REVIEW

of a dissertation for obtaining the scientific and educational degree "PhD"

in a professional direction

4.2 Chemical Sciences (Solid State Chemistry)

Author of the dissertation:

Evelina Yordanova Vasileva, SOFIA UNIVERSITY "ST. KLIMENT OHRIDSKI", FACULTY OF CHEMISTRY AND PHARMACY

Dissertation topic: **Porous metals obtained by selective dissolution of alloys - suitable electrode materials in ion batteries**

Reviewer:

Prof. Dr. Mario Yordanov Mitov, Department of Chemistry, Southwest University "Neofit Rilski" - Blagoevgrad

Brief biographical data

Evelina Vasileva graduated from Sofia University "St. Kliment Ohridski" as a Bachelor of Chemistry, majoring in "Ecochemistry" (2018) and a Master's degree, majoring in "Functional Materials" (2019). From 2019, she was appointed as a Researcher under the Project "CENTER FOR TOP ACHIEVEMENTS "NATIONAL CENTER FOR MECHATRONICS AND CLEAN TECHNOLOGIES", and from 2022 - as a Chemist at the Department of Applied Inorganic Chemistry of the Faculty of Chemistry and Pharmacy at Sofia University "St. Kliment Ohridski". In 2022, she was also enrolled as a self-taught doctoral student at the same department. Evelina Vasileva has submitted all the necessary documents for the procedure for awarding the educational and scientific degree " PhD ".

Actuality of the problem

In the context of the transition from fossil fuels to alternative ecological sources of energy, the number of research and development for the creation of new materials necessary for the efficient

functioning of a number of energy conversion and storage technologies has increased in recent decades. Since the early 1990s, lithium-ion batteries have become the primary technology for storing energy and powering the majority of portable electronic devices as well as electric cars. The growth in the production and use of these batteries is so fast that a number of researchers reasonably question how long the limited natural resources of lithium will be able to supply the growing needs. This explains the efforts aimed at developing alternative Na-ion batteries, since the natural resources of sodium compounds are significantly greater, which also determines the much lower cost of Na compared to Li. Regardless of the type of charge carrier, however, an important component determining the capacity of ion- (and of course all other types) batteries are the electrode materials, which must possess a number of characteristics such as high electrical conductivity, mechanical stability, minor structural and volume changes at charge-discharge, light weight, etc., and of course have a relatively low cost. Porous metallic materials possess many of these qualities, with additional advantages for their use as electrodes in ion batteries being their large specific surface area with many active centers, the facilitated passage of the electrolyte, and the diffusion of ions through the porous structure. In this aspect, the creation of new porous structures with high capacity is a priority direction in research aimed at developing next-generation ion batteries, which unequivocally shows that the problem that is the subject of the present dissertation - synthesis and characterization of new porous electrodes materials for ion batteries - is extremely relevant.

General characteristics of the dissertation

The dissertation is written on 116 pages, contains 54 figures and 4 tables. 230 literary sources are cited, a significant part of which were published in the last 10 years. The dissertation consists of the following sections: Introduction, Aims and objectives, Literature review, Used methods, Results and discussion, Conclusions and Scientific contributions.

In the introduction part, a brief introduction is made on the necessity of developing new electrode materials for energy storage and the advantages of porous materials for their use as electrodes in ion batteries. Several goals and specific tasks have been set, around which the overall research is focused. The Literature Review (comprising about 30% of the volume of the dissertation) presents the types of porous materials, their characteristics and properties, as well as their main applications. The various approaches and precursors for obtaining porous materials are described, and results from cited publications are presented in a summary. The literature review concludes with a chapter entitled "Porous Metal Electrodes Suitable for Ion Batteries", which highlights the advantages of porous materials reported in the literature for application in ion batteries. The significant number of cited literary sources, as well as the ability to synthesize and systematically present the results published in them, demonstrate in an indisputable way the good knowledge of the current state of

the subject on the part of the candidate. In the next section, the main principles of the methods used to obtain and characterize the studied materials are briefly presented. The variety of modern instrumental methods, selected in such a way as to characterize in depth and with the necessary precision the changes in the composition, structure and morphology of the studied materials as a result of their electrochemical treatment, is impressive.

The main results of the study and their discussion are set out in the Results and Discussion section. Alloys based on Zn-Sn and Zn-Sn-Bi, as well as a ternary alloy $Cu_{60}Ag_{30}Al_{10}$, were synthesized and characterized. Most of the alloys were obtained by the method of rapid quenching from the melt, and the binary alloy $Zn_{70}Sn_{30}$ was also obtained by normal cooling. The microstructure of the starting alloys, as well as after various electrochemical treatments, was investigated by X-ray diffraction, as well as with a transmission electron microscope. Additional information on the microstructure of the investigated alloys, as well as on their chemical composition, was obtained by energy-dispersive spectroscopy. Through electrochemical selective dissolution at selected potentials, porous metal structures were obtained from the starting alloys, some of which were tested as negative electrodes (porous Sn obtained by selective dissolution of zinc from a $Zn_{70}Sn_{30}$ alloy synthesized by the method of rapid quenching from a melt) or components of negative electrodes (porous $Cu_{60}Ag_{30}Al_{10}$ alloy material) in ion batteries. The specific surface area of the obtained porous materials was determined by the BET method, and their morphology before and after the tests as electrode materials was characterized by scanning electron microscopy. The porous structure of $Cu_{60}Ag_{30}Al_{10}$ alloy obtained by selective dissolution was used as a mechanically stable and conductive substrate on which sulfur was deposited as an active material by two approaches – from a solution and by direct dripping. The material prepared by direct sulfur deposition was tested as an electrode in a Li-ion cell. In an applied aspect, the most interesting are the results of the electrochemical tests of selected materials as potential electrodes for Li- and Na-ion batteries. With porous electrodes obtained from $Zn_{70}Sn_{30}$ alloy, an initial discharge capacity of 440 mAh g^{-1} was achieved in the lithium cell, and 205 mAh g-1 in the sodium cell. Although lower than the corresponding theoretical capacity of Sn, it should be noted that the obtained specific discharge capacities for the porous structure are without the presence of binders, which is typical for tin-based electrodes at Li- and Na-ion batteries. Despite higher initial capacitance values in the Li-ion cell, better charge-discharge cycling stability of the porous electrode was found in the Na-ion cell. With a $Cu_{60}Ag_{30}Al_{10}$ alloy electrode and deposited sulfur as the active material, a reversible specific capacity of ~ 230 mAh g^{-1} at a current density of 0.4 μA cm^{-2} was determined experimentally in a Li-ion cell. The obtained capacity of 230 mAh g^{-1} exceeds the theoretical capacity of Ag_2S (217 mAh g^{-1}), indicating the contribution of the Cu_xS component to the overall capacity of the electrode. A very good cyclic stability of the electrode was found for more than 1000 charge-discharge cycles and current densities of 1 and 2 A g^{-1}, which is associated with a substitution reaction of the active Ag_2S-Cu_xS material with Li^+ ions.

The presented discussion demonstrates the good theoretical preparation and the ability of the candidate to interpret the experimental results in the context of known facts and mechanisms published in the literature.

Conclusions summarize the most important results, but for the most part they sound more like contributions. This part should focus on observed trends and optimization of the conditions for obtaining porous materials with the potential for their use in ion batteries.

Main contributions

The main contributions of the presented dissertation can be summarized as follows:

• New eutectic-type binary and ternary alloys have been synthesized by the rapid melt quenching method.

• Porous materials were obtained by electrochemical selective dissolution of the synthesized alloys.

• The microstructure and composition of the obtained materials were characterized before and after the electrochemical selective dissolution, as well as after their testing as electrode materials in ion batteries.

• Selected porous materials have been tested as negative electrodes for Li/Na-ion batteries.

• When using porous Sn obtained by selective dissolution of zinc from $Zn_{70}Sn_{30}$ alloy, relatively high discharge capacity values were achieved in Li- and Na-ion cells, without the presence of binders.

• Very good cyclic stability was achieved when using as an electrode in a Li-ion cell a porous metal structure obtained from a $Cu_{60}Ag_{30}Al_{10}$ alloy, on which sulfur was directly deposited as an active material.

As a summary, it can be noted that the contributions of the presented dissertation are significant in both scientific and scientific-applied terms and represent further development and enrichment of knowledge in the field of synthesis and characterization of porous materials for applications as electrodes in ion batteries.

The abstract reflects clearly and precisely the main results and contributions of the dissertation.

Scientific data

The results of the dissertation are summarized in 3 scientific papers, which have been published in prestigious international journals with an impact factor - Journal of Alloys and Compounds (Q1), Dalton Transactions (Q1) and Journal of Porous Materials (Q2). In 2 of the published articles, the candidate is the first author. Although published recently, 2 citations of the publications in which Evelina Vasileva is a co-author have already been noticed. Part of the results presented in the dissertation were also reported at 2 scientific forums.

On the basis of the indicated data, it can be concluded that the scientometric indicators of Evelina Vasileva's dissertation meet and even exceed the criteria of the Law for the development of the academic staff in the Republic of Bulgaria and the regulations of the Sofia University for the claimed educational and scientific degree.

Role of the candidate in the conducted research

The fact that Evelina Vasileva is the first author in co-authorship with an authoritative scientific team in 2 of the publications used in the dissertation gives me reason to conclude that to a large extent the research presented in this dissertation is the personal work of candidate.

Criticisms, questions, recommendations

A very good impression is made by both the style and the overall layout of the dissertation and the abstract in Bulgarian and English. There are no significant grammatical and punctuation errors, which are unfortunately a common occurrence even in works of this kind.

I have a few remarks about the thesis, which are more of a technical nature:

• Each particular undertaking has one particular purpose. The goals presented in the dissertation are rather stages of achieving such a goal, namely synthesis and characterization of new porous materials for application as electrodes in ion batteries.

• Some of the figures and tables are directly copied from publications. Although the relevant publications are correctly cited, I would recommend that the dissertation be adapted accordingly to the main text in such cases.

• On page 55 it is written: "…the current increases significantly for a very short time, then slows down and begins to gradually decrease." – The "current" or more precisely the "strength of the current" can increase and decrease, but not to slow down!

• On page 60: "In summary, the curves obtained in both cells are similar to those reported in other studies ??? with similar electrode materials, which proves that the porous structure can interact

with Li^+ and Na^+ by alloying." – here the publications with which the obtained results are compared must be cited.

• In the contributions it is written: "3. It has been shown that porous structures based on Bi and Sn are suitable negative electrodes in Li/Na ion batteries operating on the principle of "alloying" with lithium/sodium." - this substantively does not correspond to the presented results, because only porous Sn obtained by selective dissolution of zinc from $Zn_{70}Sn_{30}$ alloy was tested as negative electrodes for Li/Na ion batteries.

Of course, these technical shortcomings do not detract from the results obtained in the dissertation and do not significantly affect their interpretation.

I have the following questions for the candidate:

• What do you think is the reason why melt quenched alloys have a crystalline rather than an amorphous structure?

• Have you investigated as electrodes in Li/Na ion cells some of the porous structures obtained from ternary Zn-Sn-Bi alloys?

• How could the conditions be optimized to obtain porous electrode materials with higher capacity from the same starting alloys?

Conclusion

In conclusion, I consider that the dissertation submitted for review in terms of volume, methodical level, scientific contributions and scientometric data complies with the Law for the development of the academic staff in the Republic of Bulgaria and the Regulations for its application in SU "St. Kliment Ohridski" for awarding the educational and scientific degree "DOCTOR". Bearing in mind all of the above and based primarily on the scientific contributions of the dissertation work and the candidate's level of qualification, I recommend the honorable scientific jury to vote for awarding the scientific and educational degree "DOCTOR" to **Evelina Yordanova Vasileva**.

20/09/2023 Reviewer:.....

(Prof. DSc Mario Mitov)