OPINION

By Assoc. Prof. Dr. DIMITAR DIMITROV RADEV, IGIC-BAS, member of the Scientific Jury, appointed by Order No. RD38-334/07.07.2023 of the Rector of Sofia University "St. Cl. Ohridski" for the defense of a dissertation to obtain the educational and scientific degree "doctor"

Author of the dissertation: EVELINA YORDANOVA VASILEVA, independent doctoral student at the Department of "Applied Inorganic Chemistry" at the Faculty of Chemistry and Pharmacy, Sofia University "St. Cl. Ohridski"

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

Professional direction: 4.2. Chemical Sciences (Solid State Chemistry)

The dissertation contains 116 pages, 54 figures and 4 tables, and 230 literary sources have been cited. From the attached reference for minimum requirements, is obvious that the doctoral student fully meets the requirements, and the three articles published in renowned specialized journals, in two of which Ivelina is the first author, make a pleasant impression.

The aim of the dissertation work is to obtain two- and three-component alloys: Zn-Sn, Zn-Sn-Bi and Cu-Ag-Al with porous structures and their application as electrode materials in ion batteries. From the detailed critical analysis of the literature data logically follow the methods for synthesis of porous alloys suitable for application as electrode materials, the selected type of alloys, as well as obtaining appropriate structures by means of selective dissolution of one of the components.

The syntheses were carried out using traditional methods: rapid melt quenching and standard casting. The conditions for the synthesis of the alloys were studied: the influence of the type and concentration of the electrolyte, potential values, dissolution time. The obtained data served the doctoral student to optimize the conditions for obtaining alloys with pore parameters suitable for the purposes of the dissertation. The morphological and structural properties of the materials were studied using modern methods: X-ray diffraction (XRD), transmission electron spectroscopy (TEM), energy-dispersive spectroscopy (EDS), differential scanning calorimetry (DSC). Electrochemical studies were performed in two- and three-

electrode cells, depending on the goals of the experiments. In the Zn70Sn30 alloys, by means of TEM/EDS, differences in the crystallite sizes and the compositions of the alloys synthesized by the two methods were registered. The results are presented graphically and convincingly using Zn and Sn elemental mapping. Potentiodynamic and potentiostatic electrochemical studies show different behavior of materials cast by the two methods. The selective dissolution of Zn was demonstrated by XRD, structural differences were recorded for the Zn70Sn30 alloys obtained by both methods. The observed differences in the pore structures and their size distributions are logically explained by the peculiarities of the synthesis methods. Structural and electrochemical studies show advantages of the rapid quenching synthesis method. Electrochemical charge-discharge and cycling tests in Li and Na cells of alloys obtained by rapid quenching show results similar to those cited in the literature, demonstrating that the porous structure interacts with Li and Na ions through alloying . Analogous structural and electrochemical studies were carried out on ternary alloys ZnSnBi (Zn70Sn5Bi25, Zn70Sn15Bi15, Zn70Sn25B) and Cu60Ag30Al10 obtained by quick quenching from a melt, as this method has shown advantages in previous studies. Differences in the morphology of porous structures are shown depending on the composition of the alloys. On the obtained porous CuAgAl structures, an active material-sulfur was deposited by two approaches - from a solution and by dripping. The influence of sulfur on the structural and electrochemical properties of the alloys is shown, and a comparison with modern literature data is made. Stable cycling behavior of the alloys during charge/discharge experiments was demonstrated.

The general impression of the dissertation work is that a thorough study has been done using modern methods to characterize the structural and electrochemical properties of a wide range of alloys. The experimental data obtained are logically explained, and the structure-property relationships are convincingly demonstrated. The conclusions are a logical consequence of the rich experimental material presented. The obtained results have methodological and practical significance in a rapidly developing field of inorganic materials science. In conclusion, I consider that the proposed dissertation fully satisfies the recommended criteria of the Faculty of Chemistry and Farmacy for the degree "doctor" and I recommend the honorable scientific Jury to award the doctoral student Evelina Yordanova Vasileva the educational and scientific degree "doctor" in professional direction 4.2. "Chemical Sciences" (Chemistry of the Solid State).

18.09.2023 Associate Professor Dr. D. Radev