural alterations (see data in Fig. 2, reflecting the relationship between changes in defect concentration and optical density). However, in this case, one should also take into account the factor of the magnitude of ionization losses, which characterizes the sizes of isolated structurally altered regions that arise along the trajectory of ion movement in the material. At the same time, the largest sizes will be observed for Kr^+ ions, as a result of which, with an elevation in fluence, an effect of overlapping of these structurally altered areas may arise, which in turn will result in modification effect reduction, due to the destructive effect of irradiation, which has been reported in a number of works [38, 39]. In turn, the reduction in resistance in ZnO/CoZn nanostructures can contribute to an increase in the efficiency of charge transfer during the lithiation process, and can also be used for other practical applications.

During the conducted studies it was established that ion modification using O^+ and Ar^+ ions results in capacitive characteristic retention stability growth in comparison with unmodified ZnO/CoZn nanostructures, for which a decline in charging capacity is observed after 200 consecutive charge/discharge cycles, and reaching a critical point (a decrease in charging capacity below 80 % of the initial value) occurs after 260 cycles. In the case of modified ZnO/CoZn nanostructures, irradiation with O^+ ions with fluences of 10^{10}–10^{11} ion/cm^2 leads to a rise in the degradation resistance of the anode material, and the maintenance of the value of the charging capacity within the permissible errors (deviation of no more than 3 %) is observed for 400–430 consecutive cycles, which indicates a higher stability of the modified nanostructures in comparison with unmodified ones. At the same time, fluence growth during irradiation with O^+ ions does not result in significant changes in the stability indicators and charging capacity stability maintenance. In the case of irradiation of nanostructures with Ar^+ ions, a change in the irradiation fluence from 10^{10} to 10^{11} has the opposite effect, indicating that structural defects are formed in samples irradiated with a fluence of 10^{11} ion/cm^2, which accelerate the destruction processes of the anode material during lithiation, resulting in its destabilization and a reduction in capacitive parameters. However, irradiation with Ar^+ ions with a fluence of 10^{10} ion/cm^2 leads to an

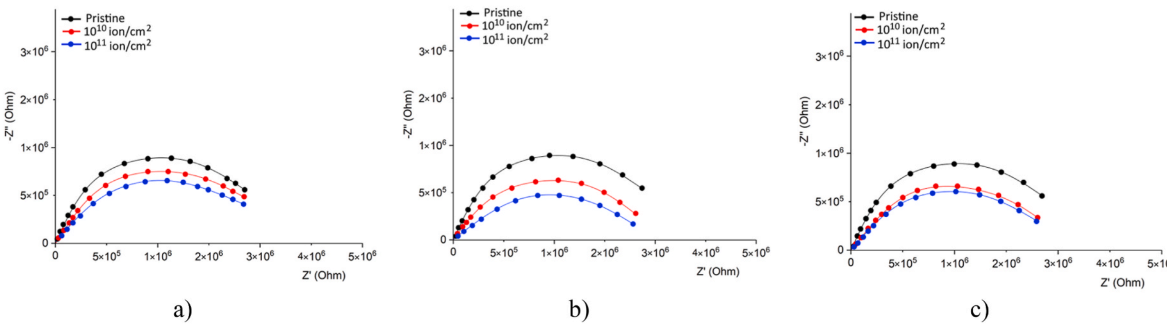

Fig. 4. Results of constructing Nyquist plots Z'‘ (Z′) for the studied samples of ZnO/CoZn nanostructures depending on the type of ion exposure: a) in case of modification by O^+ ions; b) in case of modification by Ar^+ ions; c) in case of modification by Kr^+ ions.

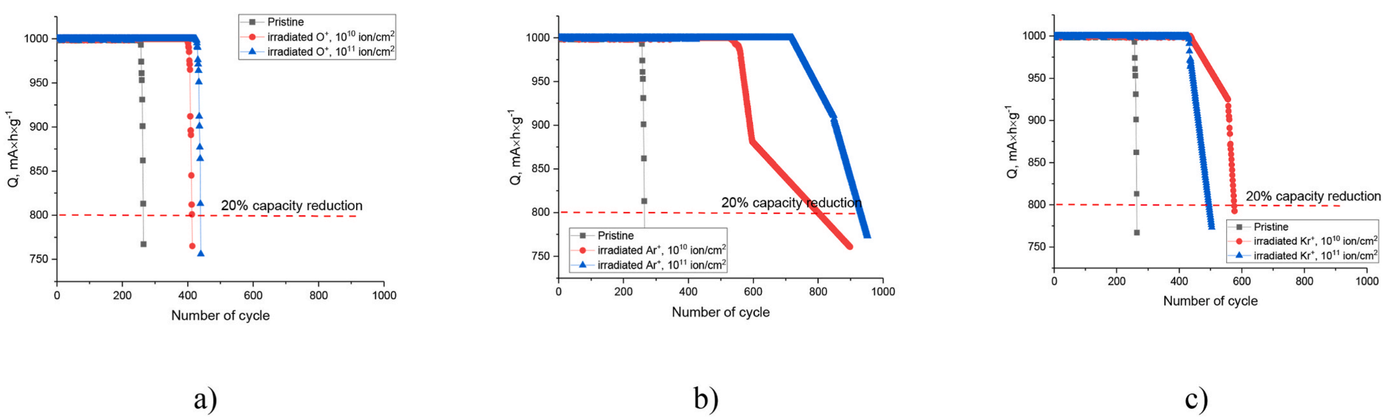

Fig. 5. Results of resource cyclic tests of the studied ZnO/CoZn nanostructures as anode materials, reflecting the change in the efficiency of their use as anode materials (The dotted line indicates the capacity value, which is 80 % of the nominal value, chosen as a value characteristic of the degradation stage of nanostructures.): a) in case of modification by O^+ ions; b) in case of modification by Ar^+ ions; c) in case of modification by Kr^+ ions.

enhancement in the preservation of the stability of the anode material's performance while maintaining the charging capacity within the error limits for 530–550 cycles, upon reaching which a slow decrease in the charging capacity indicators is observed, and the critical mark is exceeded after 740 cycles. In the case of modification with Kr^+ ions, the efficiency of using nanostructures as anode materials in comparison with the initial unmodified nanostructures increases by approximately 1.5–2 times contingent upon the irradiation fluence, while the decreasing trends are more pronounced than in the case of nanostructures modified with Ar^+ ions. This difference in the trends of accelerated degradation of the anode material with an increase in the number of cycles of resource tests of charging/discharging indicates an acceleration of oxidation processes, alongside differences in the mechanisms of containment of these processes due to ion modification of nanostructures.

Fig. 6 illustrates the results of a comparative analysis of the evaluation of the values of the number of resource test cycles, upon reaching which a decrease in capacity below 80 % of the nominal value is observed. The presented data on the number of resource test cycles at which the capacity value is more than 80 % were determined on the basis of the obtained dependencies presented in Fig. 6. The values of the number of cycles were selected for cases when the capacity value is more than 80 % of the nominal value. The results shown in the diagram characterize the efficiency of using ion irradiation to increase the stability of using ZnO/CoZn nanostructures as anode materials.

As is evident from the data presented, the use of O^+ ions leads to an enhancement in the efficiency of the operation of ZnO/CoZn nanostructures as anode materials by approximately 0.5–0.7 times in comparison with non-irradiated nanostructures, while the nature of the drop in capacitive characteristics to a critical point of 80 % of the capacity

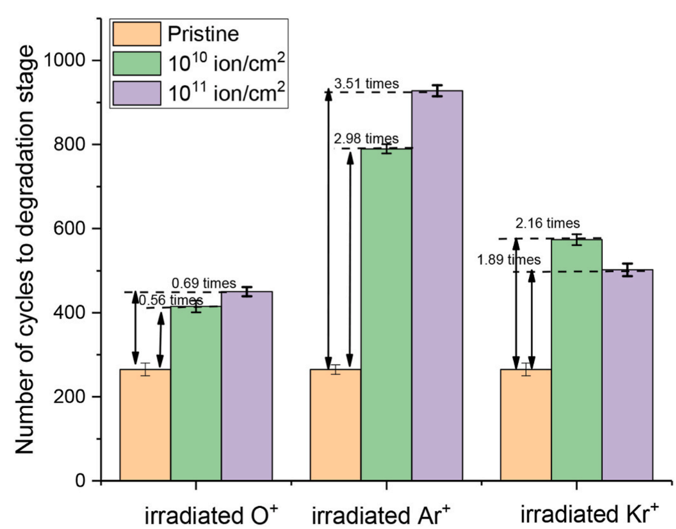

Fig. 6. Comparative diagram reflecting the number of cycles of resource tests of ZnO/CoZn nanostructures as anode materials, after which a decrease in capacity below 80 % of the nominal value is observed, the value of which is the limit of the operating mode (the dotted lines reflect the values of the increase in the number of test cycles for modified nanostructures in comparison with unmodified ZnO/CoZn nanostructures).

from the nominal value occurs quite quickly, which indicates an acceleration of the degradation rate of the anode material due to the effect of accumulation of inclusions in the anode material. The use of Ar^+ ions to modify nanostructures leads to an elevation in the number of cycles during which the capacitive characteristics are maintained above the critical value by more than 2.9–3.5 times, depending on the irradiation fluence, which indicates a fairly high efficiency due to the processes of structural changes caused by irradiation. For samples irradiated with Kr^+ ions, the irradiation fluence growth from 10^{10} to 10^{11} ion/cm^2 leads to a reduction in the trend of the efficiency of anode material degradation resistance magnification, from which it can be concluded that the possible formation of overlapping areas of defective inclusions caused by the interaction of ions with the crystal structure along the trajectory of ion movement in the material, under prolonged external influence associated with charging/discharging processes leads to a more pronounced destabilization of the anode material, which leads to a reduction in the number of resource test cycles. Small changes in the efficiency of increasing stability in the case of irradiation with Kr ions in comparison with other types of ions are due to the effect of large values of ionization losses, which leads to more pronounced changes in the distribution of electron density, and as a consequence, more pronounced structural changes, which, with an increase in irradiation fluence, have a negative effect on the stability of nanostructures to lithiation processes.

Fig. 7 reveals the assessment results of the change in capacity with variation in the charging rate ($C = 250$ mA $\times$ g^{-1}), the change of which results in the battery charging time reduction with a decrease in capacity. In this case, the variation in the charging rate is carried out in order to determine the reversibility of materials in the case of tests for a rate growth and a reverse decrease. The general appearance of the presented dependencies indicates that an elevation in the charging rate leads to a decrease in the capacitive characteristics, while in the case of a tenfold increase in the rate for unmodified samples with a rise in the number of test cycles, a destructive change is observed, leading to a decrease in capacity. The reversibility of the process with the preservation of the values of the capacitive characteristics is observed for modified nanostructures in the case of modification with O^+ and Ar^+ ions, while for samples modified with Kr^+ ions, the reversibility of the restoration of the capacitive characteristics is significantly less, which can be explained by the structural disorder degree. The reduction in capacitive parameters is due to effects associated with changes in the charge/discharge rate, the variation of which results in acceleration of degradation processes, which in turn leads to a decrease in capacitive characteristics. At the same time, as is evident from the data presented in Fig. 6, in the case of samples irradiated with ions, the variation in the charge/discharge rate does not lead to a significant decrease in capacitive parameters, which indicates sufficiently high indicators of the stability of nanostructures to accelerated lithiation processes.

Fig. 8 reveals the measurement results of the current-voltage characteristics of ZnO/CoZn nanostructures in the form of Z'‘ (Z′) diagrams, reflecting the structure degradation effect after testing in the case of resource cyclic tests carried out to determine the effectiveness of using ionic modification to magnify the degradation resistance of anode materials associated with oxidation. These diagrams are presented in comparison with the results of changes in Z'‘ (Z′) before and after life tests in order to clearly demonstrate the conductivity degradation and the resistance growth, which is caused by corrosion and oxidation processes. A comparative analysis of the observed alterations indicates that the destructive distortion of the structure associated with oxidation processes leads to a reduction in conductive properties and a steep rise in resistance, as evidenced by the data of the Z'‘ (Z′) diagrams of the initial samples after resource tests in comparison with the initial ones. At the same time, ionic modification, as is evident from the presented Z'‘ (Z′) dependencies, results in less pronounced changes in the Z'‘ (Z') dependencies, which indicates a positive effect associated with an elevation in efficiency and an elevation in degradation resistance of anode materials during the lithiation process during resource tests.

Fig. 9a–b demonstrates the results of alterations in the E_g values and optical density for ZnO/CoZn nanostructures in comparison before and after resource cyclic tests as anode materials, the changes of which reflect the degradation of the properties of the nanostructure due to oxidation and corrosion processes, alongside the associated changes in the concentration of charge carriers and degradation.

The general trend of changes in the E_g and optical density values indicates the accumulation of structural distortions in ZnO/CoZn nanostructures caused by lithiation processes and subsequent oxidation due to interaction processes with the electrolyte. At the same time, a rise in the band gap indicates a negative impact of degradation processes on the distribution of electron density, and the accumulation of structural distortions, the alteration in concentration of which is indicated by these changes in optical density. It should be noted that ionic modification in this case leads to the inhibition of processes of changes in the values of the band gap and optical density, from which one can conclude about the positive effect of ionic modification on the destructive deterioration of the properties of nanostructures. This effect in this case can be explained by structural changes caused by irradiation, the density of which, as well as the isolation of areas of structural changes arising along the trajectory of ion movement, leads to the creation of additional barriers that prevent oxidation processes associated with the introduction and subsequent migration of oxygen into the structure. In this case, the presence of isolated structural regions that stand in the way of migrating oxygen restrains its penetration into the depths, thereby preventing the acceleration of the degradation process due to the formation of oxide inclusions, the presence of which is due to lithiation processes during long-term resource tests, as was shown in the works [37,38,40,41].

4. Conclusion

The results of the conducted studies revealed that the use of irradiation with O^+ and Ar^+ ions for the targeted modification of ZnO/CoZn

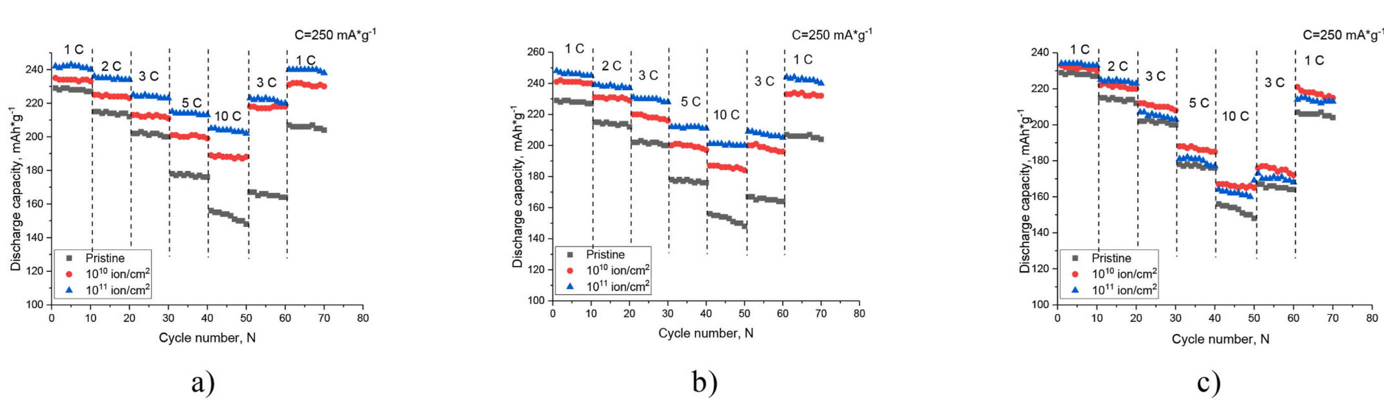

Fig. 7. Results of tests of ZnO/CoZn nanostructures as anode materials at charging rate variation: a) in case of modification of ZnO/CoZn nanostructures by O^+ ions; b) in case of modification by Ar^+ ions; c) in case of modification by Kr^+ ions.

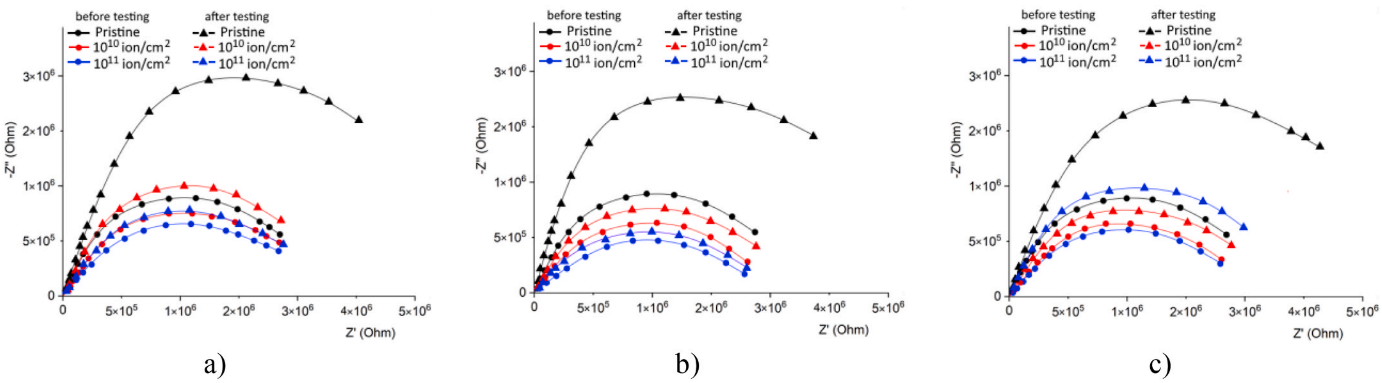

Fig. 8. Results of constructing Nyquist plots Z'' (Z′) for the studied samples in comparison before and after testing, reflecting the resistance growth caused by the degradation of the anode material associated with the lithiation and oxidation processes: a) in case of modification by O^+ ions; b) in case of modification by Ar^+ ions; c) in case of modification by Kr^+ ions.

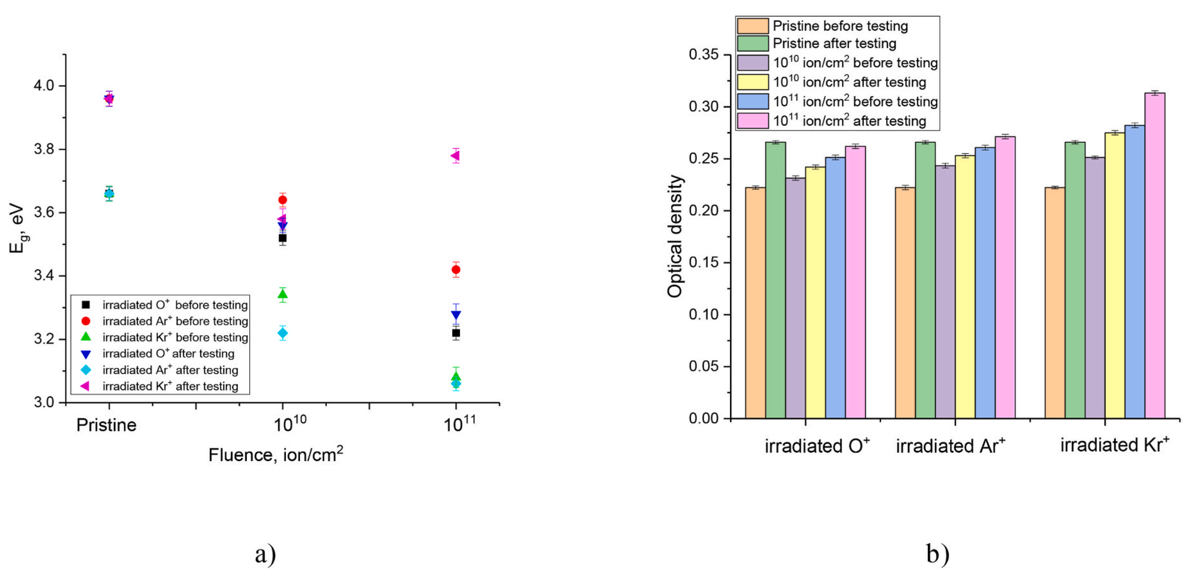

Fig. 9. a) Results of alterations in the E_g value for the studied ZnO/CoZn nanostructures before and after resource tests as anode materials; b) Results of alterations in the optical density value for ZnO/CoZn nanostructures before and after resource tests as anode materials.

nanostructures used as anode materials allows magnification of the resistance to destructive oxidation of anode materials and maintenance of capacitive characteristics by more than 2–4 times higher compared to unmodified nanostructures used as anode materials. At the same time, ionic modification also allows enhancement of the resistance to reversibility of capacitive characteristic maintenance when changing the charging rate, the variation of which results in accelerated degradation of the capacitive characteristics of batteries due to rapid lithiation processes. Determination of degradation resistance based on alterations in the values of the band gap and optical density showed that the most resistant to degradation of electronic properties, the change of which is caused by oxidation processes and the associated change in charge distribution, are nanostructures modified with O^+ and Ar^+ ions with a fluence of 10^{11} ion/cm^2, for which the degradation of these values is minimal compared to the initial values. At the same time, the analysis of Z'' (Z') diagrams showed that minimal changes in resistance are also observed for nanostructures irradiated under these conditions. Such an effect is due to the creation of isolated defects in the structure of nanowires, which have a restraining effect on oxidation processes occurring during lithiation, and also reduce the degradation rate.

The presented assessment results of the applicability of ionizing radiation used to enhance resistance to degradation caused by lithiation processes of anode materials based on ZnO/CoZn nanostructures can be further used to create process lines associated with enhancement of the efficiency of anode materials, alongside their cost reduction by increasing their service life. In this case, the use of ion modification technology, despite the rather high cost of carrying out such modifications, allows prolongation of the service life of anode materials by more than 2.5–3.5 times, which allows reduction of the costs of their replacement or the manufacture of new anode materials.

Further prospects for the use of these nanostructures include expanding the potential of their application not only as anode materials, but also as photocatalysts, as well as assessing the possibility of using ionizing radiation for targeted modification of other types of nanostructures, taking into account the obtained dependencies.

CRediT authorship contribution statement

Ainur M. Zikirina: Visualization, Software, Methodology, Funding acquisition, Formal analysis, Conceptualization. **Artem L. Kozlovskiy:** Writing – review & editing, Writing – original draft, Validation, Investigation, Formal analysis, Data curation, Conceptualization. **Inesh E. Kenzhina:** Supervision, Software, Methodology, Investigation, Data curation, Conceptualization.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

References

[1] N. Mahmood, T. Tang, Y. Hou, Nanostructured anode materials for lithium ion batteries: progress, challenge and perspective, Adv. Energy Mater. 6 (17) (2016) 1600374.
[2] Q. Wang, C. Zhao, Y. Lu, Y. Li, Y. Zheng, Y. Qi, L. Chen, Advanced nanostructured anode materials for sodium-ion batteries, Small 13 (42) (2017) 1701835.
[3] L.J. Fu, H. Liu, C. Li, Y.P. Wu, E. Rahm, R. Holze, H.Q. Wu, Surface modifications of electrode materials for lithium ion batteries, Solid State Sci. 8 (2) (2006) 113–128.
[4] J. Zhang, A. Yu, Nanostructured transition metal oxides as advanced anodes for lithium-ion batteries, Sci. Bull. 60 (9) (2015) 823–838.
[5] X.M. Bai, B.P. Uberuaga, The influence of grain boundaries on radiation-induced point defect production in materials: a review of atomistic studies, Jom. 65 (2013) 360–373.
[6] M. Hendy, M. Ponga, A multiscale and multiphysics framework to simulate radiation damage in nano-crystalline materials, J. Nucl. Mater. 578 (2023) 154347.
[7] Y.R. Lin, A. Bhattacharya, S.J. Zinkle, Analysis of position-dependent cavity parameters in irradiated metals to obtain insight on fundamental defect migration phenomena, Mater. Des. 226 (2023) 111668.
[8] Y. Xiong, S. Ma, J. Zhang, S. Huang, B. Xu, H. Fu, S. Zhao, Interactions between irradiation-induced defects and dislocations in concentrated solid solution alloys, J. Nucl. Mater. 597 (2024) 155144.
[9] K. Ma, B. Décamps, L. Huang, R.E. Schäublin, J.F. Löffler, A. Fraczkiewicz, M. Loyer-Prost, Impact of micro-alloying in ion-irradiated nickel: from the inhibition of point-defect cluster diffusion by thermal segregation to the change of dislocation loop nature, Acta Mater. 246 (2023) 118656.
[10] C.N. Singh, B.P. Uberuaga, S.J. Tobin, X.Y. Liu, Impact of radiation-induced point defects on thermal carrier decay processes in GaAs, Acta Mater. 242 (2023) 118480.
[11] X. Zhang, K. Hattar, Y. Chen, L. Shao, J. Li, C. Sun, M. Nastasi, Radiation damage in nanostructured materials, Prog. Mater. Sci. 96 (2018) 217–321.
[12] Z. Deng, Y. Liu, L. Wang, N. Fu, Y. Li, Y. Luo, H. Zhang, Challenges of thermal stability of high-energy layered oxide cathode materials for lithium-ion batteries: a review, Mater. Today (2023).
[13] C. Zhu, P. Li, G. Xu, H. Cheng, G. Gao, Recent progress and challenges of Zn anode modification materials in aqueous Zn-ion batteries, Coord. Chem. Rev. 485 (2023) 215142.
[14] P.U. Nzereogu, A.D. Omah, F.I. Ezema, E.I. Iwuoha, A.C. Nwanya, Anode materials for lithium-ion batteries: a review, Applied Surface Science Advances. 9 (2022) 100233.
[15] C. Zhang, F. Wang, J. Han, S. Bai, J. Tan, J. Liu, F. Li, Challenges and recent progress on silicon-based anode materials for next-generation lithium-ion batteries, Small Structures. 2 (6) (2021) 2100009.
[16] F.F. Bazito, R.M. Torresi, Cathodes for lithium ion batteries: the benefits of using nanostructured materials, J. Braz. Chem. Soc. 17 (2006) 627–642.
[17] R.C.K. Reddy, J. Lin, Y. Chen, C. Zeng, X. Lin, Y. Cai, C.Y. Su, Progress of nanostructured metal oxides derived from metal–organic frameworks as anode materials for lithium–ion batteries, Coord. Chem. Rev. 420 (2020) 213434.
[18] L. Zhou, K. Zhang, Z. Hu, Z. Tao, L. Mai, Y.M. Kang, J. Chen, Recent developments on and prospects for electrode materials with hierarchical structures for lithium-ion batteries, Adv. Energy Mater. 8 (6) (2018) 1701415.
[19] F. Lang, O. Shargaieva, V.V. Brus, H.C. Neitzert, J. Rappich, N.H. Nickel, Influence of radiation on the properties and the stability of hybrid perovskites, Adv. Mater. 30 (3) (2018) 1702905.
[20] R.L. Clough, High-energy radiation and polymers: a review of commercial processes and emerging applications, Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms. 185 (1–4) (2001) 8–33.
[21] M.R. Cleland, L.A. Parks, S.J.N.I. Cheng, Applications for radiation processing of materials, Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms. 208 (2003) 66–73.
[22] A.M. Zikirina, A. Temirtassova, A.L. Kozlovskiy, I.E. Kenzhina, M. Begentayev, Synthesis, characterization and evaluation of the application of CoZn nanostructures as anode materials, Batteries. 9 (8) (2023) 421.
[23] Y. Suchikova, S. Kovachov, I. Bohdanov, E. Popova, A. Moskina, A. Popov, Characterization of CdxTeyOz/CdS/ZnO heterostructures synthesized by the SILAR method, Coatings 13 (3) (2023) 639.
[24] K.K. Kadyrzhanov, A. Zikirina, K. Egizbek, A.L. Kozlovskiy, A.V. Petrov, M. V. Zdorovets, Phase transformations in CoZnO/CoZn nanostructures depending on the difference in applied potentials, Surf. Coating. Technol. 386 (2020) 125495.
[25] A. Zikirina, K.K. Kadyrzhanov, I.E. Kenzhina, A.L. Kozlovskiy, M.V. Zdorovets, Study of defect formation processes under heavy ion irradiation of ZnCo2O4 nanowires, Opt. Mater. 118 (2021) 111282.
[26] A.Zh Omarova, A.L. Kozlovskiy, G.Zh Moldabayeva, Study of the applicability of ACdSe (A – Co, Ni) thin films as catalysts for heavy metal capture, Opt. Mater. X 24 (2024) 100366.
[27] A.Z. Omarova, T. Ayazbaev, Z.S. Yesdauletova, S.A. Aldabergen, A.L. Kozlovskiy, G.Z. Moldabayeva, Evaluation of the applicability of modifying CdSe thin films by the addition of cobalt and nickel to enhance the efficiency of photocatalytic decomposition of organic dyes, Journal of Composites Science. 7 (11) (2023) 460.
[28] Thomas G. Mayerhöfer, Popp Jürgen, Beyond beer's law: revisiting the lorentz-lorenz equation, ChemPhysChem 21 (12) (2020) 1218.
[29] A.I. Popov, E. Balanzat, F centre production in CsI and CsI–Tl crystals under Kr ion irradiation at 15 K, Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms. 166 (2000) 545–549.
[30] T. Inerbaev, A. Akilbekov, D. Kenbayev, A. Dauletbekova, A. Shalaev, E. Polisadova, A.I. Popov, Color centers in BaFBr crystals: experimental study and theoretical modeling, Materials 17 (13) (2024).
[31] A.L. Kozlovskiy, M. Konuhova, D.B. Borgekov, Popov Anatoli, Study of irradiation temperature effect on radiation-induced polymorphic transformation mechanisms in ZrO2 ceramics, Opt. Mater. 156 (2024) 115994.
[32] A.L. Kozlovskiy, M. Konuhova, D.I. Shlimas, D.B. Borgekov, M.V. Zdorovets, R. I. Shakirziyanov, A.I. Popov, Study of the effect of nanostructured grains on the radiation resistance of zirconium dioxide ceramics during gas swelling under high-dose irradiation with helium ions, ES Materials & Manufacturing. 24 (2024) 1165.
[33] K.K. Kadyrzhanov, A.A. Kozlovskiy, M. Konuhova, A.I. Popov, D.D. Shlimas, D. B. Borgekov, Determination of gamma radiation shielding efficiency by radiation-resistant composite ZrO2–Al2O3–TiO2–WO3–Nb2O5 ceramics, Opt. Mater. 154 (2024) 115752.
[34] K. Dharamvir, K. Jeet, C.S. Du, N. Pan, V.K. Jindal, Structural modifications of multiwalled carbon nanotubes by swift heavy ions irradiation, J. Nano Res. 10 (2010) 1–9.
[35] A.V. Krasheninnikov, K. Nordlund, Ion and electron irradiation-induced effects in nanostructured materials, J. Appl. Phys. 107 (7) (2010) 1–10.
[36] D.J. Sprouster, R. Giulian, L.L. Araujo, P. Kluth, B. Johannessen, D.J. Cookson, M. C. Ridgway, Swift heavy-ion irradiation-induced shape and structural transformation in cobalt nanoparticles, J. Appl. Phys. 109 (11) (2011).
[37] V. Chauhan, P. Singh, R. Kumar, Ion beam-induced modifications in ZnO nanostructures and potential applications, in: Nanostructured Zinc Oxide, Elsevier, 2021, pp. 117–155.
[38] A. Kaur, R.P. Chauhan, Effect of gamma irradiation on electrical and structural properties of Zn nanowires, Radiat. Phys. Chem. 100 (2014) 59–64.
[39] A. Kaur, R.P. Chauhan, Modifications induced by silicon and nickel ion beams in the electrical conductivity of zinc nanowires, J. Mater. Sci. Mater. Electron. 24 (2013) 4302–4310.
[40] A. Kozlovskiy, S. Akhmetzhan, N. Ivanitskaya, M. Zdorovets, Study of the effect of irradiation with Ca5+ ions on the increase in Ni nanotubes lifetime, applicable as the basis for lithium-ion batteries, Mater. Res. Express. 6 (8) (2019) 085074.
[41] A. Kozlovskiy, D. Shlimas, I. Kenzhina, M. Zdorovets, Study of the use of ionizing radiation to improve the efficiency of performance of nickel nanostructures as anodes of lithium-ion batteries, Mater. Res. Express. 6 (5) (2019) 055026.