STANDPOINT

for the awarding the academic degree "Doctor"
in Professional field 4.2. Chemical sciences, Electrochemistry (incl. chemical power sources)
with candidate: Vesselina Stefanova Milusheva
Title of the PhD thesis: Fabrication and characterization of nanostructured layers of Cu and anodic aluminium oxide
Member of the scientific jury: Prof. DSc Vessela Tsvetanova Tsakova-Stancheva, Institute of Physical Chemistry, Bulgarian Academy of Sciences

1. General characteristics of the research and applied activities of the candidate1.

Vesselina Milusheva graduated in Inorganic and Electrochemical Production from the University of Chemical Technology and Metallurgy, Sofia in 1995. Subsequently she did postgraduate studies at the University of National and World Economy, Sofia in Management and Accounting. She has been working as a chemical technologist at the Department of Chemistry, Technical University of Sofia since 2013. In the period January 2018 - December 2021 she was a part-time PhD student at the Institute of Physical Chemistry (IPC), Bulgarian Academy of Sciences (BAS). Since 2023, she has been partially appointed as a chemical engineer also at IPC-BAS.

Eng. Milusheva has co-authored a total of 9 scientific publications, eight of which are included in her PhD thesis. A total of 37 citations of her scientific works have been noted.

The PhD thesis is written in 140 pages and contains a total of 69 figures and 19 tables and 163 cited references. It is structured in seven sections, of which the literature review (43 pages) and the presentation of the experimental results (68 pages including 48 original figures and 12 tables) are the main ones. The thesis of Eng. Milusheva is devoted to the development of technologies for the chemical and electrochemical deposition of copper on anodized aluminum oxide membranes supported on Al (Al/AAO) in order to obtain nanocomposite materials of Al/AAO+Cu/Cu with anisotropic electrical conductivity or layered structures of the type Al/AAO/AAO+Cu/Cu with the prospects of creating conductive copper images. The literature review of the dissertation presents in detail the conditions for the preparation of AAO nanoporous matrices and their characteristics, as well as the previously used technologies for chemical and electrochemical deposition of copper and the applications of the Cu/AAO systems. Based on the literature overview, specific well-founded tasks are formulated that address the processes of thinning of the barrier oxide layer at the Al/AAO interface, of chloride-free activation of AAO,

development of copper ions-based electrolytes for chemical deposition, compatible with the AAO chemical stability, and preparation of modified AAO on aluminum with increased chemical resistance. A wide range of methods such as scanning electron microscopy, energy dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, X-ray diffraction analysis and X-ray fluorescence spectroscopy were used to characterize the resulting nanocomposite and layered coatings.

The main results obtained in the thesis are presented in detail and well-illustrated with figures and tables. The volume of experimental work performed is very large and impressive. Optimization of the processes studied has been carried out by tracking multiple parameters (type of AAO activation, copper ion and reducing agent concentrations in the various electrolytes, temperature, pH, etc.) The morphology, thickness, chemical and phase composition of the various Cu-AAO-based coatings have been characterized by a variety of suitably applied experimental methods.

2. Main scientific and applied contributions.

The research presented in this thesis is original, has clearly stated specific objectives and well derived results with practical relevance for the preparation of nanocomposite materials and layered structures based on Cu and AAO matrices on Al supports. The main contributions of the thesis are of scientific and applied nature and can be formulated as follows:

1. As a consequence of a suitably chosen approach for electrochemical thinning of the barrier layer at the bottom of the pores of the AAO membrane on Al and a combination of chemical and electrochemical deposition in an acidic copper sulfate electrolyte, nanocomposites of the Al/AAO+Cu/Cu type have been obtained. They show anisotropic conductivity properties with high conductivity along the Cu filled-in nanopores of AAO.
2. A copper electrolyte with sodium hypophosphite as reductant, pH 4.1-6.1, containing a small amount of Ni^{2+} (1 g/L) necessary to maintain the autocatalytic nature of the copper chemical deposition process was developed. Layered structures of the type Al/AAO/AAO+Cu/Cu were obtained using this electrolyte.
3. Two copper electrolytes with phosphorous acid as reductant and copper sulfate or copper acetate salts were developed, applicable neutral and weakly alkaline solutions. These electrolytes provided also layered structures of the type Al/AAO/AAO+Cu/Cu.

4. A new approach to initiate the chemical deposition of Cu on AAO from conventional copper electrolytes with formaldehyde reductant and pH 12.8 is proposed based on the use of a thin titanium dioxide layer deposited on AAO and photochemical catalysis of the Cu ions reduction. The titanium dioxide layer improves the chemical stability of AAO in alkaline electrolytes and at the same time creates conditions for selective copper deposition through photomasks and thus for the formation of conductive copper images.

3. Citations of the candidate's scientific publications in Bulgarian and foreign literature.

The main results of the dissertation have been published in the period 2018-2022 in a total of eight scientific papers, of which three in journals with impact factor or impact rank (two articles in *Bulgarian Chemical Communications* and one in *Catalysis Science & Technology*). The remaining five publications were printed in conference proceedings (4 papers) and one in the Bulgarian journal *Nanoscience and Nanotechnology*. For the publications included in the thesis, 4 citations were noted, all from foreign authors.

4. Critical remarks and recommendations to the candidate's scientific works.

Upon reading the dissertation, several questions arise, for instance, why it is believed that during palladium activation, adsorption of Sn ions and consequent Pd activation and Cu deposition does not occur at the bottom of the AAO pores (Fig. IV.21); how correct it is to determine "coating thickness" by XRF (Table IV.7 and Fig. IV.29) in the case of island structures (Fig. IV.30) obtained at short deposition times (5 and 10 min).

Other comments on the submitted dissertation text:

- In part IV.1 "Copper filling of AAO nanopores by direct DC electrodeposition on aluminium" both galvanostatic and potentiostatic deposition is investigated and in this sense the title is inaccurate;

- the reference "Gerain and Haber" (p. 88), does not appear in the reference list;

- a decimal point and a decimal comma are used to separate decimal places in numbers (sometimes even in the same table);

- there are linguistic and punctuation errors that could be corrected by a careful reading of the text, and expressions that could be phrased more precisely.

The critical remarks made above are of technical nature and do not diminish the significance of the research presented.

Finally, I would recommend Eng. Milusheva and the team she works with to strive to publish the results of their research in journals with impact factor and impact rank in order to improve the visibility of the achieved results for the international scientific community.

CONCLUSION

In conclusion, I believe that significant scientific and applied results have been obtained, which reveal new possibilities for the practical preparation in suitable technological regimes of layered structures of the Al/Cu+AAO/Cu and Al/AAO/AAO+Cu/Cu types. The obtained composite materials have good prospects for applications in electronics, e.g. in the fabrication of metal printed circuit boards and microelectromechanical systems (MEMS).

The submitted thesis meets all the requirements for the award of the degree of Doctor according to the Law on Academic Staff Development in Republic Bulgaria and the corresponding Regulations for its application. Therefore, as a member of the Scientific Jury, I fully support the awarding of this degree to Eng. Vesselina Stefanova Milusheva.

Date: 04.12.2025 Signed: