REVIEW

on the competition for the academic position "Associate Professor" ,
cientific direction 4.2.Chemical Sciences, specialization "Electrochemistry / incl. Chemical Power Sources /" at the Institute of Physical Chemistry „"Rostislaw Kaischew",
Bulgarian Academy of Sciences,
announced in SG № 62 / 27.07.2021,
Candidate (s): Assistant Professor Dr. Nelly Boshkova,
Reviewer: Associate Professor Dr. Jenia Georgieva

1. GENERAL CHARACTERISTICS AND BRIEF BIOGRAPHICAL DATA OF THE CANDIDATE

Nelly Dimitrova Boshkova graduated at the Technical School of Chemical Industry and Bio-Technologies "Prof. A. Zlatarov ", Sofia in 1992, specialty" Technology of organic and inorganic substances ". In 1997 she graduated at the Faculty of Chemistry of the Sofia University "St. Kliment Ohridski", with qualifications Chemistry and Teacher of Chemistry and Chemical Technologies. During the period 2003 - 2008 she held the position of chemist in the section "Electrochemistry and Corrosion" at the Institute of Physical Chemistry - BAS, as her main activity is research in the field of material characterization and corrosion protection.

During the period 2015 - 2017 she is a full-time PhD student at the IPC-BAS, where she obtained the educational and scientific degree "PhD", after successful defense of her dissertation "Zinc composite coatings with embedded polymer particles - obtaining and protective ability."

In 2017 she was appointed as an Assistant, and from 2018 as an Assistant Professor in the section "Electrochemistry and Corrosion" at IPC-BAS. At the same time (2016 - 2020) she led laboratory practice in chemistry as a part-time lecturer at the Technical University, Sofia, Department of Chemistry.

Nelly Boshkova's research interests include chemistry, electrochemistry, electrodeposition of metals and alloys, protective ability of galvanic coatings, nanocomposite and hybrid coatings, inhibitors, corrosion processes and corrosion resistance.

2. DESCRIPTION OF THE SUBMITTED MATERIALS

The presented materials by the only candidate in the competition Dr. Nelly Boshkova from the section "Electrochemistry and Corrosion", IPC-BAS are in accordance with the Rules for scientific development of the academic staff of IPC-BAS and the criteria for holding the academic position "Associate Professor". All submitted works are in the scientific field of the announced competition.

The total number of points on the scientometric indicators is 585 points (indicator A - 50 points) (publications included in the dissertation - 84 points) - a total of 134 points, indicator B - 100 points, indicator D - 235 points, indicator E - 116 points) at requirement 430, according to the regulations of Law on the Development of the Academic Staff - IPC-BAS for holding the academic position "Associate Professor".

According to the submitted materials by the candidate, the total number of publications is 37, 4 book chapters and one patent. 5 of the publications are presented for the scientific and educational degree "PhD", 5 are presented as equivalent to habilitation work (with rank Q2), with 22 citations, according to Scopus. A monograph has been published, which is not presented as a major habilitation work. The presented publications are in renowned, specialized journals in the field of materials science and colloid chemistry: Coatings, Colloids and Surfaces A: Physicochemical and Engineering Aspects.

In the Scopus database to date (26.11.2021) there are 15 articles by Dr. Boshkova with 46 citations without self-citations, the Hirsch index is 5.

A list of 12 research projects is presented, funded by the National Fund "Scientific Research", the National Innovation Fund, Operational Programs, international cooperation in the framework of inter-academic contracts and agreements and companies, in which she is a participant and on another project with the National Fund "Scientific Research" she is a Project coordinator.

3. GENERAL CHARACTERISTIC OF THE RESEARCH AND APPLIED RESERARCH ACTIVITIES OF THE CANDIDATE

The research and applied research activity of Dr. Nelly Boshkova correlates with one of the main thematic priorities of IPC-BAS, related to advanced materials and technologies based on electrochemically obtained metal, alloy and modified polymer coatings with protective, decorative and electrocatalytic properties.

The main areas in which the candidate works are the following:

Area 1 - Improvement the corrosion resistance and protective ability of low carbon steel by means of electrodeposited galvanic and / or composite (hybrid) coatings; corrosion inhibitors; conversion passive films.

The main scientific subfields are:

1.1. Zinc and zinc alloy galvanic and composite (hybrid) coatings with embedded polymer nanoparticles (stabilized polymer micelles), including multilayer systems based on them;

1.2. Zinc composite (hybrid) coatings containing nanocontainers with corrosion inhibitor;

1.3. Composite (hybrid) coatings with embedded different types of inorganic or organic particles - ZnO, CuO, PANI, carbon spheres, carbon nanotubes;

1.4. Corrosion inhibitors;

1.5. Conversion surface passive films.

Area 2 - Preparation and corrosion characterization of protective systems based on sol-gel coatings.

Area 3

Corrosion monitoring

Synthesis and modeling of nanoparticle size

4. MAIN SCIENTIFIC AND APPLIED SCIENTIFIC CONTRIBUTIONS

Dr. Boshkova's contributions can be arranged as follows:

Area 1, 1.1.

Zinc and zinc alloy galvanic coatings

The conditions for electrodeposition of zinc coatings, as well as of double alloys Zn-Mn [12, 14, 20] and Zn-Co [20, 32, 34, 38, 39, 41] have been established. The corrosion behavior of these coatings in 5% NaCl was studied using different methods: polarization resistance (R_p), potentiodynamic polarization curves (PDP), electrochemical impedance (EIS) and others, in order to compare their effectiveness with respect to the classical zinc coating. The results show better corrosion resistance of both types of alloys compared to pure zinc in this medium, which can be explained by the appearance of a corrosion product with a low solubility ($10^{-14.2}$) [12, 20, 28, 34]. The protective effect of the alloying component (Mn or Co) is generally associated with a local increase in the pH of the medium, which favors the appearance of a corrosion product with a low solubility. The Zn-Co alloy coating is shiny, with a very good decorative appearance, as well as with better corrosion characteristics than zinc at a low content of the alloying component - within 1-3%. In the Zn-Mn alloy, which also shows increased corrosion resistance compared to zinc, the alloying component is in a larger quantity (about 11 wt%), and the coating is matt. Different types of multilayer systems with good corrosion resistance in the same model environment were also obtained. In them, the Zn-Mn alloy is used as a sublayer, and either a shiny zinc coating or a Zn-Co alloy is deposited as a finishing layer.

Zinc composite (hybrid) coatings

The electrochemical conditions for deposition of zinc composite coatings with four different types of polymer particles (PP) have been established [17, 20, 23, 25, 28, 34, 36, 38, 39, 40, 41]. The polymer particles are derived from two- or three-block copolymers and are of the "core-shell" type. The core is hydrophobic and is based on polypropylene oxide (PPO) or polystyrene (PS), and the shell is hydrophilic and is made of polyethylene oxide (PEO) or polyhydroxymethacrylate (PHEMA). Pre-treatment of the particles with ultraviolet light or atomic transfer radical polymerization in the presence of various reagents (macro- or photoinitiators) leads to stabilization of the particles. The size and shape of the particles embedded in the zinc matrix is determined by TEM, and the morphology of the resulting coatings - by SEM. The influence of PP on the cathodic and anodic processes of deposition and dissolution was studied using cyclic voltammetry. It has been found that in the case of zinc, the presence of PP does not lead to depolarization or overpolarization, but the cathodic (and similarly anodic) processes are more intense [17, 20]. It was found that the corrosion resistance of composite zinc coatings in 5% NaCl is higher than that of zinc, and with increasing particle concentration the protective properties in the model environment slightly deteriorate. Using the scanning-vibration electrode technique (SVET), the appearance and development of corrosion processes on the surface of the samples, as well as the distribution of cathode and anode currents were studied. It was found that the local corrosion processes are initially more intense on the surface of composite coatings, but after a short period of time the trend reverses, as the affected areas on the surface partially expand but do not develop in-depth. In these films, local corrosion is transformed into general, in contrast to the situation with zinc coatings, where local corrosion continues to develop [23, 25, 28, 29, 36]. The reason for this is the appearance of a mixed film containing zinc hydroxide chloride (ZHC) and polymer particles, the presence of which was confirmed by XRD, XPS and AFM [17, 20, 23, 28, 29, 34, 36].

Zinc alloy composite (hybrid) coatings

The influence of PP on the corrosion resistance of Zn-Co (1-3 wt%) and Zn-Mn (11 wt%) alloys was found [20, 31, 34, 38], using the same methods as for zinc. In contrast to the composite zinc coating, the presence of PP in the Zn-Co alloy somewhat deteriorates the protective properties in this medium [34]. This result is due to the different structure and morphology of the alloy. In the Zn-Mn alloy, the presence of PP improves the corrosion performance [20], and the results are confirmed by measuring the polarization resistance of the samples over a long period of time. In this alloy there is an earlier tendency to passivation in the presence of PP in the conditions of external anode polarization. The anode processes are less pronounced than those of the galvanic alloy without PP in the electrolyte [20].

Area 1, 1.2.

Zinc hybrid coatings containing polymer nanocontainers with a hematite core

Zinc composite coatings containing embedded polymer nanocontainers with a benzotriazole inhibitor were obtained [18]. An alpha-hematite core was used, which was consequently coated with two layer-by-layer polymer layers. The first layer is made of polyacrylic acid (PAA) and is negatively charged, and the second is made of polydimethyldialylammonium chloride (PDADMAC) with a positive charge. A certain amount of inhibitor is included between the two layers. Because the polymer shell is sensitive to changes in pH, it ruptures as this parameter decreases. Therefore, as the corrosion process develops, at some point the inhibitor is released from the polymer shell and begins to slow down the rate of corrosion in the area around the nanocontainers (NC). It was found that the presence of NC strongly depolarizes the cathode process and increases the speed in the anode part. Potentiodynamic studies have shown that the composite zinc coating is characterized by a lower corrosion current in a model medium of 5% NaCl under conditions of external anodic polarization [18].

Zinc hybrid coatings containing polymer nanocontainers with a kaolinite core

Kaolinite core NCs [13, 16] and benzotriazole inhibitor were obtained. Using the CVA method, the influence of NC on the cathodic deposition processes and on the anodic processes of dissolution was established. It was found that in the presence of NC, the cathode process proceeds with overvoltage compared to both pure zinc and the composite coating with embedded NC with a hematite core [13,16]. The results obtained by the methods PDP, R_p, EIS, XRD and XPS confirmed that in the model environment of 5% NaCl the composite coating has better corrosion performance - longer anode curve in the conditions of external anode polarization, higher polarization resistance in the end of a 30-day test period and increased impedance characteristics.

Zinc hybrid coatings containing polymer nanocontainers with ZnO core

These composite coatings contain nanocontainers with a ZnO core and a safranin inhibitor. ZnO nuclei are treated with polyethyleneimine (PEI) in order to further stabilize the resulting suspension, and the encapsulation of safranin is realized using the technique of "layer-by-layer". In contrast to the previous two cases, a thin sublayer of polymer-modified ZnO is initially deposited here, followed by a finishing zinc layer. Corrosion studies confirm the improved protective characteristics of the coating - a longer anode curve in external polarization and a higher value of the polarization resistance compared to ordinary zinc coating [5].

Area 1, 1.3.

Zinc hybrid coatings with embedded polymer modified ZnO particles

Polymer-modified ZnO particles are incorporated directly into the coating without the presence of NC with an inhibitor [5]. The same assessment methods were used and it was found that even in the absence of an inhibitor, the presence of these particles leads to increased anti-corrosion performance compared to conventional zinc coating, although not to the extent recorded in the presence of NC with inhibitor.

Zinc hybrid coatings with embedded polymer modified CuO particles

These coatings have been developed with purpose their possible combined application against local corrosion and biocorrosion, given the proven bactericidal properties of CuO. The research is still in an initial stage.

Zinc hybrid coatings with embedded PANI particles

Hybrid zinc-based coatings with embedded PANI particles in the metal matrix were obtained in a one-step process by electrodeposition on low-carbon steel substrates [11, 15]. The aim is to directly use the inhibitory properties of polyaniline (PANI) for improved corrosion protection in a medium containing chlorine ions (5% NaCl solution). Studies with CVA have shown that the presence of PANI particles definitely affects the cathode and anode processes. In the cathode zone, a strong depolarization of about 100 mV is observed compared to the same deposition process of ordinary zinc coating, but at a lower current value. A slower process is registered in the anode region than in zinc. Corrosion studies have confirmed the beneficial effect of these particles on the protective ability of these coatings - higher Rp values after 50 days in 5% NaCl and lower corrosion current and longer anode curve in external polarization. Using XRD and XPS methods, the composition of the newly formed mixed layer of corrosion products was determined, where the main component is ZHC, but PANI particles are also present, which have an inhibitory effect on the development of corrosion processes [11]. These particles are also subjected to additional polymer modifications using amphiphilic triblock copolymer Pluronic F127 [10], as well as with polyethyleneimine (PEI) [4]. In both cases, the presence of PANI particles was found to facilitate the cathodic coating deposition process. The conducted experiments confirm the increased protective characteristics of the composite coatings compared to the ordinary zinc.

Zinc hybrid coatings with embedded polymer modified carbon spheres

A possible way of preparing a stable aqueous suspension of positively charged carbon spheres for simultaneous electrodeposition with zinc on a low carbon steel substrate is described [9]. The particles are embedded simultaneously in the zinc coating during electrodeposition. The influence of carbon spheres on the cathode and anode processes was evaluated by cyclic voltammetric studies. Electrochemical studies were performed in 5% NaCl solution with pH 6.7 by PDP, R_p and EIS methods and the higher protective ability of the hybrid coating compared to that of the ordinary zinc was confirmed [9].

Nickel composite coatings with embedded carbon nanotubes

Shiny and semi-shiny nickel composite coatings were electrochemically obtained. They are characterized by good physical and mechanical properties, decorative appearance and increased corrosion resistance in two model corrosion media - 0.5M Na_2SO_4 and 0.5M H_3BO_3 [26]. Studies show that these coatings have increased corrosion resistance and protective ability in this model environment under external polarization. Another study [35] showed the possibility to obtain with special equipment two types of nickel nanocomposite coatings with embedded carbon nanospheres and TiO_2 particles. The obtained materials are characterized in terms of their photocatalytic properties for possible practical application.

Area 1, 1.4.

Nitrogen-containing heterocyclic bi-cation compounds with antioxidant properties were synthesized, which were characterized by NMR spectroscopy. Their corrosion inhibitory effect for the protection of steel and galvanized steel has been investigated by electrochemical polarization methods to assess the potential suitability of these compounds to be included as an inhibitor in hybrid zinc galvanic coatings [8]. This study found that the compounds have a well-defined protective effect against corrosion in a model environment of 5% NaCl - lower corrosion current and higher polarization resistance for 70 days, which makes them suitable for this future purpose.

Area 1, 1.5.

In a model medium of an aerated 5% NaCl solution, the protective ability of different types of chromatic passivating films (based on conversion solutions containing Cr^{3+} compounds) on galvanic and composite zinc coatings was evaluated [19, 25, 29, 30]. Conversion films of different colors were obtained - transparent, gray-black and light green. The last film demonstrated the best protective characteristics when tested in the Salt Spray Test Chamber – estimation marks of 10 for 22 cycles [19]. Studies confirm the possibility of obtaining Cr^{3+} - containing and chromium - free films on zinc and Zn-Co alloy with low cobalt content. To characterize these coatings and films, well-established and standardized test methods were used - PDP, R_p, EIS, SVET, Salt Spray Test Chamber (NSS) [19, 21, 25, 27, 29, 30, 32], XPS and XRD. Conversion films have also been obtained on zinc alloy coatings [12, 27, 32]. The obtained results showed an improvement in the protective properties of chromium - containing films in contrast to chromium - free ones.

Area 2

Increased corrosion resistance of low carbon steel has been achieved through multilayer environmentally friendly systems with barrier properties based on sol-gel coatings of ZrO_2 (surface layer) and TiO_2 (sublayer). The zirconium precursor solution is kept constant, while the TiO_2 solution is modified with two different types of polymers, added separately to it. Both types of polymer modifications demonstrate increased protective properties on the corrosion resistance of coatings under conditions of external polarization, compared to the unmodified titanium layer. In addition, the amorphous structure of the zirconium layer and its relatively dense and hydrophobic surface also improve the anti-corrosion characteristics of the system in this environment [3]. Similar studies have been performed for multilayer systems of the same initial components. The systems are amorphous and dense, demonstrating increased corrosion resistance compared to low-carbon steel in a model environment with chlorine ions. In another study, dense, highly textured, hydrophobic coatings of ZrO_2-TiO_2 (1: 1) with an amorphous structure were obtained, respectively, using an organic or inorganic zirconium precursor [2]. Their protective ability in 5% NaCl was studied. The coatings show good corrosion resistance, which is demonstrated both by the weighting method and by means of potentiodynamic polarization curves. The samples were characterized by XRD, XPS [7], AFM, infrared spectroscopy (IRS), SEM, differential thermal analysis (DTA-TG), contact angle measurement. It has been found that the degree of influence of some factors, such as heat treatment temperature (TT) and the type of zirconium precursor is different. The potentiodynamic curves of samples, thermally treated at 400 °C show a better effect of the zirconium precursor compared to TT, as the application of an organic zirconium salt worsens the zones of anodic passivation. In contrast, coatings derived from organic and inorganic zirconium precursors show similar corrosion resistance, i.e. the influence of the precursor is minimized.

Increased corrosion resistance of low carbon steel is achieved by a newly developed hybrid multilayer coating consisting of a zinc sublayer (1 micron), a middle layer of chitosan (CS) and a sol-gel coating of ZrO_2 as a finishing layer. Samples were characterized using DTA-TG, XRD, XPS and AFM. The hydrophobicity of the coatings was assessed by measuring the contact angle. Two electrochemical tests - PDP and EIS were used to determine the corrosion resistance and the protective ability of the coatings in 5% NaCl. The results show that sandwich systems reliably protect the steel substrate in this corrosive environment. The newly obtained hybrid multilayer systems with an intermediate layer of CS have a dense structure and hydrophobic character. They demonstrate positive effects on the protective ability under external polarization, regardless of various characteristics such as morphology, grain size, roughness and contact angle [1].

Area 3

Corrosion monitoring

Research and corrosion monitoring of austenitic (18Cr10NiTi) and low-carbon (38GN2MFA) steels used to make some of the structures at Kozloduy NPP in model environments, containing the most common corrosion agents were performed. The beneficial effect of monoethanolamine as a mixed inhibitor has been established. Potentiodynamic studies were performed in conditions close to the water chemical regime, used in the plant. An electrode has been designed to simulate corrosion processes in cracks (the size of which can be changed if necessary) and preliminary studies have been carried out [22].

Synthesis and modeling of nanoparticle size

Together with the Technical University in Tbilisi, Georgia, equipment and methodology have been developed for the production of metal and oxide nanoparticles, as well as for adjusting their size, using a rotating electrode (cathode) in a two-layer bath of immiscible aqueous and organic solvents. The facility provides the ability to control various parameters, including the nucleation and growth of the resulting nanoparticles, depending on the time of stay in the medium and the speed of rotation of the cathode [24].

5. IMPACT OF THE CANDIDATE'S SCIENTIFIC PUBLICATIONS IN THE BULGARIAN AND FOREIGH LITERATURE

Dr. Nelly Boshkova presented 80 citations in the documentation, of which 58 are not included in her dissertation. The reference in Scopus to date gives 68 citations without self-citations. However, as is well known, the Scopus and Web of Knowledge databases reduce the number of citations as they omit citations from dissertations as well as those in conference proceedings. From the general list of Dr. Boshkova's works, the most cited are the articles [13, 18, 39] - 10 times. Dr. Nelly Boshkova has participated in presentations at 25 international and 23 national forums. The documentation submitted for the competition shows that Dr. Nelly Boshkova has won two awards:, International Award for Best

Publication: ICEMC 2018, 20th International Conference on Electrochemical Methods in Corrosion, April 12-13, 2018, Venice, Italy and II prize for oral presentation, Vth Scientific Seminar in Physical Chemistry for PhD students and young scientists, 2015.

In general, it can be concluded that the works of the candidate are excellently reflected in the scientific community.

6. CRITICAL REMARKS AND RECOMMENDATIONS TO THE SCIENTIFIC PAPERS OF THE CANDIDATE

Technical inaccuracies have been noted: two of the publications [40, 41] are not presented with a complete bibliography: the title of the conference proceedings "Nanostructured Materials in Electroplating, Proceedings of the International Workshop" and the date of the conference 25-30 March, 2006 are omitted. The chapters of books in group Г [4, 5, 10] would be good to have a larger volume, to be more convincing as scientific works of this scale.

For the future development of Dr. Nelly Boshkova I could recommend the attraction of students, as well as the scientific guidance of PhD students in this current scientific field.

7. PERSONAL IMPRESSIONS OF THE REVIEWER ABOUT THE CANDIDATE

I know Dr. Nelly Boshkova personally and over the years I have direct impressions of her as a colleague, as well as of the group at IPC - BAS, in which she follows her career development. That is why her achieved scientific results give me the conviction to believe that she has excellent prospects to make her personal contribution to the future development of this topical issue.

CONCLUSION

The documents presented by Dr. Nelly Boshkova, the only candidate in the announced competition for "Associate Professor" at IPC - BAS, correspond to the topic of scientific specialty in direction 4.2. Chemical Sciences, specialty "Electrochemistry"/ incl. Chemical Power Sources /" for the needs of the Institute of Physical Chemistry "Acad. R. Kaishew", Bulgarian Academy of Sciences, section "Electrochemistry and Corrosion", satisfying and exceeding the requirements of Law on the Development of Academic Staff in the Republic of Bulgaria (LASRB), The Regulations for its implementation in the Republic of Bulgaria and the Regulations for its implementation in IPC - BAS. The candidate's contributions are indisputable and clearly distinguishable in the scientific community.

The analysis of the overall and research work gives me a reason to believe with confidence to support the candidacy of Assistant Professor Dr. Nelly Boshkova and to recommend to the members of the respected Scientific Jury for the competition and the esteemed Scientific Council of IPC-BAS to award her the academic position of "Associate Professor".

Date: 06.12.2021

Prepared by:

/Assoc. Prof. Dr. Jenia Georgieva/