Институт по ФИЗИКОХИМИЯ при БАН
Вх. №171
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REVIEW

On a thesis for the scientific and educational degree "DOCTOR" of (Philosophy Doctor, PhD), professional field, 4.2 Chemical Sciences, scientific specialty "Electrochemistry"

Scientific organization: Institute of Physical Chemistry, Bulgarian Academy of Sciences, "Acad. R. Kaishev".

Reviewer: Professor Dr. Branimir Ivanov Banov IEES-BAS, member of the Scientific Jury, appointed by Order of the Director of Institute of Physical Chemistry - BAS.

1. General information and brief biographical data about the candidate

Marina Hristova Arnaudova was born on 07.05.1979 in the city of Sofia. In 1996 she entered the University of Chemical Technology and Metallurgy, Sofia, where in 2001 she obtained a Master's degree in the Department of Electrochemistry and Corrosion of the University of Chemical Technology and Metallurgy. In 2002 she entered the Institute of Chemical Engineering-BAS, as a chemist.

In the period 2002-2008 she was a chemist, then a research associate III degree 2008-2011, and in the period 2011-2024 she was an assistant. During the same time, she was a doctoral student in free training in the group of Assoc. Prof. Rashko Rashkov. Since the beginning of 2024, she has been working as a chemist again. I do not personally know Chemical Engineer Marina Hristova Arnaudova and I have no direct observations on her work and scientific growth, so in my judgment I will base only on the documents and materials provided to me for this purpose and the impressions gained from her pre-defense. The good theoretical preparation that Eng. Chem. Marina Arnaudova has received and the good command of English (B2) have allowed the candidate not only to develop interesting and achieve excellent results on the topic, but to present them at national and international forums in the best way to the scientific community and for them to be noticed and evaluated. This is reflected in the more than 36 citations noted so far, which she has included in her PhD thesis. The achieved results are natural and are due to both the PhD student and the working team and the long experimental experience gained in the period 2001-2024, to the work of the PhD student at the Institute of Physical Chemistry.

2. Description of the submitted materials and relevance of the topic of the PhD thesis

The materials submitted by the candidate include the documents required by the procedure, namely:

- PhD thesis,
- Abstract,
- Reference to the minimum requirements for the competition,
- Reference to the Contributions of the PhD thesis,
- List of scientific papers included in the thesis,
- List of all scientific papers,
- List of noted citations,
- Creative CV
- Appendix 1
- Appendix 2
- Separation protocol

• Application for PhD thesis official presentation

Formally presented documents correspond exactly to the requirements set by law and allow the evaluation of the PhD thesis work to be complete, accurate and fully justified, thanks to the comprehensive information provided in them. The thesis is written on 98 pages and contains 40 figures and 14 tables 80 literary sources are cited.

The thesis itself is based on five (5) publications, as follows: one (1) Q1, one (1) Q2 and three (3) non-indexed. The works thus proposed carry a total of 45 points with a required minimum of 30 points, which shows that the candidate has made an effort in his presentation, exceeding the required minimum by more than 1.5 times. The number of citations noted now and included in the PhD thesis work is 36, which carry an additional 72 points. It should also be noted that in only one of the 5 works presented, from those in Q1, Eng. Chem. M. Arnaudova is in second place, while in all other presented publications she occupies first place, which is a guarantee of her competence and initiative and a leading place in the work done on the topic.

Participation in national and international forums, as well as national ones with international participation, can only be praised for the high activity of both the PhD thesis candidate and the team. Participation in national scientific forums with a report - 11, of which M. Arnaudova is in second place in only three, and in 8 in first.

Presentations at national forums with international participation and at international conferences include 14 appearances, in 7 of which M. Arnaudova, Chemical Engineer, is in first place. This reinforces the belief that M. Arnaudova can present scientific results in the best way for the audience and make an impression on the national and international scientific community.

Participation in Contracts

Several groups can be formed here, as follows: starting from 2006, with a national scientific program, "New Technologies in Energy", IPC, UZU, IEES, "Building Scientific Potential", 2008, Scientific Research Fund, in a team of IPC, UZU, Plovdiv University and IEES-BAS. The activity of the team does not fail to actively participate in the national scientific program E-Plus, again in partnership between IFH, UZU, Plovdiv University and IEES-BAS. Again, active participation is recorded in the construction of the scientific infrastructure "INFRAMAT" of IPC. The project started in 2020 and continues until 2023, was successfully completed. Meanwhile, the PhD thesis candidate is an active participant in two other projects in the period 2014-2018 for catalysts not containing precious metals for hydrogen generation, such as a bilateral agreement between the Bulgarian Academy of Sciences and the Bulgarian Academy of Sciences, and research on magnetic multilayers and alloys obtained through oscillating electrochemical reactions 2016-2018.

Structure of the PhD thesis.

The thesis is structured according to a classical scheme, Introduction, Theoretical part, Goals and objectives, Experimental part, Physicochemical and electrochemical characterization of the obtained samples, Results and discussion. The theoretical part is very well structured and allows one to enter the specific topic quickly and easily, demonstrating the in-depth knowledge of the PhD thesis candidate in the field of theoretical electrochemistry. The experimental part describes the electrolytes used, the preliminary preparation of the samples, the preparation of alloys and composites on a copper substrate, followed by physicochemical and electrochemical characterization, as well as coatings and alloys on carbon fibers with their physicochemical and electrochemical characterization. Everything is

well arranged and precisely described, so that it is clear what is being done and why. The language is precise, clear and understandable.

Relevance of the topic.

The last ten years have been marked by the ever-increasing threat of a gradual rise in the temperature of the planet, which is largely due to unreasonable human activity, attitude towards nature and the generated huge amounts of greenhouse gas - carbon dioxide. To this end, the EU has proposed to rapidly develop and implement new technological solutions that will lead to carbon-neutral industrial production. The only solution to the problem lies in the widespread use of hydrogen, as a clean energy carrier with a zero carbon footprint, obtained through the electrolysis of water with electricity from renewable sources. The industrial production of hydrogen dates back to the end of the 19th century, using the conversion of natural gas for this purpose. Unfortunately, this process also generates carbon dioxide, considered the main threat to the increase in global temperature, which is why new solutions are being sought to obtain "green" hydrogen.

"Green" hydrogen is produced by electrolysis of water and theoretically consumes 45 kWh/kg of electrical energy. The real value of the required energy, however, is about 55 kWh/kg, and the amount of water required is 9 dm3. And currently there are industrial electrolyzers that consume 55 - 51 kWh/kg of electricity and 10 dm^3, not counting the cooling water and its losses, since the process is carried out at high temperature (about 80°C) in order to reduce the overvoltage of the electrolysis cells and increase the energy efficiency of the system. That is why the development of suitable electrodes with catalysts for the hydrogen evolution process (HER) is of utmost importance, both for theory and practice.

Based on the above, it can be concluded that the research conducted is more than relevant and timely. This is also evidenced by the fact that there are more than 120 noted citations in the works of the PhD student, although of course only 30 are included in the PhD thesis. This fact confirms that we have not only a successful PhD student, but also a fully developed scientist with his own contribution and vision in the subject.

3. General characteristics of scientific research

The aim of this PhD thesis is the electrochemical preparation of alloy and composite coatings of nickel with W, Mo and TiOx, determination of their structure, morphology, chemical composition and the influence of these characteristics on the electrocatalytic and corrosion properties, with the aim of their application as active electrode materials for use in hydrogen evolution reaction (HER).

The following tasks arise from the goal set thus:

- Electrochemical preparation of alloy and composite coatings of nickel with W, Mo and TiOx, on copper and carbon fiber substrates,
- Selection of electrolyte and conditions for conducting the electrochemical process, temperature, stirring speed, time,
- Physicochemical characterization of the obtained coatings with SEM/EDS (scanning electron microscopy/energy dispersive spectroscopy), XRF (X-ray fluorescence analysis), XRD (X-ray diffraction analysis), XPS (photoelectron spectroscopy), as well as electrochemical characterization using CVA (cyclic voltammetry), potentiodynamic polarization curves, polarization resistance Rp and electrochemical impedance spectroscopy – EIS,

- Investigation of the electrocatalytic activity of the obtained coatings in terms of the hydrogen evolution reaction (HER),
- Model studies of corrosion resistance in acidic (0.5M H_2SO_4) and alkaline environments (6M KOH).

In order to meet the set tasks, systematic studies have been conducted to determine the technological scheme for processing the samples, the composition of the electrolytes, the temperature, the pH of the solution, and the deposition time. The results are summarized and presented in a tabular form, which allows the reviewer to easily navigate. The corresponding conclusions have been made about the W content in the alloys and the dependence on the potential. The stirring speed for non-stoichiometric titanium oxides has been determined. The electrochemical activity of the samples thus obtained has been determined and graphically compared.

From the analysis of the polarization curves, a mixed mechanism, Folmer-Heyrovsky hydrogen evolution (HER), was established, with the highest electrochemical activity at low current densities demonstrated by the NiMoW alloy samples, while at high current densities the NiWTiOx samples approached those used in industry. The samples thus obtained were subjected to long-term corrosion tests to determine their suitability for industrial application. The studies were carried out in two model electrolytes, acidic (0.5M H_2SO_4) and alkaline (6M KOH) for a duration of 336 hours (14 days). The results show that W and Mo are incorporated into the FCC nickel crystal lattice without changing it and are present in it in the form of 4+ and 6+ valent cations. NiW and NiWTiOx coatings show the best corrosion resistance from the studied series of samples, which is due to the formation of the $H_{0.33}O_3W$ and H_2O_4W phases on the surface due to partial dissolution of nickel from the matrix. In alkaline media, the corrosion resistance is high due to the formation of mixed oxy-hydroxy structures of the NiMeO(OH)x type where Me=Mo or W. The NiMoW alloy shows the highest polarization resistance, which is due to the stability of the formed mixed oxy-hydroxyl film.

After successfully studying the series of alloys and composites formed on a copper substrate, the PhD thesis student turned to studying the behavior of the same coatings deposited on a non-metal - carbon fiber, in two modifications, oxidized and non-oxidized. Samples of NiW, NiWTiOx, NiMo and NiMoW were studied. Non-stoichiometric titanium oxides represent a homogeneous mixture of Ti_4O_7, Ti_6O_{11}, Ti_8O_{16}, with Ti_4O_7 being the predominant oxide in the mixture. Physicochemical studies of the samples show that in the NiW, NiWTiOx samples, the globular structure is more clearly expressed on the oxidized carbon fibers, while in the NiMo and NiMoW coatings the globular character is observed on the non-oxidized ones. Systematic electrochemical studies of the samples were carried out using polarization curves and EIS. From the obtained Tafel curves, the electrochemical activity of the coatings and the hydrogen evolution efficiency (HER) were determined, as the studies were conducted again in the two model electrolytes, for acidic (0.5M H_2SO_4) and alkaline media (6M KOH). Due to the complex nature of the hydrogen evolution reaction, the EIS equivalent circuit turned out to be quite complicated, for which a CPE element was added. From the experiments conducted and described in this way, the following conclusions were made: alloy and composite coatings of NiW, NiWTiOx, NiMo and NiMoW were successfully obtained on oxidized and non-oxidized carbon fibers, which were characterized in terms of the hydrogen evolution reaction (HER). Oxidized carbon fibers show better electrochemical activity, and NiWTiOx can be indicated as a favorite.

The interpretation of the obtained data is very good, gives a complete and adequate picture of the conducted research, and correctly interprets the obtained results. The PhD thesis author has tried to illustrate and explain all the steps and obtained results, both textually and

graphically. The presented graphic materials correctly reflect and illustrate the experimental results, showing a deep understanding of the ongoing and studied processes and demonstrating serious theoretical preparation combined with excellent practical skills, which inevitably leads to positive results.

4. Main scientific and applied scientific contributions of the PhD thesis

The main scientific and scientifically applied contributions are determined and defined by the PhD thesis, with which I completely agree and allow myself to quote with a minor edit:

- Alloys and composite materials based on nickel with W, Mo, TiOx have been successfully obtained on a copper substrate and carbon fiber, both pure and oxidized. The dependence of the composition and morphology of the obtained coatings on the parameters of the electrolysis process has been established. Physicochemical, chemical and electrochemical studies have been carried out to determine the necessary conditions for obtaining samples with specified parameters. The optimal conditions for obtaining coatings with the desired morphology and electrochemical characteristics have been selected.
- Through a series of electrochemical tests, the electrocatalytic activity of the various obtained alloy and composite samples in terms of the hydrogen evolution reaction (HER) was determined and compared. All alloy and composite samples have higher electrocatalytic activity compared to pure nickel coating. The highest electrocatalytic activity in terms of the hydrogen evolution reaction (HER) in alkaline medium is possessed by nickel molybdenum alloy coatings
- Systematic and in-depth studies of the corrosion behavior of the prepared alloy and composite samples in two model environments, acidic (0.5M H_2SO_4) and alkaline (6M KOH), were carried out using various modern electrochemical methods including EIS. It was found that in acidic environments, the NiW alloy and the NiWTiOx composite showed the best corrosion resistance, which is due to the formation of a stable tungstate phase ($H_{0.33}O_3W$ and H_2O_4W) in the form of filamentary crystals on the surface, at the expense of partial dissolution of the nickel matrix. In alkaline environments, all studied samples showed high corrosion resistance, as well as good catalytic activity. These samples can be successfully used as effective electrode materials for hydrogen evolution in industrial production in alkaline environments.

5. Reflection of the candidate's scientific publications in Bulgarian and international literature

Chemical Eng. Marina Hristova Arnaudova has provided the full list and copies of the publications included in the PhD thesis, from which the results achieved and presented to the broad national and international scientific community are very clearly visible.

The thesis itself, as already mentioned, is based on five (5) publications, as follows: one (1) in Q1, one (1) in Q2 and three unindexed. The works selected in this way carry 45 points with a required minimum of 30 points, which shows that the candidate has made enough effort for his presentation, exceeding the required minimum by more than 1.5 times. The PhD thesis candidate Marina Hristova Arnaudova is the lead author in four out of five publications, which is a recognition of the team for her leading role in the conducted research, processing of the results, interpretation, as well as their presentation to the broad national and international scientific community. 36 citations have been noted on the submitted publications (only from the first work in Q1). From the academic reference, according to the LDASRB and the Regulations of the Institute of Physical Chemistry - BAS, it is clear that the PhD thesis candidate not only covers, but also exceeds the minimum requirements many times over.

The additional materials provided, such as publications not included in the PhD thesis and the number of citations (an impressive 119!) show that Chemical Engineer Marina Hristova Arnaudova is a fully established scientist with an established reputation and a recognizable international name.

6. Critical remarks, recommendations and questions

I do not have any critical remarks and recommendations for the PhD thesis, but a rather theoretically applied question has arisen in me that I would like to clarify.

- Does it matter what kind of reference electrode is used when determining and setting the working potentials of the electrode under study?
- What conditions must the reference electrode meet in relation to the system under study (electrolyte - purely theoretically and practically)?
- Can the same reference electrode SCE be used to conduct model studies in acidic 0.5M H2SO4 and alkaline 6M KOH environments?

7. Personal impressions

I do not know the PhD student personally and have no common publications with her, but the materials presented at the pre-thesis presentation very pleasantly surprised me. Clear Bulgarian language and expression, combined with deep knowledge and understanding of the matter and processes, she comments on. The PhD thesis work is written with skill and understanding, again in clear Bulgarian language, precise expression, understanding and in-depth theoretical and professional knowledge in the field.

8. CONCLUSIONS

Active scientific research activity defines Chemical Engineer Marina Hristova Arnaudova as a young and ambitious scientist in the field of electroplating, complex alloys and composite coatings, as catalysts for hydrogen evolution reaction (HER) or, in general, as new materials for highly efficient electrocatalysts, new structural materials for industry with increased corrosion resistance and environmental protection, improved energy efficiency.

The scientific contributions of the doctoral candidate, chemical engineer Marina Hristova Arnaudova and the material submitted for review are up-to-date and fully cover and exceed many times the requirements of the Law on the Bulgarian Academy of Sciences and the Regulations on the conditions and procedure for acquiring scientific degrees and occupying academic positions at the Institute of Physical Chemistry-BAS "Acad. R. Kaishev".

The presented materials give me full reason to recommend with conviction to the Honorable Jury to support my positive assessment for the doctoral student, chemical engineer Marina Hristova Arnaudova, and to vote for awarding the scientific and educational degree "DOCTOR" (Doctor of Philosophy - PhD) in the professional field 4.2 Chemical Sciences, the scientific specialty "Electrochemistry".

Sofia **Reviewer:**

09.07.2025