REVIEW

on a competition for the academic position of "Professor" at the Institute of Physical Chemistry (IPC), Bulgarian Academy of Sciences (BAS), Sofia, announced in State Gazette No. 99/13.12.2022 under Professional direction 4.2. Chemical sciences, scientific specialty "Electrochemistry (including chemical current sources)" with a single candidate Associate Professor Dr. Maria Hristova Petrova-Nikolova

Member of the scientific jury: Professor Dr. Nikolai Stoyanov Boshkov, IPC-BAS

1. Brief biographical data about the candidate

Associate Professor Dr. Maria Hristova Petrova-Nikolova was born on 04.12.1963. For the period 1976–1981, she studied at the 91-st German Language High School. Then, in 1981–1986, she completed higher education at the Chemical-Technological and Metallurgical University, Sofia, specialty "Electrochemistry". For the period 1987-1990, she was a full-time doctoral student at IPC-BAS and obtained the PhD Degree in 1991. From 1995 until now, she has been a part-time lecturer at the Technical University, Sofia - leading lectures and exercises in chemistry in German. In 2005, she became a Senior research associate, currently an Associate Professor. She was the Scientific secretary of the IPC-BAS for the years 2008 - 2012. From 2008 to the present, she is a member of the Scientific Council of the IPC-BAS, and from 2018 until now, she is a member of the Academic Council at the Training Center at BAS. In her research activities, M. Petrova uses German and English languages.

2. Description and evaluation of the presented materials

In the competition in which she participated, Associate Professor Petrova presented evidence for the following scientific production by groups of indicators according to the minimum requirements of the IPC-BAS, adopted by the Scientific Council of the institute (Appendix No. 1 of the Rules for the Terms and Conditions for the Acquisition of scientific degrees and for occupying academic positions at IPC-BAS):

2.1. Group of indicators A, Indicator 1: PhD Thesis for awarding the educational and scientific degree "Doctor" - Diploma No. 2745/20.11.1991 (Protocol No. 17 of the Higher Attestation Commission - VAK) for a protected dissertation on the topic "Mechanism of electroextraction of zinc from sulfate electrolytes in the presence of inorganic impurities and organic additives", which carries 50 points. Additionally, data are presented for three publications in Q2-ranked journals that relate to the PhD Thesis and are not scored:

2.2. Group of indicators C, Indicator 4: Habilitation work - scientific publications in journals that are referenced and indexed in world-renowned databases with scientific information. According to this indicator, information is given on a total of 5 articles with co-authors, published in international journals with rank Q2, respectively in 2011, 2012, 2013, 2014 and 2016, which carry a total of 100 points, as are the legally required for this group of indicators. All five publications were published after receiving the PhD Degree "Doctor" and after the habilitation of the candidate, i.e. the legal requirements are met.

2.3. Group of indicators G:

- ***Indicator 7***: Scientific publications in journals that are referenced and indexed in world-renowned databases with scientific information (Web of Science and Scopus) outside of the habilitation work. A list of a total of 22 publications is presented, all with co-authors, of which one issue was published in a Q1 journal and carries 25 points; 12 issues are out of print in Q2-ranked journals and carry a total of 240 points; 3 issues are in journals with rank Q3 and carry a total of 45 points; 4 issues are in journals with rank Q4 - a total of 48 points. Additionally, there are 2 publications that are published in SJR journals without IF (20 points). All publications under this indicator have been published after receiving the PhD Degree "Doctor" and after the candidate's habilitation and are valued at a total of 378 points.
- ***Indicator 9***: Invention, patent or utility model for which a protective document has been issued in due course. Associate Professor Petrova is a participant in the collectives of three issued patents (respectively in 2009, 2018 and 2021), which carry another 75 points. All three patents were approved by the Patent Office after the candidate's habilitation. Together with the points under Indicator 7, the total number of points in this group becomes 453, i.e. just over twice the minimum requirements for the procedure.

In an additional list for information, the participation of the candidate with poster and oral reports (86 in total) at international and national scientific forums is presented.

2.4. Group of indicators D:

- ***Indicator 11***: Citations in scientific publications, monographs, collective volumes and patents, referenced and indexed in world-renowned databases of scientific information (Web of Science and Scopus). According to the attached reference, a total of 489 citations have been found in the SCOPUS database, of which 437 are for the period after taking the academic position of "Associate Professor". Therefore, according to this group of indicators, there are 874 points, i.e. about seven times more than stipulated in the Minimal requirements according to Appendix 1 of the Regulations of IPC-BAS.

2.5. Group of indicators E:

- ***Indicator 13***: Guidance of a successfully defended PhD student – there is one successfully defended PhD student (in 2015), which carries 50 points;

- ***Indicator 14***: Participation in a national scientific or educational project – information on six projects was provided, which brings a total of 60 points;
- ***Indicator 15***: Participation in an international scientific or educational project – the candidate has participated in two such projects, which is estimated at a total of 40 points;
- ***Indicator 16***: Management of a national scientific or educational project – data on 4 such projects are shown, which is estimated at a total of 80 points;
- ***Indicator 18***: Attracted funds for projects led by the applicant - information was presented certifying the attraction of a total amount of BGN 855112, which, under the required conditions, gives another 171 points;
- ***Indicator 20***: Published university textbook or textbook that is used in the school network - there is a co-authored chemistry laboratory textbook published in 2011, which equals 10 points after dividing by the number of authors.

Therefore, according to this group of indicators, a total of 411 points are collected, which is nearly three times (2.7 times) above the required minimum according to Appendix 1 of the IPC-BAS Regulations.

From the information provided, it is obvious that the candidate has scientific contacts with a wide group of Bulgarian and foreign co-authors given the complexity of the researched objects. Some of the journals in which she has published are extremely prestigious such as: Journal of Applied Electrochemistry, Journal of The Electrochemical Society (Rank Q1) and others. These facts clearly show that the professional qualification and high scientific erudition of the candidate are beyond doubt.

Attached to the materials provided to me is a list of the publications she used in her PhD Thesis - a total of 7 publications that do not match those on the list for the current competition. In another list, the publications from the competition for her habilitation (24 items) are presented. From the list of publications in the current competition, it can be seen that Associate Professor Petrova participated as the first author in a total of 11 articles, and as the second author - also in 11 issues. Her place in the authors' collectives proves indisputably her active contribution in the preparation of these scientific publications.

In conclusion, it can be said that all presented materials correspond to the theme of the competition. Scientific and other indicators in almost all groups significantly exceed the minimum requirements of IPC-BAS for acquiring a scientific degree and for holding academic positions (Appendix 1 of the Regulations on the terms and conditions for acquiring scientific degrees and for holding academic positions in IPC - BAS):

For "Professor": Group A - 50 points (with required 50 points); Group B – 100 points (with 100 points required); Group D - 453 points (with required 220 points); Group D - 874 points (with required 120 points); Group E – 411 points (with required 220 points).

3. General characteristics of the candidate's scientific-research and scientific-applied activities

In her activity so far, Associate Professor Petrova has carried out her scientific and scientific-applied research in the following main areas:

- Research area 1 – Chemical deposition of nickel/phosphorus and copper dispersion coatings on solid (non-metallic and metallic) substrates;
- Research area 2 – Chemical deposition of nickel/phosphorus and copper dispersion coatings on flexible substrates.

Research area 1 - Some of the publications refer to the pretreatment of non-metallic substrates [60,70] before the chemical metallization of the thermoplastic copolymer acrylonitrile butadiene styrene (ABS). Studies have been conducted with selected compositions for degreasing and pickling aiming to produce a Ni-P chemical coating. Due to the smooth surface of the polymer samples, additional roughening (swelling) was carried out with organic solvents - toluene, xylene, acetone.

Another part is related to the chemical deposition of dispersed coatings with micro- and nanoparticles on non-metallic (ABS) and metallic substrates [32-37,41,42,57]. Chemical metallization was performed in the presence of nano- (TiO_2 - 30nm; 60nm) or microparticles (diamond - 14μm – 20μm) [33,57]. The influence of TiO_2 nanoparticles on the thickness of Ni-P coatings, as well as the corrosion resistance and microhardness of Ni-P coatings with incorporated diamond particles at two pH values, was investigated. Increasing the pH of the electrolyte leads to an increase in thickness and microhardness, and decreases the P content. The weight loss of particle coatings in a salt spray chamber is greater, and in sulfate medium the coatings do not completely dissolve up to the oxygen evolution potential.

Studies have been conducted with acidic and alkaline nickel electrolytes for the deposition of nano- and microparticle coatings on metal substrates (Al, Fe, Ti, Ni, Cu) - [37, 41]. Some nanoparticles (Al_2O_3 and SiO_2) greatly reduce the rate of the reduction process, while others (TiO_2) increase it [33, 35]. A suitable activating solution and an economically viable technology for the electroless deposition of Ni-P and nanodispersed Ni-P coatings have been established [32, 34, 37]. The latter have a good morphology, and their microhardness is more than 30% greater compared to the ordinary Ni-P-coatings.

Environmentally friendly solutions have been proposed for the chemical deposition of copper layers using tin ions, which are previously adsorbed on the surface of the dielectric. A comparison was made between copper layers obtained by two different schemes: 1/. with environmentally friendly electrolyte for chemical copper plating; 2/. with copper trilonate electrolyte with formaldehyde

reducer [62,65,66]. A metal-ceramic composite material with a low coefficient of thermal expansion of the Cu/ZrW_2O_8 type was created [67]. The deposition processes of chemical copper on a matrix of nanoporous anodic alumina (AAO) on an aluminum substrate have also been investigated [58,63]. Systematic studies of combined Al-O-Ag coatings on technical grade aluminum AA1050 have been carried out [59].

Coatings were deposited on 3D-printed substrates - ABS samples with different filling densities of the inner layers and compared with those obtained by injection molding [64]. Four copper and nickel electrolytes were used, respectively with and without reducers. It was found that as the activation temperature increased, the sample roughening and metallization rate increased.

Research Area 2 - Research in this area concerns the preparation of composite coatings incorporating different types and sizes of dispersoids - diamond, ZrO_2, SiC, Al_2O_3, TiO_2, α-hexagonal (hBN) and cubic (cBN) boron nitride - characterized by high wear resistance and microhardness [50,53,56]. The influence of temperature and certain surfactants on the quality of the obtained coatings, which can be used for the production of abrasive, cutting and polishing tools [69], was established. Copper dispersion coatings were obtained with incorporated dispersoids with nano- (SiO_2, Al_2O_3 and TiO_2 [47]) or micro-sizes (graphite [47], SiC [48, 53]), which differ significantly from electrochemically obtained ones [43, 44, Patent 2].

4. Basic scientific and scientific-applied contributions

The main contributions of the candidate can be summarized as follows:

Dispersed materials combining to a certain extent the properties of metals and non-metals have been obtained, including chemical copper dispersion coatings with diamond or BN dispersoid size (α-hBN and cubic cBN) from 3/7μm up to 100/125μm on a flexible PET substrate [45,46,49]. Hydrodynamic mode and particle processing are optimized. It has been confirmed that non-metallized [49, 51] and pre-metallized [52] grains of BN can be incorporated into the copper matrix, and it is more expedient to work with the smaller fractions. Metallization of cBN grains (non-metallized and pre-metallized with Ti) with nickel and cobalt was carried out in order to obtain abrasive tools by high-temperature sintering [52] and it was found that the titanium layer did not affect the rate and structure of the subsequent nickel plating and cobalt plating.

- ***Research Area 1*** – Three organic solvents were applied to roughen the surface of polymers and the effect of temperature and processing time on the thickness and adhesion of deposited chemical copper or nickel coatings was determined. It was established that using acetone produces uniform copper and Ni-P coatings over the entire surface of the polymers.

It was found that the nature of the solid nanoparticles embedded in the coating does not influence the deposition kinetics of NiP-dispersed coatings on ABS if they are of similar size, surface microgeometry and electrical charge.

The optimal conditions of preliminary preparation of the various metal substrates (Al, Fe, Ti, Ni) during their chemical metallization have been determined. It was found that the presence of nanoparticles in the electrolyte strongly affects the kinetics of the process, but not the choice of substrate. A new generation of activating solution based on palladium sulfate and a complexing agent is proposed. A technology has been developed for the production of printed circuit boards by depositing a two-layer Ni/Au coating on copper surfaces.

The optimal concentrations of compositions for degreasing, pickling, reduction, pre-activation have been determined, and the optimal compositions and regimes of the copper electrolyte have been established [61,63]. A model has been proposed regarding the kinetics of formation of complex Al-O-Ag coatings and the interrelationship between the applied growth conditions and the obtained characteristics, properties and morphology [59].

It has been proven that the standard technology for metallization of cast ABS-polymer samples can also be applied to 3D-printed ABS samples.

Research Area 2 - A technology for pre-treating of a PET substrate prior to the deposition of metal coatings has been established and the compositions and conditions for the chemical deposition of copper and nickel metal coatings have been established.

The effect of the microparticles used on the thickness of the coating, the amount of the dispersed phase in the coating and its distribution in the copper and nickel-matrix system was established - the degree of inclusion of untreated particles strongly depends on their size. After metallization, the degree of incorporation increases significantly. These coatings can be used as an abrasive material for grinding.

Coatings of uniform thickness, semi-bright and with a good decorative appearance were obtained, which can be used against electromagnetic interference.

In conclusion, based on the submitted materials, I believe that a considerable amount of experimental activity has been carried out in relation to the studied materials and selected environments. The conducted research is correct, precise and at a modern methodological level, with a clearly defined and current topic, whose benefit and significance for science and practice is beyond doubt.

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

Associate Professor Petrova submitted information on a total of 489 citations to her articles found in the SCOPUS system. Of these citations, 437 came out after her habilitation, i.e. after 2005. A total of 114 citations were found for one (No. 14) of her articles, of which 113 were after her habilitation. Another article (No. 15) was cited 82 times, respectively 81 citations were after habilitation. There is also an article (No. 11) with 56 citations – of which 54 are after 2005. All these data unequivocally confirm the extremely high interest in the topics studied by the candidate.

6. Critical notes and recommendations

I have no critical remarks about the materials provided for my review. Although there are three patents in place, I believe there is great scope for applying for more patents and/or utility models given the high interest in this type of material. I also believe that the candidate has the potential and experimental results to write a monograph/monograph chapter or review article on the current topic.

7. Personal impressions of the candidate

I have known Associate Professor Dr. Maria Petrova since my admission to IPC-BAS. In my opinion, she is an example of an extremely fair and responsible researcher. From the available information about her scientific activity, I can responsibly state that, in my opinion, the experimental activity was carried out competently and at a very high professional level. In addition, I believe that the conducted research is largely her personal work, which is unequivocally confirmed by the place and authorships of the available publications, posters and reports at scientific forums. The analyzes of the obtained experimental data, their interpretation, as well as the proposed conclusions in the publications are logical and very well founded.

CONCLUSION

From the materials presented by Associate Professor Dr. Maria Petrova on the competition, I can conclude that, in terms of quantity and quality, her scientific output is more than sufficient in terms of the Minimum requirements of the recommended criteria for occupying the academic position "Professor" at IPC-BAS (Appendix 1 of the Regulations on the terms and conditions for acquiring scientific degrees and for holding academic positions at IPC-BAS), and in some cases it significantly exceeds them. The candidate is a fully formed scientist, with high scientific qualifications and erudition. On the basis of all this, I strongly propose to the Honorable Scientific Jury to elect Associate Professor Dr. Maria Hristova Petrova-Nikolova as "Professor" in Professional Direction 4.2. Chemical sciences, scientific specialty "Electrochemistry (including chemical current sources)".

Signature:

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Sofia, 28.04.2023