REVIEW

of Dissertation work entitled: "**Porous metals obtained by selective dissolution of alloys - suitable electrode materials in ion batteries**"
for awarding the educational and scientific degree "Doctor of Philosophy",
professional specialty: 4.2 Chemical Sciences (Solid State Chemistry)

PhD candidate: Evelina Yordanova Vassileva
academic supervisor: Prof. Tony Spassov, DSc.
scientific consultant: Assist. Prof. Lyuben Mihaylov, PhD.

reviewer: Assoc. Prof. Georgi Yordanov (DSc.), Faculty of Chemistry and Pharmacy, SU

Biographical and scientometric data

Evelina Yordanova Vassileva completed her higher education with a bachelor's degree in "Ecochemistry" at the Sofia University "St. Kliment Ohridski", Faculty of Chemistry and Pharmacy. After that, she continued her education in the same Faculty and received a Master degree in the specialty "Functional Materials". Since 2019, she has been a researcher at the Center for Excellence project "National Center for Mechatronics and Clean Technologies". From 2022, she was also appointed as a chemist at the Department of Applied Inorganic Chemistry of the Faculty of Chemistry and Pharmacy at SU "St. Kliment Ohridski", where she was enrolled in the doctoral course for the period 14.11.2022 - 21.06.2023. A total of 6 scientific publications with her as a coauthor and 8 independent citations were found in the Scopus system. Evelina Vassileva is a participant in the projects "Center for Excellence "National Center for Mechatronics and Clean Technologies"" and "National Scientific Infrastructure INFRAMAT".

Aims of the dissertation and actuality of the research topic

The dissertation is dedicated to the development of new porous metals as electrode materials for ion batteries. The advantages of porous materials as electrodes in ion batteries are their large specific surface area, facilitating the passage of the electrolyte and the diffusion of ions. A general analysis of literature and previous research on the subject was made and on its basis the aims of the dissertation work were clearly and specifically defined: production of two-component (Zn-Sn) and three-component (Zn-Sn-Bi and Cu-Ag-Al) alloys at different crystallization conditions from a melt and achieving selective electrochemical dissolution of the less noble metal from the alloys to produce

porous structures. The literature review and the results presented in the dissertation work are in full accordance with the set goals. The topic of the dissertation falls in the field of materials science and in particular in the field of materials for efficient energy storage, which is an extremely fast-developing and modern scientific field, uniting different parts of inorganic chemistry, chemical technology and electrochemistry.

Dissertation review and evaluation of results

The dissertation is written in Bulgarian and contains 116 pages, which include 54 figures and 4 tables. 230 literary sources are cited. The Autoreferat is presented on 52 pages, correctly and fully reflecting the main results and contributions of the dissertation work. The results were published in 3 scientific publications in prestigious international journals, which have already received independent citations in the scientific literature. The studies are of an interdisciplinary nature, in which both the preparation and structural characterization of the materials are described, as well as electrochemical studies in connection with their application in ion batteries. Evelina Vassileva is the first author in two of the scientific publications, which suggests that she has a leading contribution to the works presented. Attached is a list of 2 participations in scientific forums related to the topic of the dissertation, where she is the first author of the reports presented.

The dissertation is structured in the following parts: introduction (1 page), aims and objectives (1 page), literature review (32 pages, 2 figures, 1 table), used methods (9 pages, 6 figures), results and discussion (42 pages, 46 figures, 3 tables), conclusions and scientific contributions (3 pages), bibliographic description of the cited literary sources (22 pages).

The literature review (section I) examines in the necessary depth and detail various methods of preparation, description of properties and physicochemical characterization of various electrode materials for ion batteries, which is directly related to the goals and tasks of the dissertation work. Within the framework of the literature review, 216 literature sources are cited, mostly related to the preparation, properties and applications of various porous materials and, in particular, porous metal structures. Their application for ion batteries is described. Section II gives a general description of the methods used for obtaining and analyzing the studied materials. The principles on which the instrumental methods for physicochemical characterization are based are briefly described. The detailed description of the experiments and the specific apparatus is given also in section III (results and discussion).

Section III (results and discussion) gives a detailed and correct description of the synthesis procedures, performed analyzes and tests of the obtained materials. The

research and presented results are mainly concentrated on alloys with the composition $Zn_{70}Sn_{30}$ and Zn-Sn-Bi and the corresponding porous materials obtained after the selective dissolution of the zinc component, as well as on the alloy with the composition $Cu_{60}Ag_{30}Al_{10}$ and the corresponding porous material obtained after its selective dissolution and modification. The starting alloys were obtained in most cases by induction heating and melting, followed by rapid cooling/quenching on a rotating metal disc. Porous materials suitable for electrode materials in ion batteries have been obtained by electrochemical dissolution of the less noble components of the alloys. The main results can be summarized as follows:

i) Alloys with composition $Zn_{70}Sn_{30}$ were obtained by rapid quenching and by normal cooling and casting on a ceramic surface. The established difference in the microstructure of the alloys (smaller crystallite size and more homogeneous distribution of phases in the alloy obtained with faster cooling) is associated with a difference in the porosity of the corresponding materials obtained by the selective dissolution of the alloys. The material obtained by selective dissolution of the quenched alloy, characterized by a better combination of properties (mechanical stability, strip thickness, smaller pores and their homogeneous distribution on the surface), was investigated as an electrode for Li/Na ion batteries. In doing so, a better charge-discharge cycling stability was found in the Na-ion cell (compared to a Li-cell).

ii) A series of Zn-Sn-Bi alloys with different Sn/Bi molar ratio were obtained by rapid quenching. Differences in the starting ratio of the components lead to different ratios of ternary eutectic and the other two crystalline phases in the resulting alloys. After electrochemically selective dissolution of the zinc component, porous materials with different morphology and pore size were obtained, the difference in porosity being the result of the different initial chemical and phase composition.

iii) A microcrystalline alloy with the composition $Cu_{60}Ag_{30}Al_{10}$ was obtained, from which, after selective electrochemical dissolution under appropriate conditions, a silver-enriched mechanically stable and conductive porous material was obtained. An active layer of $Ag_2S–Cu_xS$ was deposited on the porous surface and the resulting electrode was tested in a Li-ion cell, where very good cycling stability was found for more than 1000 cycles. The cyclic stability is explained by an ongoing reaction of replacing the metal ions from the active Ag_2S-Cu_xS layer with Li^+ ions. During the reduction of the metal ions from the sulfide layer, Ag and Cu are deposited on the surface and form dendritic structures on the Li_2S matrix. The process proceeds in the opposite direction during charging. By limiting the dissolution of the polysulfide intermediates, destruction of the

electrode is largely avoided. Electrode material studies after more than 1000 cycles found preservation of pore morphology and mechanical integrity.

Dissertation Contributions

The contributions of the dissertation can be summarized as follows:

1. Double (Zn-Sn) and triple (Zn-Sn-Bi, Cu-Ag-Al) alloys with fine crystal micro-structure and homogeneous distribution of phases were obtained by induction melting and rapid quenching.
2. Appropriate conditions were established for electrochemical selective dissolution of the prepared alloys, in which porous nanostructures were obtained.
3. Sn-based porous structures have been shown to be suitable as electrodes in Li/Na ion batteries.
4. A new approach was applied to investigate the capacity and stability of lithium-sulfur batteries using a porous silver-enriched material as a mechanically stable and conductive substrate on which an active layer of $Ag_2S–Cu_xS$ was deposited.

Contributions are supported by the evidence presented and generally contain useful information. The resulting materials have an interesting nano-architecture and promising application.

Recommendations

I have some remarks on the technical layout of the dissertation submitted for review, which in no way detract from the otherwise high scientific quality of the dissertation work. For example, in the bibliographic description of the literature used (Section V) different styles were used. It is recommended to use a uniform style, format and punctuation scheme when describing the cited information resources. A slight confusion in the reader is caused by the use of the term "alloy" in several places in the text both for the starting alloy $Zn_{70}Sn_{30}$ and for the porous material obtained after its selective dissolution (for example, in the text under Fig. 20 in the dissertation).

Conclusion

The large volume of research carried out, the knowledge and experience of the PhD candidate in the use of various experimental methods and approaches, as well as the quality of the main conclusions and scientific publications in prestigious scientific journals, convinced me that the presented dissertation work has fulfilled its scientific and educational purpose and fully meets the the requirements of ZRASRB and the Regulations of SU "St. Kliment Ohridski". Therefore, I strongly recommend to the

respected members of the scientific jury to award Evelina Yordanova Vassileva the educational and scientific degree "Doctor of Philosophy" in professional specialty 4.2 Chemical Sciences (Chemistry of the Solid State).

Sofia, 12.09.2023

Reviewer:.....
/ Assoc. Prof. G. Yordanov/