STANDPOINT

**for the awarding the academic degree "Doctor",
field of higher education 4. Natural sciences, mathematics and computer science,
Professional field 4.2. Chemical sciences, doctoral program „Electrochemistry“
with candidate: Marina Hristova Arnaudova - chemist at the "Electrochemistry and Corrosion" section, IPC-BAS
Title of the PhD thesis: *Preparation and characterization of electrochemical nickel-based coatings Ni-M, where M = W, Mo, TiO_x***
Member of the scientific jury: Assoc. Prof. Dr Zhenya Stefanova Georgieva, Institute of Physical Chemistry, Bulgarian Academy of Sciences

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

Marina Arnaudova graduated from the University of Chemical Technology and Metallurgy - Sofia, Department of Electrochemistry and Corrosion in 2001. Since 2002, she has been appointed as a chemist at the Institute of Physical Chemistry "Acad. Rostislaw Kaishew", subsequently as a Res. Assoc. III degree and Assistant. In 2020, she was enrolled as a PhD student of independent study at the Institute of Physical Chemistry, where she has a permanent employment contract till now.

Since then, she has been working in the field of electrochemical preparation of nickel-based alloy coatings, with the aim of using them as electrodes for hydrogen production. These materials are a promising alternative for replacing precious metal catalysts with those that have the same catalytic activity, but at a lower price. The subject is topical, with a practical focus and is of great interest to researchers.

The dissertation is written on 100 pages and contains a total of 40 figures and 14 tables. 80 references are cited. Based on the detailed literature review, clear and well-formulated specific tasks of the dissertation are made. In chapter V. Experimental results and discussion, after the shown results for each of the investigated coatings, the corresponding conclusions are presented.

The dissertation is devoted to the preparation and characterization of three types of alloy and composite materials of nickel with W, Mo and non-stoichiometric TiO_x. Electrolytes and conditions for the preparation of these materials were selected. The catalysts were characterized physicochemically with different experimental methods: scanning electron microscopy and energy-dispersive spectroscopy (SEM/EDS), X-ray fluorescence analysis (XRF), X-ray diffraction analysis (XRD) and X-ray photoelectron spectroscopy (XPS). Electrochemical experiments were conducted to study the catalytic activity towards the hydrogen evolution reaction (HER) of the obtained coatings, deposited on different substrates. Their corrosion resistance was evaluated in two model environments (0.5 M H_2SO_4 and 6M KOH). Various electrochemical techniques were used: cyclic voltammetry (CV), potentiodynamic polarization curves method, polarization resistance (R_p) and electrochemical impedance spectroscopy (EIS).

Overall, I believe that the results presented in the dissertation are original, have no analogue in the scientific literature, the dissertation work has a clearly defined aim and well-formulated conclusions and contributions. Some of the experimental results have been reported to various scientific forums with oral and poster presentations. The PhD student has participated in five national projects and one EBR project - a bilateral cooperation between the Hungarian Academy of Sciences and the Bulgarian Academy of Sciences.

2. Main scientific and applied contributions

The following scientific and scientific-applied results were achieved during the conducted research:

Nickel-based alloy and composite coatings with W, Mo, TiO_x were electrochemically obtained on various substrates and the optimal conditions were selected in view of the desired characteristics. The electrocatalytic activity of the obtained materials towards hydrogen evolution reaction was studied using different electrochemical methods. It was found that all coatings demonstrate better electrocatalytic behavior compared to pure nickel coating, as alloys containing molybdenum show the best electrocatalytic activity for HER in alkaline medium. Corrosion studies were carried out in two model environments. It was found that in acidic medium (0.5M H_2SO_4) the NiW alloy and the $NiWTiO_x$ composite show the best corrosion resistance, while in alkaline medium (6M KOH) all studied coatings demonstrate significant corrosion resistance. These coatings could be successfully used as an electrode material for hydrogen production.

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

The PhD student is a co-author in a total of 15 publications, printed in Bulgarian and international journals. 119 citations were noticed. The main results of the dissertation have been published in the period 2006-2024 r. in five scientific papers in Bulgarian and international journals. Two of them have an impact factor or impact rank: International Journal of Hydrogen Energy and Journal of Solid State Electrochemistry. On the publications included in the dissertation, 41 citations were noticed, almost all of them from foreign authors.

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

Critical remarks on the dissertation: there are some punctuation errors. In Chapter VI. CONTRIBUTIONS of the dissertation, in the third contribution I have one remark. In my opinion, instead of "Along with the good catalytic activity in this environment, they could be successfully used as an electrode material for hydrogen production" it is more correct to formulate "Along with the good corrosion resistance and catalytic activity in this environment, they could be successfully used as an electrode material for hydrogen production".

These critical remarks are of a technical nature and do not reduce the significance of the presented research.

I would like to recommend to Marina Arnaudova to maintain her desire and persistence in experimental work, expanding her field of vision for preparation and electrocatalytic studies for a wider range of electrode materials.

CONCLUSION

I have known Marina Arnaudova since she started working at the Institute of Physical Chemistry. In addition to being a wonderful colleague, over the years I have observed her development as a reliable and dedicated experimenter who enters with desire and enthusiasm into various aspects of research. My impressions are that she treats the experimental tasks assigned with responsibility and criticality and spares no effort until she herself is satisfied with the achieved results.

The presented dissertation meets and even exceeds the requirements for awarding the educational and scientific degree "Doctor" in the Regulations on the conditions and procedure for acquiring scientific degrees and for holding academic positions at the Institute of Physical

Chemistry. Therefore, I strongly recommend to the respected members of the Scientific Jury to vote for the awarding of the educational and scientific degree "Doctor" in Professional field 4.2. Chemical Sciences, doctoral program "Electrochemistry" to chemist Marina Hristova Arnaudova.

Date: 20.06. 2025 г.

Prepared the standpoind:

/ Prof. Dr Zhenya Georgieva /