REVIEW

on the competition for the occupation of the academic position "PROFESSOR", announced in SG No. 99/13.12.2022 from the Institute of Physical Chemistry "Academician Rostislav Kaishev", BAS – Sofia, (IPC-BAS) in professional direction 4.2. "Chemical sciences", scientific specialty "Electrochemistry" for the needs of the "Electrochemistry and Corrosion" section

Reviewer: *prof. DSc. Assen Girginov, Ph.D., Department of "Physical chemistry", UCTM - Sofia*

The only candidate in the announced competition is Associate Professor Maria Hristova Petrova-Nikolova, Ph.D., Eng. The only candidate in the announced competition is assoc. prof. eng. Maria Hristova Petrova-Nikolova, Ph.D. from IPC-BAS, "Electrochemistry and Corrosion" section, who has submitted all the necessary documents for participation in the competition.

GENERAL AND BRIEF BIOGRAPHICAL INFORMATION ABOUT THE CANDIDATE

In ***1981***, Maria Petrova completed her secondary education at the German Language High School in Sofia;

In the period ***1981-1986***, Mrs. Petrova was a full-time student at the University of Chemical Technology and Metallurgy - Sofia, graduating as a Master of science (chemical engineer), majoring in "Electrochemistry";

1987 – 1990 she was a full-time doctoral student at the Institute of Physical Chemistry - BAS and in ***1991*** she defended her dissertation on the topic "Mechanism of electroextraction of zinc from sulfate electrolytes in the presence of inorganic impurities and organic additives" thus obtaining the educational and scientific degree "Philosophical doctor";

Since ***1990***, she has been working at IPC-BAS successively as a chemist, research associate (III-I) degree;

In ***2005***, Dr. Petrova occupied the position "Associate Professor" and is currently working in the "Electrochemistry and Corrosion" section.

DESCRIPTION OF THE SUBMITTED MATERIALS

Prof. Petrova participates in the announced competition with **39** scientific publications, **5** of which were summarized as a habilitation thesis.

It should immediately be noted that these materials cover her activities since her habilitation as "Associate Professor" (after 2005). In fact, the total number of her scientific publications is **70** (dissertation **7**, habilitation for "Associate professor" **24**, in the current competition **39**).

It is worth noting Dr. Petrova's active participation with oral and poster presentations at international and national scientific forums: **87** (**16** before and **71** after habilitation). Assoc. prof. Petrova is the supervisor of **one** full-time doctoral student who has successfully sustained his thesis.

Also, her participations in **6** national and **2** international scientific/educational projects are presented. Assoc. prof. Petrova has managed **4** national projects and has attracted financial resources from **5** projects she managed.

From 1995 to this day, she has been a part-time lecturer at TU-Sofia, where she has had lectures and exercises in "Chemistry" in German language. In addition, she is the co-author of a textbook "Chemistry" (in German). She has always received very high grades from both students and colleagues in the department for her teaching activity.

The materials with which assoc. Prof. Maria Petrova participates in the competition for the academic position "Professor" in accordance with the current regulations of the IPC-BAS are systematized and evaluated in the following table.

Group of metrics	№	Indicator	Points	Minimal requirements "Professor"	Collected points	Comment
A	1	Dissertation "Philosophical doctor"	50	**50**	**50**	
C	4	Habilitation thesis - **5** publications	$5Q_i$= 5x20 =100	**100**	**100**	Points are collected only from publications accepted after the habilitation "associate professor"
D	7	**29** scientific papers in Scopus and **3** patents	$1Q_i$= 1x25 = 25 $12Q_i$=12x20 = 240 $3Q_i$=3x15=45 $4Q_i$=4x12=48 2SJR without IF=2x10=20 3 patents x25 =75	**220**	**453**	Points are calculated only from the publications issued after the habilitation "associate professor"
E	11	Citations of **35** papers in scientific journals (*Web of Science* and *Scopus*)	437 x 2 points/citation	**120**	**874**	The points are collected from the citations of all publications of Dr. Petrova, but were not used in the habilitation for associate professor
F	13	Successfully graduated doctoral student	50		**50**	
	14	Participation in **6** national scientific/educational projects	x 10 points/project		**60**	Points are calculated only from participation in projects after the habilitation "associate professor"
	15	Participation in **2** international scientific/educational projects	x 20 points/project		**40**	
	16	Management of **4** national scientific / educational projects	x 20 points/project		**80**	
	18	Attracted funds for **5** projects	x1 point/5000 BGN		**170**	
	20	**1** teaching aid	20/n		**10**	
				640	**1887**	

In general, assoc. prof. Petrova's scientific works have been published in renowned international and specialized Bulgarian scientific journals.

• A total of **five** publications are included in the habilitation work (group B indicators): **two** in *Materiale Plastice* (Q2), **two** in *Transactions of the IMF* (Q2) and **one** in *Archives of Metallurgy and Materials* (Q2).

• The scientific publications out of the habilitation (group D indicators) are published in refereed and indexed in Web of Science and Scopus publications such as "*Transactions of the IMF*", "Galvanotechnik", "Journal of the Electrochemical Society", "Journal of International Scientific Publication: Materials, Methods & Technologies", "Bulgarian Chemical Communications", "Compt. rend. Acad. bulg. Sci.".

Assoc. prof. Petrova's literary awareness is beyond doubt. Most of the literary sources cited in her works were published in recent years. Given the complexity of the investigated systems and the numerous methods used, Dr. Petrova works with various Bulgarian and foreign colleagues. There is no doubt, however, that in all the scientific production presented, assoc. prof. Petrova is the main researcher.

GENERAL CHARACTERISTICS OF THE CANDIDATE'S SCIENTIFIC RESEARCH AND APPLIED ACTIVITY

The peer-reviewed scientific works (**39** items, of which **29** in Scopus) refer to one of the main sections of material science related to the development of technologies for the elaboration of advanced materials through chemical and electrochemical formation of metal, alloy and modified coatings on numerous types of dielectrics, including on 3D-printed materials. Various functional coatings with immediate practical application have been formed. As already noted, the results of the conducted research were published mainly in specialized journals, as well as in full text in proceedings of symposia, congresses and conferences with Bulgarian and foreign participation. Assoc. prof. Petrova is the co-author of **one** educational handbook and **three** patents.

BASIC SCIENTIFIC AND SCIENTIFIC-APPLIED CONTRIBUTIONS

HABILITATION

The inclusion of dispersed particles in the metal layers chemically deposited on flexible substrates makes it possible to combine the properties of metals (strength, plasticity, elasticity, electrical and thermal conductivity, etc.) with those of non-metals (hardness, chemical and thermal resistance, etc.).

Copper coatings deposited on flexible substrates were systematically investigated with the implementation of a different dispersed phase: diamond and boron nitride. The best results were obtained on polyethylene terephthalate (PET) substrates, which enables the use of works of different shapes (fibers, sheets, etc.). For the first time, copper coatings were chemically formed in a wide range (from 3/7 μm to 100/125 μm) of diamond and boron nitride dispersed phase sizes. The optimal hydrodynamic regime was determined, as well as the procedures for processing the dispersed particles. The coatings are characterized in detail, showing the possibility of incorporating boron nitride in other types of matrices (metal, ceramic, polymer).

A technology has been developed for the chemical deposition of dispersed coatings with diamond particles (from 3/7 μm to 225/300 μm) and in a nickel matrix. The influence of the main technological parameters (pH of the solution, temperature, hydrodynamics and duration, amount of incorporated particles) on the thickness and properties of the coatings was investigated. Test samples of abrasive tools were produced.

SCIENTIFIC PAPERS OUT OF THE HABILITATION

1. CHEMICAL DEPOSITION OF NICKEL/PHOSPHORUS AND COPPER DISPERSION COATINGS ON SOLID (NON-METALLIC AND METALLIC) SUBSTRATES

Pretreatment of non-metallic substrates

It is known that non-metallic (dielectric) substrates do not have their own catalytic action, which requires them to go through a preliminary surface treatment before their metallization. In it, one of the main operations is degreasing and pickling.

Systematic studies of various solution compositions and operating modes of degreasing and pickling of acrylonitrile butadiene styrene (ABS) substrates prior to the formation of nickel-phosphorus coatings were conducted. Changes in surface morphology were assessed with appropriate instrumental methods. The influence of various additives on the thickness and adhesion of the coatings was investigated.

To improve the effect of surface treatments, extensive research has also been carried out on an additional operation called "swelling", which increases the surface roughness. The experiments were carried out with three organic solvents (toluene, xylene and acetone), at different temperatures and processing times. As a result of this treatment, it was found that uniform coatings with very good adhesion were deposited on the substrate.

Chemical deposition of dispersed coatings with various micro- and nanoparticles

Systematic studies have been carried out on the deposition of nickel/phosphorus and copper dispersion coatings with various micro- and nanoparticles on non-metallic and metallic substrates.

Nickel/phosphorus dispersion coatings

• The chemical deposition of these coatings on acrylonitrile butadiene styrene (ABS) substrates was carried out by sequential degreasing and pickling, activation, acceleration and chemical metallization. The influence of the content of nanoparticles of TiO_2 and SiO_2 (30 – 60 nm) on the electrical resistance of the coatings was studied with equipment designed and manufactured at the Technical University in Sofia. The corrosion resistance and microhardness of coatings containing diamond particles (14 – 20 μm) were also studied. The influence of pH of the electrolyte on the composition, thickness and microhardness of the coatings was investigated.

• Nickel/phosphorus coatings are formed on various metal substrates (Al, Fe, Ti, Ni, Cu). Original methods of chemical metallization are applied. The optimal conditions for the preliminary preparation of the different metal substrates have been determined, so that the production of quality coatings was ensured.

• Special attention is paid to the formation of nickel/phosphorus coatings on copper substrates in view of their wide application in the production of printed circuit boards. Preliminary activation with palladium salt has been studied in detail, as a new innovative activating solution in which coatings with increased microhardness are formed.

Copper dispersion coatings

The mechanism of copper dispersion coatings deposition on acrylonitrile butadiene styrene (ABS) substrates was studied. The optimal composition of the copper electrolyte ensuring a constant deposition rate was determined. The structure of the formed copper coatings was also investigated.

Copper coatings from electrolytes with low pH, not containing formaldehyde

Copper deposition on dielectrics is a typical reduction process of metal ions on a catalytically active surface. The classic reducing agents (hydrogen-containing compounds) used in working electrolytes are highly toxic. This necessitates conducting research on the creation of new (environmentally friendly) solutions that do not contain toxic reducers. Experiments were carried out with reducing Sn^{2+} ions, which were previously adsorbed on the surface of the dielectric.

Deposition solutions were investigated by varying copper ion concentration, pH, temperature and deposition time. By applying modern experimental methods, the chemical composition, thickness and morphology of the formed coatings were determined.

Experiments were carried out on chemical deposition of copper and on ZrW_2O_8 particles, suitable for the creation of functional metal-ceramic composites.

It is worth noting that the development of new innovative environmentally friendly electrolytes is an important step towards finding a combined approach for chemical and eventual subsequent electrochemical deposition.

Chemical deposition of coatings on 3D-printed substrates

In recent years, 3D printing has been increasingly used in various manufacturing sectors. Through 3D-printing, parts of various shapes can be made from polymers, which can be covered with suitable metal layers.

• The properties of metallized 3D printed samples of acrylonitrile butadiene styrene (ABS) obtained by different technological modes were investigated and compared. The coatings obtained from four different copper and nickel electrolytes, containing and respectively not containing reducers, were investigated. The formed coatings are characterized in detail: morphology, structure, elemental composition, surface roughness and adhesion to the polymer substrate.

• Metallized 3D printed polylactate (PLA) samples were systematically studied. A detailed technological scheme has been compiled for the operations and the optimal values of the parameters in which reproducible and high-quality nickel/phosphorus coatings are obtained.

2. CHEMICAL DEPOSITION OF NICKEL/PHOSPHORUS AND COPPER DISPERSION COATINGS ON FLEXIBLE SUBSTRATES

A technology has been created for the formation of metal coatings on flexible polyethylene terephthalate (PET) substrates. Pretreatment conditions, electrolyte compositions and all parameters of chemical deposition of copper and nickel/phosphorus coatings are strictly defined. The resulting metal composite coatings with particles of different nature and sizes of the dispersed phase have demonstrated increased wear resistance and microhardness.

Nickel/phosphorus dispersion coatings

The influence of temperature, the presence of stabilizers and surfactants on the characteristics of the formed coatings has been studied in detail. It has been convincingly shown that this type of dispersion coating is particularly promising for the production of abrasive tools, an alternative to those based on hard chromium.

Copper dispersion coatings

Different compositions of solutions for chemical copper plating of a flexible polyethylene terephthalate (PET) substrate were investigated. A technology has been created for obtaining nano-dispersed copper coatings with different nano-sized (SiO_2, Al_2O_3 and TiO_2) and micro-sized (graphite, SiC) particles on woven and non-woven textile substrates. The conditions for obtaining reproducible layers of uniform thickness are strictly defined. Their polishing effect has been studied in laboratory conditions on various materials. The results have clearly shown that these coatings are suitable for a wide variety of industrial, agricultural and domestic applications.

3. FORMATION OF ANODIC OXIDE FILMS ON ALUMINUM

Anodic aluminum oxides (AAO) were electrochemically formed on the AA1050 aluminum alloy. Silver is incorporated into the pores of the oxide matrix by AC-polarization. The obtained (AAO/Ag)-layers were characterized by various instrumental methods (SEM, AFM, EDX, XPS and nanoindentation). A model was created describing the mechanism of their formation and the correlation between their characteristics and formation conditions. These layers are widely used as innovative functional coatings.

It is worth noting that in all the research conducted by Prof. Petrova, various experimental techniques, a large number of methods and reasonable calculation procedures were used, which is a guarantee of the high reliability of the obtained results.

REFLECTION OF THE CANDIDATE'S PUBLICATIONS IN BULGARIAN AND FOREIGN LITERATURE

489 citations were noticed on **37** of all the papers authored by assoc. prof. Petrova. Of these, **53** were used in the competition for "Associate professor". In this sense, in the current competition for "Professor" **437** of them should be taken into account (on **35** papers).

It is noteworthy that some of these articles are repeatedly cited in the international specialized literature, and for illustration I will present just one example. Dr. Petrova's paper:

Ivanov I., Stefanov Y., Noncheva Z., Petrova M., Dobrev Ts., Mirkova L., Vermeersch R., Demaerel J.P., "Insoluble anodes used in hydrometallurgy Part I. Corrosion resistance of lead and lead alloy anodes", *Hydrometallurgy*, 57 (2), (**2000**), 109-124

published after her habilitation, was cited more than **113** times.

It should also be noted that in many of the citations, the results obtained by assoc. prof. Petrova are commented on. This shows that Dr. Petrova's publications represent an indisputable contribution to the research field.

CRITICAL NOTES AND RECOMMENDATIONS TO THE CANDIDATE'S RESEARCH PAPERS

I have essentially no objections to the presented materials. I would like to make a recommendation to the candidate: I believe that my colleague Prof. Petrova has the necessary theoretical knowledge and experience to summarize the essential results obtained in a review article (or a chapter in a monographic publication). It could present both the mechanisms and the complex description of the processes in the chemical metallization of works from different materials.

REVIEWER'S PERSONAL IMPRESSIONS OF THE CANDIDATE

Unfortunately, I have no immediate impressions of the scientific activity of assoc. prof. eng. Maria Petrova, Ph.D. However, my acquaintance with the presented materials convinces me that she is an erudite researcher with a wide range of interests and high competence in the field of developing technologies for the creation of cutting-edge materials through chemical formation of metal, alloy and modified coatings. Over the years, Dr. Petrova has excellently presented the results of the conducted research in a large number of prestigious publications and specialized scientific forums. She is a desired and sought-after partner for participation in international and national research projects. Assoc. prof. Petrova enjoys high authority in the foreign and Bulgarian physicochemical and electrochemical collegium, which also defines her as one of the very good scientists at IPC-BAS.

CONCLUSION

It is necessary to note that the field in which the main scientific and scientific-applied results were achieved by assoc. prof. Dr. Petrova is both leading and very important. It is relevant because it is closely related to the technologies for depositing metal coatings on various surfaces for the needs of a wide range of industries. It is also important because it opens up many opportunities for fundamental research in the field of physical chemistry and electrochemistry. Assoc. prof. Petrova has perfomed a thorough analysis of a number of problems in the researched area and has systematically aimed at solving them.

The research activity of Dr. Petrova fully meets the thematic priorities of IPC-BAS, related to the creation and research of new materials.

Assoc. prof. Petrova's scientific contributions, as already noted, are substantial and have received wide international appreciation. The results have been achieved through significant volume of complex research conducted at a high level on sophisticated systems and phenomena. Her scientometric indicators are extremely good, which is a clear criterion for the level of research conducted and the results obtained.

Given the above, there is no doubt in my mind that we have before us the successful work of a fully formed and thorough scientist. Her scientific activity, international performance,

contributions, scientific indicators (impact factor, citability) and competence fully meet the requirements of the regulations of IPC-BAS for holding the academic position "Professor".

Therefore, I confidently allow myself to recommend to the Honorable Scientific Jury to propose to the Scientific Council of IPC-BAS to give **assoc. prof. eng. Maria Hristova Petrova-Nikolova, Ph. D.**, the academic position **PROFESSOR** in professional direction 4.2. Chemical sciences, scientific specialty "Physical chemistry" (01.05.05).

Sofia, 18.04.2023 **Reviewer:**