DOI 10.31489/2023PH3/98-106

UDC 538.971, 620.97

M.M. Kubenova[1], K.A. Kuterbekov[1], M.Kh. Balapanov[2], R.Kh. Ishembetov[2], K.Zh. Bekmyrza[1], A.M. Kabyshev[1], Sh. Afroze[1], R.Sh. Palymbetov[1], Zh.A. Mukhanova[1], E. Shukalov[1]

[1]L.N. Gumilyov Eurasian National University, 2 Satpayev str., 010008 Astana, Kazakhstan;
[2]Ufa University of Science and Technology, 32 Zaki Validi str., 450076 Ufa, Bashkortostan, Russia
(E-mail: kubenova.m@yandex.kz)

Analysis of the problems of synthesis of new nanocrystalline chalcogenide materials for thermoelectric generators and sodium-ion batteries

The paper analyzes the problems of the synthesis of new nanocrystalline chalcogenide materials for thermoelectric generators and sodium-ion batteries. The objectives of the synthesis will determine the best method to use to create chalcogenide materials for electrodes in real-world applications. The method of direct solid-phase reaction in a vacuum or in an environment of pure inert gas is the most effective way to generate novel chalcogenide materials in tiny amounts for the investigation of physicochemical and other features.With this approach, which is more dependable, it is feasible to produce a pure result free of contaminants that are inescapable when working with other solvents and precursors. Additionally, in a consistent synthesis regime, it is differentiated by the stability of the acquired attributes of the compounds. Synthesis modes, reagents, and post-processing depend on the specific material. The method of synthesizing alloys in a melt media made up of a combination of potassium and sodium hydroxides is one of the key techniques employed in the present research. The melting point drops to 165 °C at a certain ratio of the concentrations of these hydroxides, allowing for the execution of salt exchange processes in the melt. The size of the resultant chalcogenide particles can be reduced to a few nanometers by lowering the synthesis temperature, adding water, and shortening the annealing period.

Keywords: thermoelectric materials, copper sulfide, crystal structure, conductivity, diffusion, thermal conductivity, Seebeck coefficient, superionic conductors.

Introduction

The main reason hindering the creation of competitive sodium-ion batteries (SIB) is the low efficiency of the available electrode materials. The aim of this research is to generate a very energy-intensive nanostructured electrode material for sodium-ion batteries that operate at ambient temperature and can be recharged several times.

SIB cannot currently work at large current densities due to a significant disadvantage of the sodium-ion electrochemical system, which is a relatively long charge/discharge time. For this reason, one of the goals of the work is also to increase the rate of charge and discharge processes in SIB electrode materials by increasing the chemical diffusion coefficient.

As candidates for cathode materials in the framework of this study, highly non-stoichiometric phases of copper sulfide (digenite and anilite) in the nanoscale state are considered, which can exhibit superionic properties at room temperature and, in addition, have a high electronic conductivity of the order of 10^2 — $10^3 Om^{-1}cm^{-1}$. The structure of digenite and anilite contains many copper vacancies, which can reduce lattice mechanical stresses and extend the cycle life of the cathode to 100 or furthermore.

Transition metal chalcogenides (TMCh), such as cobalt sulfides, molybdenum sulfides, and tin sulfides, have been extensively investigated as potential anode materials with high sodium content, easy availability, and improved safety [1]. However, transition metal chalcogenides have certain defects and disadvantages, such as low conductivity and large volume changes, which can prevent the diffusion of Na + ions and reduce the operating current of the cells, and large volume changes can accelerate particle reunification and grinding (crushing) of active materials. These two unfavorable factors significantly limit the widespread use of transition metal chalcogenides, which are used exclusively in NIB. Therefore, to minimize volume expansion and enhance Na^+ diffusivity, transition metal chalcogenides are typically coupled with conductive carbon materials [1].

CPM electrodes for NIB based on carbon have been stated fairly often nowadays. The Mai group, for instance, developed a unique method for synthesizing a mesoporous “yolk” consisting of cobalt sulfide and an alveolar carbon shell (M-CoS@C) [2]. A mesoporous cobalt sulfide “yolk” and an alveoloid-like carbon shell (M-CoS@C) emerged after annealing, etching in HF, coating with silica and resorcinol formaldehyde, and annealing.

After 100 cycles at 0.2 A g^{-1}, the M-CoS@C electrode still has a high reversible capacity of 532 mAh g^{-1}, corresponding to a retention of 87.2 % capacity. On the contrary, the capacity of M-CoS rapidly decreased to 55 mAh g^{-1} within five cycles, indicating deterioration of the structure due to a shortage of the spatially constrained structure provided by the carbon shell.

In addition, the structure of the "yolk" shell also endowed the M-Co@C electrode with impressive speed characteristics with capacities of 635, 570, 530, 490, 440, 360, 295, and 190 mAh g^{-1} at 0.1, 0.2, 0.5, 1, 2, 5, 10 and 20 A g^{-1} respectively.

A study by Zhang et. al. [3] obtained self-organizing polygonal CoS_2 nanoparticles doped with nitrogen and coated with a carbon layer (N-CoS_2@C composites) as an anode electrode for NIB. Figures A and B depict the configuration and microstructure of N-CoS2@C, where high magnification TEM images show that the ordered CoS_2 is tightly encapsulated in a carbon layer with an average thickness of 0.5 nm, which should provide a strong barrier to protect intermediate reactants from being dissolved in electrolyte and create a better conductive path for active materials [1].

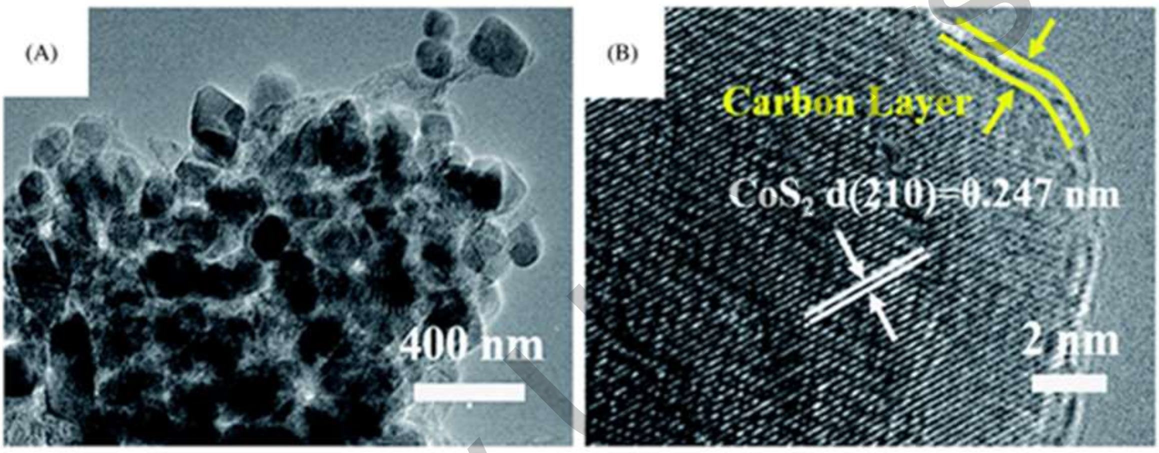

Figure 1 — (A) TEM and (B) HREM images of N-CoS2@C composites by [1]

N-CoS_2@C provides sodium incorporation reversibility, demonstrating a high incorporation rate. At a current density of 0.1 A g-1, the N-CoS_2@C electrode exhibits an initial high discharge capacity of 814 mA h g -1. The material showed an impressive reversible capacity of 559 mAh g^{-1} after 1000 cycles at 1 A g^{-1}. This is indicative of the excellent stability and reliability of the carbon-coated structure. The data obtained show that CoS_2 nanostructures with high sodium storage capacity, easy accessibility, low losses, and excellent safety can serve as promising anode materials for NIB [1].

Copper chalcogenides.

J. -S. Kim et al. were the first to investigate rechargeable batteries based on sodium/copper sulfide (Na/Cu_2S) [4] using the liquid electrolyte 1M $NaCF_3SO_3$-TEGDME at room temperature. The initial discharge curve of Na/Cu_2S cells had a slanting form and no apparent plateau area. After 20 cycles, the capacity dropped to 220 mAh g^{-1} from 294 mAh g^{-1} at the initial discharge. The integration of sodium into the Cu_2S chalcocite lattice without disentanglement in the second phase explains how the discharge mechanism occurs.

In the work of J. -L. Yue et. al. [5] Cu_2Se electrodes on a copper grid substrate were directly fabricated by a simple post-selenization method and tested as a positive electrode for sodium-ion batteries. Cu_2Se showed a large reversible capacity (about 250 mAh g^{-1}), good cyclic stability, and low polarization. These findings demonstrate that Cu_2Se is a promising candidate as a NIB cathode material.

J.Y. Park et. al. [6] obtained and studied electrodes from covellin CuS nanoplates in a sodium-ion cell. CuS undergoes a series of crystallographic rearrangements throughout the intercalation procedure, and many of the intermediate phases share crystal structures with one another. A novel capacity recovery behavior is also demonstrated by the material, which is in stark contrast to the normal conversion reaction systems, which suffer from substantial capacity loss upon cycling.

After the initial 13 cycles, the capacity of CuS nanoplatelets with a current density of 0.2 C rapidly declines to 80 mAh/g. The capacity progressively upsurges to ≈570 mAh/g, which is near the theoretical capacity, during the course of the following 90 cycles. The capacity recovers after the initial decline to ≈ 246 mAh g^{-1} in under 20 cycles at a greater current density (i.e., 3 C), which is an intriguing finding.

When exposed to different current densities between 1 and 5 C, bulk CuS with particle sizes in the hundreds of micrometers demonstrates outstanding stability. Bulk CuS also offers long-term cyclic stability; after 1000 cycles at 1C and 5C currents, respectively, the specific capacities were 415 and 406 mAh/g, correspondingly. With ≈ 93 % capacity retention after the second cycle, cyclic stability is preserved even after 2100 cycles. Akin to CuS nanoplates, bulk CuS also exhibited capacitance recovery, electrical property changes, and a plateau in the discharge. The capacity of CuS initially decreases significantly to 392 mAh/g over the initial 8 cycles at 1C current. The capacity does, nevertheless, return to 429 mAh/g during the next 500 cycles. After a more significant capacity lessening to 276 mAh g^{-1}, the capacity recovers more hastily after 100 cycles at a greater current density of 5 C [6].

According to the conclusions of the authors of [6], the ability of Na_xCuS nanoplates to regain their electrode capacity and resistance to grinding is facilitated by the development of stable grain boundaries and interphase boundaries. Astoundingly, the aforementioned process is applicable to all materials, as bulk coarse-grained CuS also shows electrochemical characteristics resembling those of nanowafers.

CuS can be beheld as a potential anode contender for sodium-ion batteries based on contrasts with its equivalents in lithium-ion batteries. As an outcome, it can be hypothesized that the crystallographic bonds between the sodium intercalation phases are a crucial part of materials that can be cycled mechanically with high levels of reliability for sodium-ion battery high-performance conversion processes.

Evaluation of existing methods for the synthesis of chalcogenides.

The intentions of the synthesis will determine the best technique for producing chalcogenide materials for oxygen reduction catalysts. It is quickly accomplished using the direct solid-phase reaction approach in a vacuum or in an environment of pure inert gas to synthesize novel chalcogenide materials in tiny quantities for the investigation of their physicochemical and other features. With this approach, which is more dependable, it is feasible to produce a pure result free of contaminants that are inescapable when working with other solvents and precursors. Furthermore, in a consistent synthesis regime, it is differentiated by the stability of the acquired attributes of the compounds. Synthesis regimes, reagents, and subsequent processing depend on the specific material and are developed in this work for binary and complex sulfides, selenides, tellurides of monovalent and transition metals, substituted or doped with other metals, and having different nonstoichiometry.

The key objective of synthesizing a catalytic material features of which are recognized for profit-making applications is to provide low-cost goods while preserving valuable qualities discovered via laboratory research. Since this is thought to lower manufacturing expenditures, nearly all topmost laboratories now working on functional materials use “soft” chemistry techniques that allow for synthesis at low temperatures, ideally close to room temperature.

A process for synthesizing alloys in a melt media made of an amalgamation of potassium and sodium hydroxides was devised. It is feasible to conduct exchange reactions between salts in the melt when the melting point drips to 165 °C at a certain ratio of the concentrations of these hydroxides. The size of the resultant chalcogenide particles can be abridged to a few nanometers by lowering the synthesis temperature and cutting the annealing period.

Synthesis of nanocrystals of metal sulfides.

Metal sulfide nanoparticles were manufactured using a number of techniques, such as solvothermal synthesis [7], microwave radiation [8], ultrasonication [9], and surface-passivating high-boiling solvents used in the thermolysis of precursors from a single source [10-13]. In order to synthesize CuS nanocrystals, various methods [14–17] for obtaining nanoparticles were also used with different morphologies, such as nanotubes [18, 9], nanowires [19], and nanoplates [20, 11, etc. [21, 22]. Among the methods for synthesizing nanocrystals, the method of a single precursor source allows for the acquisition of nanocrystals with good monodispersity [23], and studies showed that the size and shape of the obtained nanocrystals depended on the precursor concentration [24], reaction time [25], and temperature [26]. Due to the distinctiveness of the size-dependent physical and chemical features of nanocrystals [27, 28], researchers continue to pay close attention to the synthesis of monodisperse nanocrystals [29, 30].

Synthesis of nanocrystals of copper sulfides.

Longer alkyl chain precursors result in the development of nanosheets, whereas shorter alkyl chain precursors yield two-dimensional nanosheets. It has also been investigated how one specific precursor mechanism works. Cu-dithiocarbamate, for instance, is used to create nanowires, quantum dots, and nanobarrels.

In recent years, most research has focused on the colloidal solution-based synthesis method. Typically, two separate copper and sulfur precursors are dissolved in an organic solvent such as oleylamine (OLA). CuCl and copper acetylacetonate are the two utmost prominent copper precursors. The most common form of sulfur is elemental sulfur. A 7:3 amalgamation of oleylamine (OLA) and octadecene (ODE) was employed to dissolve the precursors CuCl and element S for the $Cu_{2-x}S$ synthesis, for instance.

The heating technique and the hot injection method are two categories for solution-based synthesis. In the heating method, the reaction temperature is reached after heating two precursors that have been combined at a low temperature. Using CuCl and S powder as precursors and a solution of oleylamine and octadecene as solvents, it was possible to grow monodisperse CuS nanoplatelets. In addition, it was found that changing the ratio of Cu to S can preciously modify the plasma characteristics of CuS particles without altering their shape and size.

To make assured $Cu_{2-x}S$ nanoparticles are used industrially, it is necessary to develop a scalable and reliable synthesis. In order to accomplish this goal, Robinson's team of researchers [31] developed an ultra-high concentration heating method and synthesized more than 200 g (80 % yield) of nanoparticles as a result of a single synthesis. In addition, even the large-scale synthesis of 8 — nm roxbyite ($Cu_{1,81}S$) had a size dispersion of fewer than 10 %. CuCl and S were employed as precursors in this synthesis, while an oleylamine (OLA)/octadecene (ODE) (7:3) combination was used as the solvent. Distinctively, dissolving CuCl and S, they are then combined at 50 °C and heated for two hours at 185 °C. The items are then centrifuged three times while being cleaned with acetone-hexane. The high concentration of the precursor is indispensable for this process (1000 mMCuCl and 5000 mM S).

Apart from the heating technique, the hot injection technique is yet another sort of colloidal synthesis. In this case, the sulfur forerunner is usually introduced into the copper forerunner solution at the reaction temperature. Due to the high stirring temperature, the hot injection reaction is completed much faster compared to the heating method. For example, $Cu_{2-x}S$ monodisperse particles ranging in size from 2.8 nm to 13.5 nm can be synthesized by hot injection within 1.5-3 minutes. Size change can be achieved with variations in injection temperatures (115 °C — 140 °C). Moreover, the choice of solvent strongly affects the phase of the synthesized $Cu_{2-x}S$ particle. While OLA is used as a solvent, jarleite ($Cu_{1.94}S$) and oleic acid (OA) are produced, and these substances then cause the covellin (CuS) phase to develop in the form of particles [32].

Electrochemical deposition, or anodizing, is another simple, inexpensive, and high-throughput method for directly fabricating a copper sulfide nanostructure on a substrate. Like many other metal oxides, copper sulfide nanostructures are also grown on Cu substrates or Cu foil as the anode and Ti metal as the cathode in a voltage range of 1.5 — 8 V in an aqueous solution of Na_2S. Accordingly, Cu_2S and CuS nanorod and nanowall arrays were obtained by controlling the voltage and reaction temperature [32].

Hydrothermal method. It is currently one of the methods for synthesis that are employed most frequently for nanomaterials. The technique makes it possible to increase the solubility of the reagents in the solvent and accelerate the chemical reaction, achieving rapid supersaturation at elevated temperatures and pressure. The application of stabilizing/coating agents is also widely used to stabilize narrow size distributions in 0D and specific high-energy surfaces in 1D and 2D copper sulfide nanostructures. Although the hydrothermal method is commonly used for slow-growing large single-crystal particles, it demonstrated that it could create $Cu_{2-x}S$ nanocrystals with different morphologies. $Cu_{2-x}S$ nanowires, nanotubes, and nanovesicular structures synthesized employing the hydrothermal synthesis technique effectively. 1-D structures consist of self-assemblies of $Cu_{2-x}S$ nanoplates and nanoparticles. In addition, it demonstrated that the methods of hydrothermal and solvothermal synthesis were efficient in the synthesis of $Cu_{2-x}S$ 3-D superstructures. A three-dimensional structure made of four hexagonal CuS plates, for instance, was generated by heating copper nitrate and sulfur powder to 140 °C for 24 hours. It measured 200 nm in thickness and 1 to 1.5 microns in diameter. The 14 chambers in this material, which may be used for applications like photocatalysts, are intriguing. Other layered structures of CuS, such as color-like structures and nanospheres, are also synthesized [32, 33].

Experimental part

Synthesis of nanodispersed phases with sodium-ion conductivity $Na_xCu_{2-y}S$ ($0<x<0.25$, $0<y<0.25$).

As a priority synthesis method, low-temperature chemical synthesis in a liquid medium was considered, which requires a minimum of time and ensures the yield of a sufficiently pure product in a nanoscale form.

Nanomaterials based on superionic copper sulfide, $Cu_{2-x}S$ were chosen as electrode materials.

To select the optimal synthesis technique, an analysis was made of the available literature on the synthesis of copper chalcogenides over the past decade.

Due to its promising qualities, copper sulfide is the copper chalcogenide that was examined the most. The direct band gap of $Cu_{2-x}S$, a p-type semiconductor, ranges from 1.2 eV (Cu_2S) to 2.0 eV (CuS). Since it consists of non-toxic and common elements in the earth's crust, it is environmentally friendly. In addition, numerous non-stoichiometric defects contribute to the ability to control the density of current carriers, and thus the electrical conductivity of the material, by changing the ratio of Cu to S during synthesis. Compared to most noble metal nanocrystals, the tunability of the carrier concentration is unique. Controlling the phase composition, size, and shape of $Cu_{2-x}S$ nanoparticles advanced significantly over the past ten years as a result of the benefits highlighted above. Numerous synthesis techniques are taken into account, such as solvent-free synthesis, hydrothermal synthesis, solvothermal synthesis, and colloidal hot injection techniques.

Shorter alkyl chains of the precursor cause the emergence of two-dimensional nanosheets, nonetheless, a longer chain results in the fabrication of nanosheets. In another work, for the synthesis of nanobarrels, quantum dots, and $Cu_{2-x}S$ nanowires, Cu-dithiocarbamate is employed.

In a melt of NaOH and KOH hydroxides, a method established for the manufacture of nanocrystalline copper sulfides, $Cu_{2-x}S$.

The research is carried out in a fume hood with a coating resistant to heated alkalis and equipped with a forced ventilation system. The Teflon vessel, in which the reaction is carried out in an alkaline melt, is reinforced on the outside with a strong metal edging to prevent rupture due to increased pressure inside during the reaction.

In a Teflon jar, the produced combination of sodium and potassium hydroxides is put in the proper ratio and heated to melt (about 165 °C). Heat is supplied to the vessel both from below and along the side walls, for uniform heating throughout the volume. The lid of the vessel should not be tight so that excess vapors can freely escape from the vessel. The power of the heater after boiling is reduced to a minimum in order to avoid violent boiling. The operator must wear a respirator and protective gloves.

All reagents (CuCl, Na_2S*9H_2O) are pre-weighed in the calculated proportion and simultaneously heating put into a Teflon container.

The vessel is then firmly sealed with an argon fill once the charge has been full, and a steam release hole is drilled in the screw cap. During the reaction, a small flow of argon continues to flow into the top section of the vessel, which creates some excess pressure above the melt surface.

$Cu_{2-x}S$ nanoparticles are formed after several hours, usually 15 hours are maintained. The formed crystals are in the melt in the form of a gel. By incorporating a little amount of water into the melt, nanocrystal sizes can be lessened. The final result, which takes the shape of a gel clot, is cleaned three times with warm distilled water before being cleaned again with pure ethanol and allowed to air dry. Particle sizes ranging from 15 to 90 nm make up the majority of the resultant powder. The process of sedimentation in an alcohol-filled column is used to separate distinct particle fractions according to size.

Low-temperature liquid-phase chemical synthesis requires less time and cost to obtain a synthesis product, but has a number of features. Residues of organic components used in the synthesis are difficult to completely remove, which does not always allow for the acquisition of a chemically pure product, and the presence of several percent of foreign components in the synthesized phase is almost inevitable. In this case, X-ray phase analysis does not fix the presence of foreign phases, but the presence of impurities is manifested in studies on a scanning electron microscope and in spectral chemical analysis. Homogenization at a temperature not lower than 400 °C allows for minimizing the content of volatile components and increasing the repeatability of the outcomes of investigations of electronic kinetic coefficients (conductivity, thermal conductivity, etc.).

In the chemical synthesis of copper chalcogenide nanopowder, the result strongly depends on the reaction time. The size of the resultant nanocrystals may be dwindled to 8–12 nm by cutting the annealing period to 5-8 hours. The use of a dispersing medium (for example, diethylene glycol) changes the shape of the nanocrystals and reduces their size. In the synthesis of $Na_xCu_{2-x}S$ superionic materials, the incorporation of a trace quantity of water also makes it possible to vary the size of the obtained nanocrystals.

Electron microscopy.

An examination of the periphery of the samples using a MIRA3 TESCAN scanning electron microscope confirmed the estimate of the crystallite sizes from the X-ray line half-width. In figures 2-5 below, the materials have a loose structure of blocks of crystallites separated by large pores.

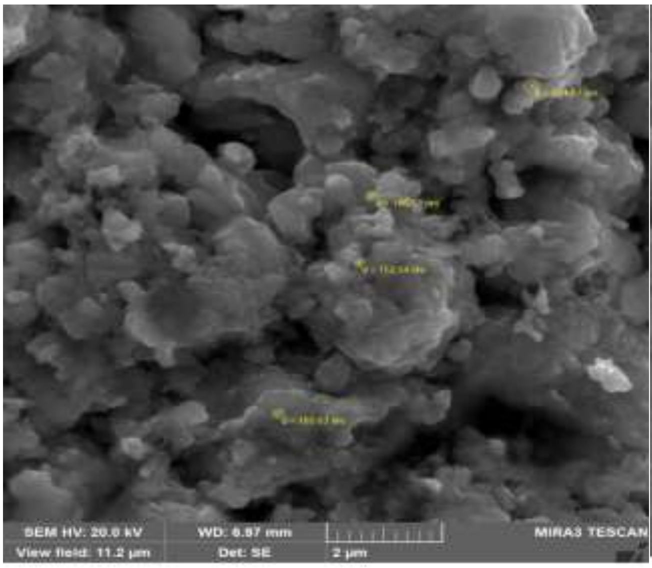

Figure 2 — Photograph of the etched $Na_{0.15}Cu_{1.85}S$ surface on a MIRA3 TESCAN scanning electron microscope. Visible loose nanocrystalline structure

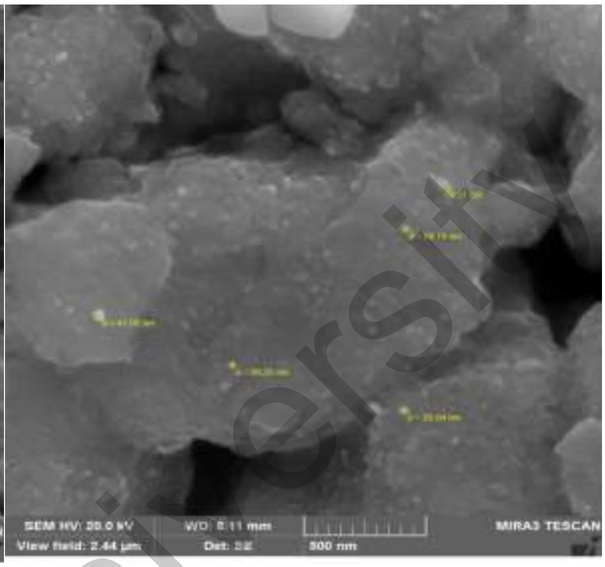

Figure 3 — Photograph of another area of the etched $Na_{0.15}Cu_{1.85}S$ surface on a MIRA3 TESCAN scanning electron microscope. Visible nanocrystalline grain structure and large pores

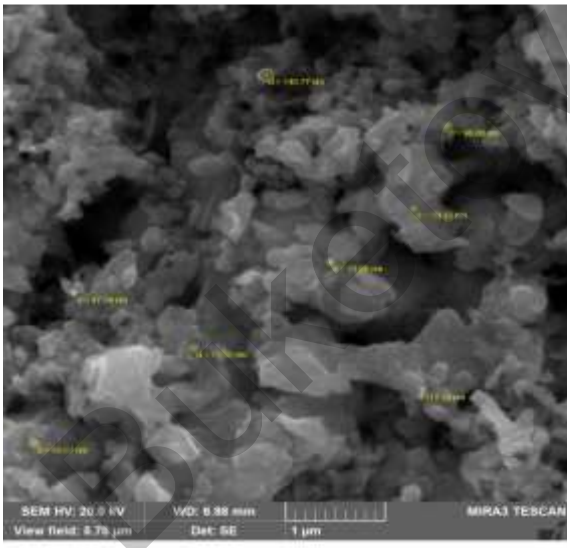

Figure 4 — Photograph of the etched $Na_{0.125}Cu_{1.75}S$ surface on a MIRA3 TESCAN scanning electron microscope. Loose nanocrystalline structure and pores are visible

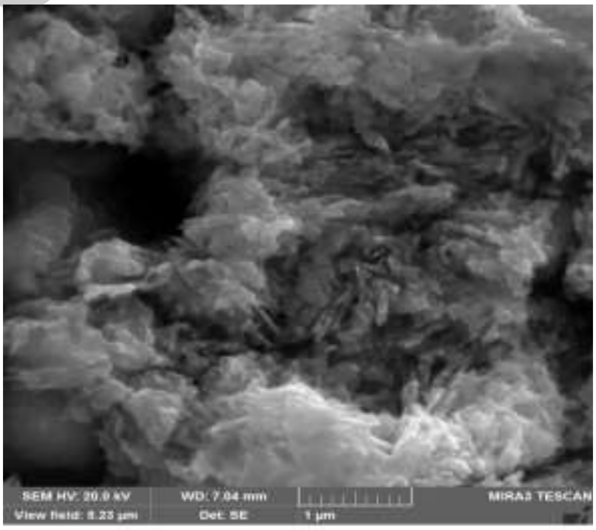

Figure 5 — Photograph of another area of the etched $Na_{0.125}Cu_{1.75}S$ surface on a MIRA3 TESCAN scanning electron microscope. Loose nanocrystalline structure and pores are visible

Conclusion

Depending on the purposes of the synthesis, the best technique for producing chalcogenide materials for sodium-ion battery electrodes will be chosen. It is ideal to use the direct solid-phase reaction approach in a vacuum or in an environment of pure inert gas when synthesizing a novel chalcogenide material in tiny quantities for the investigation of its physicochemical and other features. With this approach, which is more dependable, it is feasible to produce a pure result free of contaminants that are inescapable when working with other solvents and precursors. Additionally, in a consistent synthesis regime, it is differentiated by the stability of the acquired attributes of the compounds. Synthesis modes, reagents, and post-processing depend on the specific material.

The main challenge in the synthesis of an electrode material features of which are known for commercial applications is to produce low-cost goods while keeping relevant qualities discovered in laboratory investigations. Due to the lower manufacturing costs, nearly all top laboratories now working on functional materials use “soft” chemistry techniques that enable synthesis at low enough temperatures.

In this work, as one of the main ones, it is used to generate alloys using a procedure that involves melting a combination of potassium and sodium hydroxides. The melting point drips to 165 °C at a certain ratio of the concentrations of these hydroxides, letting for the conduct of exchange processes between salts in the melt. The resultant chalcogenide particles can be shrunk to a few nanometers in size by lowering the temperature during synthesis, adding water, and shortening the annealing period.

As studies of recent years show, one of the promising materials for electrodes in sodium-ion batteries is currently considered covelline CuS. Hundreds of micrometer-sized particles in bulk CuS reveal outstanding stability and high capacity for a range of current densities from 1 to 5 C. Bulk CuS also offers long-term cyclic stability, with a specific capacity retention of 406 mAh/g at high current densities (5C) after 1000 cycles. In Na_xCuS nanoplates, the development of stable grain boundaries and interfacial boundaries also helps to restore the electrode capacity and resistance to grinding, prolonging the service life of the cathode.

In light of the results of recent research, the greatest success in the development of electrodes for sodium-ion batteries can be achieved for composites that combine the active material with nanosized carbon materials, including those that create a protective shell for particles of the electrode material, which increases the resistance of the electrode to repeated overcharging.

In consequence, in line with the current trend of looking for novel electrode materials for sodium-ion batteries, work on the synthesis of copper sulfides of varied compositions and morphologies offers optimism that the acquired materials may soon be used in practical applications.

Acknowledgments

The Science Committee of the Republic of Kazakhstan, which is part of the Ministry of Science and Higher Education, provided funding for this research (No. AP14871197).

References

1 Tang, Zh. & Yang, H. (2020). Advanced Nanomaterials for Electrochemical Energy Conversion and Storage. CHAPTER 11: Transition metal chalcogenides for energy storage and conversion. *ELSEVIER,* P. 355-391.

2 Li, Q., Li, L., Owusu, K.A., Luo, W., An, Q. & Wei, Q. (2017). Self-adaptive mesoporous CoS@alveolus-like carbon yolk-shell microsphere for alkali cations storage. *Nano Energy, Vol. 41,* P. 109-116.

3 Pan, Y., Cheng, X., Gong, L., Shi, L., Deng, Y. & Zhang, H. (2018). Highly reversible Na ion storage in N-doped polyhedral carbon-coated transition-metal chalcogenides by optimizing the nanostructure and surface engineering. *J. Mater. Chem. A., Vol. 6,* P. 18967-18978.

4 Kim, J.-S., Kim, D.-Y., Cho, G.-B., Nam, T.-H., Kim, K.-W., Ryu, H.-S., Ahn, J.-H. & Ahn, H.-J. (2009). The electrochemical properties of copper sulfide as cathode material for rechargeable sodium cell at room temperature. *J. Power Sources, Vol. 189,* P. 864-868.

5 Yue, J.-L., Sun, Q. & Fu, Z.-W. (2013). Cu_2Se with facile synthesis as a cathode material for rechargeable sodium batteries. *Chem. Commun, Vol. 49,* P. 5868-5870.

6 Park, J.Y., Kim, S.J., Yim, K., Dae, K.S., Lee, Y., Dao, K.P., Park, J.S., Jeong, H.B., Chang, J.H. & Seo, H. (2019). Pulverization-Tolerance and Capacity Recovery of Copper Sulfide for High-Performance Sodium Storage. *Adv. Sci,* P. 1900264.

7 Park, J., Joo, J., Kwon, S.G., Jang, Y. & Hyeon, T. (2007). Synthesis of monodisperse spherical nanocrystals. *Angew. Chem. Int. Ed., Vol. 46,* P. 4630-4660.

8 Wada, Y., Kuramoto, H., Anand, J., Kitamura, T., Sakata, T., Mori, H. & Yanagida S. (2001). Microwave-assisted size control of CdSnanocrystallites. *J. Mater. Chem, Vol. 11,* P. 1936-1940.

9 Ghows, N. & Entezari, M.H. (2011). A novel method for the synthesis of CdS nanoparticles without surfactant. *Ultrason. Sonochem, Vol. 18,* P. 269-275.

10 Sohrabnezhad, S.H. & Pourahmad. (2010). A. CdS semiconductor nanoparticles embedded in AlMCM-41 by solid-state reaction. *J. Alloys Compd., Vol. 505,* P. 324-327.

11 Nirmal, R.M., Pandian, K. & Sivakumur, K. (2011). Cadmium (II) pyrrolidinedithiocarbamate complex as single source precursor for the preparation of CdS nanocrystals by microwave irradiation and conventional heating process. *Appl. Surf. Sci., Vol. 257,* P. 2745-2751.

12 Trindade, T. & O’Brien, P. (1997). Synthesis of CdS and CdSeNanocrystallites Using a Novel Single-Molecule Precursors Approach. *Chem. Mater., Vol. 9*, P. 523-530.

13 Zhang, Y.C., Wang, G.Y. & Hu, X.Y. (2007). Solvothermal synthesis of hexagonal CdS nanostructures from a single-source molecular precursor. *J. Alloys Compd., Vol. 437,* P. 47-52.

14 Huang, Y., Xiao, H., Chen, S. & Wang, C. (2009). Preparation and characterization of CuS hollow spheres. *Cer Inter., Vol. 35,* P. 905-907.

15 Dhassade, S.S., Patil, J.S., Han, S.H., Rath, M.C. & Fulari, V.J. (2013). Copper sulfide nanorods grown at room temperature for photovoltaic application. *Mater. Lett, Vol. 90,* P. 138-141.

16 Maji, S.K., Mukherjee, N., Dutta, A.K., Srivastaca, D.N., Paul, P., Karmakar, B., Mondal, A. & Adhikary, B. (2011). Deposition of nanocrystallineCuS thin film from a single precursor: Structural, optical and electrical properties. *Mater. Chem. Phys., Vol. 130,* P. 392-397.

17 Ma, G., Zhou, Y., Li, X., Sun, K., Liu, S., Hu, J. & Kotov, N.A. (2013). Self-assembly of copper sulfide nanoparticles into nanoribbons with continuous crystallinity. *ACS Nano, Vol. 7,* P. 9010-9018.

18 Zhang, H.T., Wu, G. & Chen, X.H. (2006). Controlled synthesis and characterization of covellite (CuS) nanoflakes. *Mater. Chem. Phys., Vol. 98,* P. 293-303.

19 Wu, C., Shi, J.B., Chen, C.J., Chen, Y.C., Lin, Y.T., Wu, P.F. & Wei, S.Y. (2008). Synthesis and optical properties of CuS nanowires fabricated by electrodeposition with anodic alumina membrane. *Mater. Lett, Vol. 62,* P. 1074-1077.

20 Liu, J. & Xue, D.F. (2009). Solvothermal synthesis of CuS semiconductor hollow spheres based on a bubble template route. *J. Cryst. Growth, Vol. 311,* P. 500-503.

21 Thongtem, T., Phuruangrat, A. & Thongstem, S. (2009). Formation of CuS with flower-like, hollow spherical, and tubular structures using the solvothermal-microwave process. *Curr. Appl. Phys., Vol. 9,* P. 195-200.

22 Tan, C.H., Lu, R., Xue, P.C., Bao, C.Y. & Zhao, Y.Y. (2008). Synthesis of CuS nanoribbons templated by hydrogel. *Mater. Chem. Phys., Vol. 112,* P. 500-503.

23 Pradhan, N., Katz, B. & Efrima, S. (2003). Synthesis of High-Quality Metal Sulfide Nanoparticles from Alkyl Xanthate. Single Precursors in Alkylamine Solvents. *J. Phys. Chem. B., Vol. 107,* P. 13843-13854.

24 Mondal, G., Acharjya, M., Santra, A., Bera, P., Jana, S., Pramanik, N.C., Mondal, A. & Bera P. (2015). A new pyrazolyldithioate function in the precursor for the shape controlled growth of CdS nanocrystals: Optical and photocatalytic activities. *New J. Chem., Vol. 39,* P. 9487-9497.

25 Flor, J., Marques de Lima, S.A. & Davalos, M.R. (2004). Effect of reaction time on the particle size of ZnO and ZnO: Ce obtained by a sol-gel method. *Prog. Colloid Polym. Sci., Vol. 128,* P. 239-243.

26 Sharma, K.N., Joshi, H., Prakash, O., Sharma, A.K., Bhaskar, R. & Singh, A.K. (2015). Pyrazole-Stabilized Dinuclear Palladium (II) Chalcogenolates Formed by Oxidative Addition of Bis [2-(4-bromopyrazol-1-yl) ethyl] Dichalcogenides to Palladium (II)–Tailoring of Pd–S/Se Nanoparticles. *Eur. J. Inorg. Chem., Vol. 29,* P. 4829-4838.

27 Deori, K., Ujjain, S.K., Sharma, R.K. & Deka, S. (2013). Morphology controlled synthesis of nanoporous Co3O4 nanostructures and their charge storage characteristics in supercapacitors. ACS Appl. *Mater. Interfaces, Vol. 5,* P. 10665-10672.

28 Coe, S., Woo, W.K., Bawendi, M. & Bulovic, Y. (2002). Electroluminescence from single monolayers of nanocrystals in molecular organic devices. *Nature, Vol. 420,* P. 800-803.

29 Ajibade, P.A. & Botha, N.L. (2017). Synthesis, Optical and Structural Properties of Copper Sulfide Nanocrystals from Single Molecule Precursors. *Nanomaterials, Vol. 7,* P. 32.

30 Lot, M., Machani, T., Rossi, D.P. & Plass, K.E. (2011). Alpha-Chalcocite Nanoparticle Synthesis and Stability. *Chem. Mater., Vol. 23,* P. 3032-3038.

31 Williamson, C.B., Nevers, D.R., Hanrath, T. & Robinson, R.D. (2015). Prodigious Effects of Concentration Intensification on Nanoparticle Synthesis: A High-Quality, Scalable Approach. *J. Am. Chem. Soc., Vol. 137,* P. 15843-51.

32 Yao, Y. (2018). Reaction Mechanism and Size dependent Electrochemical Properties Study of $Cu_{2-x}S$ Versus Li. *A Thesis of Master of Science of Cornell University,* 85 p.

33 Lu, Q., Gao, F. & Zhao, D. (2002). One-Step Synthesis and Assembly of Copper Sulfide Nanoparticles to Nanowires, Nanotubes, and Nanovesicles by a Simple Organic Amine-Assisted Hydrothermal Process. *Nano Lett., Vol. 2,* P. 725-728.

М.М. Кубенова, К.А. Кутербеков, М.Х. Балапанов, Р.Х. Ишембетов, К.Ж. Бекмырза, А.М. Кабышев, Ш. Афрозе, Р.Ш. Палымбетов, Ж.А. Мұханова, Е. Шукалов

Термоэлектрлік генераторлар мен натрий-ионды аккумуляторларға арналған жаңа нанокристалды халькогенидті материалдарды синтездеу мәселелерін талдау

Мақалада термоэлектрлік генераторлар мен натрий-ионды аккумуляторларға арналған жаңа нанокристалды халькогенидті материалдарды синтездеу мәселелері талданған. Практикалық электродтар үшін халькогенидті материалдарды синтездеудің оңтайлы технологиясы синтез мақсаттарына байланысты. Физика-химиялық және басқа да қасиеттерді зерттеу үшін аз мөлшерде жаңа халькогенидті материалды синтездеу вакуумда немесе тазартылған инертті газ атмосферасында тікелей қатты фазалы реакция әдісімен оңтайлы жүргізіледі. Бұл әдіс сенімдірек және әртүрлі еріткіштер мен прекурсорларды пайдалану кезінде сөзсіз қоспасыз таза өнімді алуға мүмкіндік береді. Сонымен қатар, ол тұрақты синтез режиміне сәйкес алынған қосылыстардың қасиеттерінің тұрақтылығымен ерекшеленеді. Синтез режимдері, реагенттер, кейінгі өңдеу нақты материалға байланысты. Бұл жұмыста калий және натрий гидроксидтері қоспасының балқыма ортасындағы қорытпаларды синтездеу негізгі қолданылатын әдістердің бірі. Осы гидроксидтердің концентрациясының белгілі бір қатынасында балқу температурасы 165 °C дейін төмендейді, бұл қорытпадағы тұздар арасында алмасу реакцияларын жүргізуге мүмкіндік береді. Синтез температурасының төмендеуі, судың қосылуы және күйдіру уақытының қысқаруы нәтижесінде пайда болған халькогенид бөлшектерінің мөлшерін бірнеше нанометрге дейін азайтуға мүмкіндік береді.

Кілт сөздер: термоэлектрлік материалдар, мыс сульфиді, кристалдық құрылым, өткізгіштік, диффузия, жылу өткізгіштік, Зебек коэффициенті, суперионды өткізгіштер.

М.М. Кубенова, К.А. Кутербеков, М.Х. Балапанов, Р.Х. Ишембетов, К.Ж. Бекмырза, А.М. Кабышев, Ш. Афрозе, Р.Ш. Палымбетов, Ж.А. Мұханова, Е. Шукалов

Анализ проблем синтеза новых нанокристаллических халькогенидных материалов для термоэлектрических генераторов и натрий-ионных аккумуляторов

В статье проанализированы проблемы синтеза новых нанокристаллических халькогенидных материалов для термоэлектрических генераторов и натрий-ионных аккумуляторов. Оптимальная технология синтеза халькогенидных материалов для электродов практического применения зависит от целей синтеза. Синтез нового халькогенидного материала в малых количествах для изучения физико-химических и других свойств оптимально проводить методом прямой твердофазной реакции в вакууме или в атмосфере очищенного инертного газа. Этот метод более надежен и позволяет получить чистый продукт, не содержащий примесей, неизбежных при использовании различных растворителей и прекурсоров. Кроме того, его отличает стабильность свойств получаемых соединений при соблюдении постоянного режима синтеза. Режимы синтеза, реагенты, постобработка зависят от конкретного материала. В настоящей работе в качестве одного из основных используется метод синтеза сплавов в среде расплава смеси гидроксидов калия и натрия. При определенном соотношении концентраций этих гидроксидов температура плавления снижается до 165°C, что позволяет проводить обменные реакции между солями в расплаве. Снижение температуры синтеза, добавление воды и сокращение времени отжига позволяют уменьшить размер образующихся частиц халькогенидов до нескольких нанометров.

Ключевые слова: термоэлектрические материалы, сульфид меди, кристаллическая структура, проводимость, диффузия, теплопроводность, коэффициент Зеебека, суперионные проводники.