STATEMENT

on the PhD Thesis of **Evelina Yordanova Vassileva**
for earning the educational and scientific degree "Doctor"
in professional area 4.2. Chemical Sciences,
PhD program "Solid State Chemistry"
Title: "Porous metals obtained by selective dissolution of alloys – suitable electrode materials for ion batteries"

MEMBER OF THE SCIENTIFIC JURY (by order of the Rector of Sofia University "St. Kliment Ohridski № RD-38-334/04.07.2023)**:**
Prof. Dr. Ekaterina Zhecheva from the Institute of General and Inorganic Chemistry of the Bulgarian Academy of Sciences

The PhD thesis of Evelina Vassileva contains 116 pages with 54 figures, 41 tables and 230 references. The thesis fully meets the requirements for obtaining the educational and scientific degree "Doctor" in terms of size, structure and design.

Research on the synthesis and functional properties of porous metals is a rapidly developing topic that reveals wide application. The intensive search for new electrode materials with improved performance has drawn attention to use porous structures as electrodes in rechargeable ion batteries. For the development of high-performance lithium and sodium ion batteries porous metal anodes offer a number of advantages in respect of better electrode/electrolyte contact, easier charge transfer reactions, shorter diffusion paths, full utilization of the active material and absence of binders. In recent years selective dissolution of multicomponent metal alloys become an effective tool for the preparation of nanoporous metals, owing to the possibility of modeling the pore size and shape through the chemical and phase composition of the initial alloy and its microstructure. The research carried out by Evelina Vassileva falls in this topic.

The thesis is entitled "Porous metals obtained by selective dissolution of alloys - suitable electrode materials for ion batteries" and it shows experimental results on the synthesis of two-component Zn-Sn and three-component Zn-Sn-Bi and Cu-Ag-Al alloys by melt crystallization, the preparation of porous structures on their basis using selective electrochemical dissolution of the less noble metal and the possibility to use them as anodes in lithium/sodium ion batteries. The composition of the starting alloys is selected with a view to obtain electrochemically active porous structures.

In the thesis a review on the basics of porous materials is made, including their characteristics, properties and production. Literature data on the preparation of porous metal struc-

tures by selective dissolution of various metal precursors are summarized. The advantage to use porous metals as anodes in lithium-ion batteries has been analyzed. The review reveals that the candidate has well covered the available literature on the subject of the thesis. During the research work the candidate has adapted a lot of physicochemical and electrochemical experimental methods, which were well combined to characterize the structure, composition, morphology and electrochemical behaviour of the materials studied.

The main research contributions of the thesis are as follows:

● Eutectic Zn-Sn-(Bi) and Cu-Ag-Al alloys with homogeneous phase distribution and fine crystalline microstructure were synthesized. The conditions of their electrochemical selective dissolution were optimized and porous structures with nanometric ligaments and homogeneously distributed nanometric pores were obtained.

● The Porous Zn-Sn-(Bi) alloys are mechanically stable and can be used directly as anodes in Li- and Na-ion electrochemical cells without using binders and conductive additives. The electrochemical interaction of the porous Sn structures with lithium and sodium proceeds via alloying.

● The Cu-Ag metallic porous structures are suitable as stable current collectors for sulfur-based electrodes. Surface deposition of sulfur on the Cu-Ag structures leads to the formation of an $Ag_2S–Cu_xS$ coating, which is electrochemically active towards lithium. Most likely, the mechanism of electrochemical interaction with lithium involves displacement reactions with lithium ions in metal sulfide phases, as well as alloying/de-alloying with Ag and S redox processes. The material exhibits good capacity stability when cycled as an anode in lithium cells for extended periods at relatively high cycling rates.

The general impression of the thesis is that a systematic and precise research work has been carried out, and the aims and objectives of the study have been achieved. The thesis is clearly written, well-formed and the data obtained are correctly explained. The initial results on the electrochemical behavior of porous structures based on Zn-Sn alloys as anodes in alkaline ion batteries are encouraging and they can certainly be improved upon further optimization of the chemical and phase composition of the alloys as well as the microstructure and pore size. The proposed approach for using porous Cu-Ag structures as precursors for sulfur-based electrodes deserves further attention regarding the development of new electrodes for thin Li-ion batteries. Thus, I believe that the thesis of Evelina Vassileva would be interesting both for researchers interested in porous metals and electrochemists dealing with rechargeable ion batteries.

The abstract is in accordance with the requirements and correctly reflects the content and the research contributions of the thesis.

The results of the thesis are included in 3 publications, of which two in Q1 journals (Journal of Alloys and Compounds and Dalton Transactions) and one in a Q2 journal (Journal of Porous Metals), which indicates a high research level. Results are reported at two national scientific forums.

Conclusion: The PhD thesis of Evelina Vassileva fulfills the requirements of the Act on Development of the Academic Staff in the Republic of Bulgaria and the Regulations for the terms and conditions for acquiring academic degrees and occupying academic positions at the Sofia University "St. Kliment Ohridski". The candidate has acquired appropriate competence in the field of solid state chemistry and has obtained interesting and reliable scientific results. Based on this, I evaluate the thesis positively and recommend the Scientific jury to award the educational and scientific degree "Doctor" in professional area 4.2 "Chemical Sciences" (Solid State Chemistry) to Evelina Yordanova Vassileva.

Member of the Scientific juri:

(Prof. Dr. Ekaterina Zhecheva)

12.09.2023.