REVIEW

in competition for the academic position Professor of professional field "4.2. Chemical Sciences" and scientific specialty "Physical chemistry" for the needs of the "Phase formation, crystalline and amorphous materials" department at IPC-BAS, announced in SG No. 107 of 20.12.2024 with a candidate Dr Svetlozar Dimitrov Ivanov.

Reviewer: Professor Anton Momchilov

1. Background and brief biographical details of the candidate.

The only candidate ин the competition for the academic position of "Professor" for the needs of the field "Phase Formation, Crystalline and Amorphous Materials" of the Institute of Philosophical Chemistry - BAS is Associate Professor Dr. Svetlozar Dimitrov Ivanov. The documents comply with the requirements of the Academic Staff Development Act and the Regulations for its implementation, as well as the Regulations of the Institute of Academic Staff Development - BAS.

Mr. Svetozar Ivanov has completed his secondary education at Dobri Chintulov Natural and Mathematical High School, Sofia, Bulgaria. Chemistry in 1995. He studied at the Faculty of Chemistry of Sofia University, graduating with a specialization in "Pure and Particularly Pure Substances and Materials Based on Them" in 2000. The same year he joined the Institute of Physical Chemistry at the Bulgarian Academy of Sciences as a chemist. Since 2001 he has been a PhD student at the same institute. He received the BAS award for the young scientist under 30 in 2003. He defended his thesis on "Modification of conductive polyaniline coatings by current and currentless deposition of metal particles" in 2006. Since 2007 he has been a research fellow at the IHF, and in 2010-2011 he was a postdoctoral fellow at Bar Ilan University, Ramat Gan in Israel. After postdoctoral studies he was accepted as a research fellow at TU Ilmenau, Ilmenau, Germany. Mr. Ivanov habilitated at the "Faculty of Electrical Engineering and Information Technology" of the same university in 2019. The topic of his habilitation thesis is "New materials and advanced analytical techniques for application in the research and technology of lithium-ion batteries". He gives lectures and seminars on "Electrocrystallization" and "Electrochemistry and Corrosion". He has been a scientific supervisor of Bachelors, Masters and PhD students. He has developed a laboratory practicum on electrochemical energy storage and galvanotechnics. He has also been the leader, co-leader and participant in many research projects.

2. Evaluation of the submitted materials.

The materials submitted by Assoc. Prof. Dr. Ivanov are in the thematic area of the competition and meet the eligibility requirements. His scientific activity is presented in accordance with the requirements of Article 29, paragraph (1), item 5 of the Law on Research and Development and the minimum requirements adopted by the IHF SC.

In the group of indicators A 50 points of the defended dissertation for the scientific and educational degree "PhD" are covered.

In indicator group B, 135 points have been collected with a minimum requirement of 100 points. Points have been collected from 6 publications submitted in indicator 4 of this group. The publications are in journals with Q1 - three and with Q2 - three.

From indicator group "Г", 250 points were collected from indicators 7, 8 and 10 at a requirement of 220 points. The points were collected from 6 publications in Q1 journals (150 points) and two in Q2 journals (40 points). Two book chapters in indicator 8 (30 pts) and two US patents (30 pts) were also submitted.

In indicator "Д", 63 citations are presented from only three publications, thus accumulating 126 pts. at a requirement of 120 pts. One of the publications has 37 citations, which is impressive. An additional list presents 60 citations from 8 more publications that are not presented in the minimum requirements reference.

In group of indicators "Е", 343 points were collected with a requirement of 150 points, of which 75 points were from doctoral students who defended their thesis, participation in national and international projects – 60 points,

leadership of a Bulgarian team in an international project – 50 points. From funds attracted for projects led by the candidate – 158.

3. General characteristic of the candidate's scientific research and applied activity.

Associate Professor Dr. Svetlozar Ivanov is an established scientist in the field of physical chemistry, electrochemistry and materials science. His H-index in Research Gate is 22 and the so-called i10-index in Google Scholar is 36. The results of his research have been reported in 75 scientific papers, 18 have been printed in conference proceedings, and two US patents have been granted. He has presented papers at 19 scientific conferences. Early in his scientific career he worked on the preparation of polyaniline layers on which metal particles are deposited. The conditions for the preparation of the layers and for the deposition of the metal particles (Cu, Ag) were studied. The results are published in seven papers. Another direction in the candidate's research work is the preparation and characterization of negative active materials for lithium-ion batteries. The conditions for obtaining the layers and for depositing the metal particles (Cu, Ag) were studied. The results were published in seven articles. Another area of the candidate's research is the preparation and characterization of negative active materials for lithium-ion batteries. Ordered titanium dioxide nanotubes (amorphous and crystalline) have been studied in two types of electrolytes. Silicon deposited on a substrate of titanium dioxide tubes has also been studied. The resulting active material shows a stable capacity as of the 200th cycle of 1150 mA h g-1. Another negative active material was obtained by doping non-stoichiometric titanium dioxide nanoparticles with carbon and sulfur. The doped nanomaterial has a stable capacity (initial values of 210 mAh g-1) and very fast electrochemical kinetics. A thin composite layer containing silicon was electrochemically deposited on a copper substrate at a constant potential in an ionic liquid-based electrolyte. The composite exhibits stable galvanostatic behavior with a capacity of about 1200 mAh g-1 and 80% capacity retention after 300 cycles in a standard electrolyte. A pulsed current technique was used to prepare SnO2 nanoparticles. The electrode material demonstrated an initial capacity in the first cycle of about 680 mAh g-1. The same method was used to synthesize MOx–C (M = Sn, Ni) supports and Pt/MO x –C catalysts for application in direct alcohol fuel cells. The "self-combustion" method resulted in a positive active material with improved capacity and high cycling stability. A thin-film calorimeter has been developed to study the thermodynamic properties of thin films, including energy storage materials. A novel approach has been chosen, employing high-temperature stable piezoelectric resonators as a highly sensitive planar temperature sensor. In another work, the technique was used to study intercalation-induced macroscopic expansion of electrodes for lithium-ion batteries. Multilayer nanocomposites of polyaniline and gold nanoparticles were formed by layer-by-layer deposition. The introduction of citrate ions provides stable doping of the PANI structure, leading to significant electroactivity and conductivity at near-neutral pH values. The layer-by-layer adsorption technique was used to deposit a novel electrocatalytic material consisting of palladium nanoparticles and polyaniline. The resulting nanocomposites were investigated as electrocatalytic materials for hydrazine oxidation. The same technique was used to prepare thin composite layers consisting of polyaniline and palladium particles. The composites were used for the reduction of hydrogen peroxide at neutral pH. Fourteen publications were submitted in the professorship competition, two of which are reviews. These works can be summarized in the following areas: synthesis of Si for Li- and Na-ion batteries, synthesis of Ni/NiO for negative active material, study of the SEI film, corrosion processes in Li-ion batteries, synthesis of catalysts for the oxidation of ascorbic acid and methanol. Two US patents were also presented. In my opinion, both patents have a very great value for the competition. Silicon was electrochemically deposited from a sulfolane-based electrolyte. Thin Si layers with low roughness and minimal inclusion of organic contaminants were obtained (Electrochem. Commun, 103, 37-11, 2019). The process of electrodeposition of silicon in sulfolane-based electrolytes and ionic liquid has been studied. More efficient deposition is observed on metal electrodes (copper, nickel). When using glassy carbon, successful deposition can only be achieved in ionic liquid (2020, ACS Appl. Mater. Interfaces 12 (51), 57526-57538). The electrochemical nucleation and growth of silicon on glassy carbon in an ionic liquid was investigated in paper 2020, J. Crystal Growth, 531, 125346. A theoretical model for three-dimensional nucleation was applied, taking into account the propagation and overlap of diffusion zones. The

obtained active material was tested as an anode for sodium-ion batteries, where it showed high specific capacity, long-term electrochemical stability, retaining a capacity of 540 mAh g−1 for at least 400 cycles (2022, Energy Technology 10 (5), 2101164). An electrochemically formed porous copper substrate was used for electrochemical deposition of silicon. The modified electrode was tested as an anode, without a binder and a conductivity enhancing component (2021, Electrochim. Acta 380, 138216). Nickel microfibers with a rough nanostructured surface were synthesized and further partially oxidized. The resulting Ni/NiO was tested as an anode, showing higher reversible capacity and improved stability. The influence of soluble polysulfides and lithium nitrate on the characteristics of the SEI film on the Li surface before electrochemical cycling was investigated. The change of the Li surface upon cycling in two electrolytes was investigated (2019, Journal of Chemistry, (1), 4102382). An electrochemical quartz microbalance (EQCM) was used for real-time analysis of SEI film formation in modified electrolytes (2019, ChemPhysChem, 20 (5), 655-664). The Taguchi (TM) method was used to determine the relative influence of various parameters on the intensity of the corrosion process in lithium-ion batteries (2020, Electrochim. Acta 360, 137011). SEI formation was investigated by in situ electrochemical dilatometry upon the addition of vinyl carbonate. Its influence on the graphite anode was determined (2020, J. Power Sources 457, 228020). The corrosion of lithium in contact with a copper substrate was studied using the in situ ZRA (Zero-Resistance-Amperometry)-QCM method. This new technique allows the measurement of a gravimetric response due to electrochemical deposition or dissolution in parallel with the galvanic current (2023, Electrochim. Acta 463, 142853). Polyaniline layers doped with poly(2-acrylamido-2-methyl-1-propanesulfonic acid) were synthesized under various conditions. The electrocatalytic activity of PANI for the oxidation of ascorbic acid was investigated (2013, Chemical Papers 67, 1002-1011). Pt(Cu)/TiO2/Ti electrodes were prepared by a multi-step method and spontaneous substitution of Cu by Pt. The oxidation of methanol on rutile-rich platinized electrodes proceeds at significant rates and can be further enhanced under UV illumination (2012, J. Electrochem. Sci. Eng. 2 (4), 155-169). The first review article describes a methodology for separating faradaic, pseudocapacitive, and capacitive charge storage using conventional electrochemical methods. Exemplary electrochemical energy storage systems that combine battery, capacitor, and pseudo capacitor features are described (2022, Electrochim. Acta 412, 140072). The first review article describes a methodology for separating faradaic, pseudocapacitive and capacitive charge storage using conventional electrochemical methods. A description of exemplary electrochemical energy storage systems that combine battery, capacitor and pseudo capacitor characteristics is provided (2022, Electrochim. Acta 412, 140072). An updated critical review of the main strategies for structuring 3D copper current collector, methodologies for analyzing these structures, and approaches for effective control over their properties is provided. These methods are described in the context of their practical utility (2023, Energies 16 (13), 4933). The next review is a critical review of the mechanisms of aluminum corrosion in lithium-ion batteries, methodologies for analyzing this phenomenon, and approaches for its effective inhibition. Relevant examples of important factors such as electrolyte composition, temperature conditions, and electrochemical parameters are presented (2021, J. Energy Storage 43).

4. Basic scientific and applied scientific contributions of the candidate.

In the works of the PhD thesis: Polyaniline layers have been successfully synthesized, on which for the first time metal particles of Cu and Ag have been deposited. It has been established that the type of active sites for silver nucleation changes depending on the thickness of the polymer layer. Crystalline and amorphous titanium dioxide nanotubes have been obtained and the better electrochemical behavior of the amorphous material has been demonstrated (2013, Electrochim. Acta, 104, 228-235). It was found that the resulting Ti/TiO2HT–Si structures have excellent cyclability in ionic liquid (2014, J. Electroanal. Chem. 731, 6-13). Nanoporous Si was obtained, having stable reversible capacitance in EC/DMC electrolyte. The poorer cycling in ionic liquid was explained (2014, J. Appl. Electrochem., 44, 159-168). Anatase, S and C nanoparticles have been synthesized and the presence of sulfur in the S^{6+} sulfate form, without the presence of Ti-S and C-S chemical bonds, with good photovoltaic behavior (2016, Nanoscale Research Letters, 11, 140) and accelerated and stable reversible Li+ incorporation (2016, J. Power Sources, 326, 270-278) has been demonstrated. Composite layers with Si were obtained by electroreduction and the processes involved were established. Its good

electrochemical behavior was demonstrated and analyzed (2015, Electrochim. Acta 168, 403-413). Using acoustic impedance and corresponding theoretical models, a change in the influence of viscoelasticity and morphology with the deposition time of silicon-containing layers has been shown (2016, Electrochim. Acta 219, 251-257). SnO2 nanoparticles were obtained and their good behavior as a lithium anode was shown (2016, J. App. Electrochem. 46, 527-538). An original method for preparing MOx–C (M = Sn, Ni) supports and Pt/MO x –C catalysts has been proposed for direct methanol fuel cells in acidic or alkaline electrolyte (2016, J. Appl. Electrochem. 46, 245–1260). A LiNi0.6Mn0.2Co0.15Al0.025Fe0.025O2 material was obtained using the "self-combustion" method and its parameters responsible for good cycling characteristics were determined (2014, J. Power Sources, 268, 414-422). A thin-film calorimeter has been developed to study the thermodynamic properties of thin films and has been applied to study the thermodynamic parameters of materials for lithium-ion batteries (2015, J. Electrochem. Soc. 162, A727-A736, 2013, J. Mater. Sci. 48, 6585-6596, 2017, Int. J. Mater. Res. 108, 904-019, 2013, J. Appl. Electrochem. 43, 559 – 565). "In situ" dilatometry and a developed theoretical approach for estimating reversible electrode expansion have been applied to an NMC(1:1:1) – graphite cell (2017, J. Power Sources, 342, 939-946). A macroscopic electrochemical-mechanical model of a lithium-ion cell has been developed and applied. The model has been validated and applied to assess the consequences of elevated pressure conditions (2018, J. Power Sources, 378, 235-247). A conductometric technique has been proposed for electrocatalytic chemical sensors based on conductive polymers (2006, Electrochem. Commun., 8 (4), 643-646). TiO2-polyaniline (PANI) composite layers have been prepared electrochemically and characterized electrochemically and photoelectrochemically. It has been found that the bilayer structures have up to three times higher photocurrents than the composite single layers (2008, J. App. Electrochem. 38, 63-69). A method for obtaining multilayer polymer structures has been developed (2009, Macromol. Mater. Eng., 294 (6-7), 441-444). Multilayer PANI-AuNPs structures have been obtained, with the introduction of citrate ions leading to significant electroactivity and conductivity at close to neutral pH values (2010, J. Solid State Electrochem., 14, 1261-1268). The sensitivity of PANI-AuNPs for the oxidation of dopamine and uric acid was established in terms of the different limitations for the two oxidation reactions (2011, Electrochim. Acta 56 (10), 3693-3699). A new electrocatalytic material consisting of palladium nanoparticles (Pd NPs) and polyaniline (PANI) was obtained, and a linear response was established upon hydrazine oxidation (Sensors and Actuators B: Chemical 150 (1), 271-278, 2010, Pure App. Chem. 83 (2), 345-358). Two types of composites of PANI-Pd NPs and (PANI-PSS)Pdeless were prepared and their high amperometric sensitivity was established (2013, Electrochim. Acta 90, 157-165). Electrochemically deposited Si was obtained from a sulfolane-based electrolyte for the first time (2019, Electrochem. Commun, 103, 37-11). In a study of the electrodeposition of Si by electrolyte and ionic liquid, it was found that on a metal substrate it was successful in both cases, while on glassy carbon it was only possible by the ionic liquid (2020, ACS Appl. Mater. Interfaces 12(51), 57526-57538). A theoretical model of three-dimensional nucleation was applied to quantitatively characterize Si deposition on glassy carbon (2020, J. Crystal Growth, 531, 125346). The electrodeposited Si has a good and stable capacity as an explanation of its behavior was also found (2022, Energy Technology 10 (5), 2101164). A porous copper substrate was found to improve the mechanical and electrochemical stability of electrodeposited silicon derived from a sulfolane electrolyte (2021, Electrochim. Acta 380, 138216). Nickel microfibers with rough nanostructured surface were prepared at low temperature and magnetic field with further oxidation. The material was found to exhibit higher reversible capacity and improved cyclic stability (2021, J. Appl. Electrochem., 51, 815-828). In other work, polysulfides and LiNO3 were found to reduce the resistive behavior of the SEI film, and the interface exhibited a rough and inhomogeneous morphology (2019, Journal of Chemistry, (1), 4102382). The difference in SEI film growth in electrolytes with different additives is shown by electrochemical quartz microbalance (2019, ChemPhysChem, 20(5), 655-664). The Taguchi method was used to analyze the corrosion process in lithium-ion batteries. The partial influence of the factors in the corrosion process was established (2020, Electrochim. Acta 360, 137011). The addition of vinyl carbonate was found to reduce the irreversible expansion of the graphite anode by in situ electrochemical dilatometry (2020, J. Power Sources 457, 228020). It was found that an adsorbed layer of polyethylene oxide on the copper surface could be applied to inhibit corrosion by a combined in situ ZRA -QCM method (2023, Electrochim. Acta 463, 142853). In a work (2013, Chemical Papers 67, 1002-

1011) it was found that the type of inorganic component in the polymerization solution has a pronounced effect on the degree of doping and on the redox activity in the preparation of PANI layers doped with poly(2-acrylamido-2-methyl-1-propanesulfonic acid) and the activity of PANI for the oxidation of ascorbic acid depends on the preparation. Pt(Cu)/TiO2/Ti electrodes have been obtained that oxidize methanol at significant rates and can be enhanced with UV illumination in the photoelectrochemical oxidation of methanol (2012, J. Electrochem. Sci. Eng. 2 (4), 155-169).

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

The candidate has provided a total of 1057 citations from his papers. The citations for group 'Д' of the two lists are 123. In Google scholar the i-10 index is 36. Eight papers have more than 50 citations, one of which has 120 citations.

6. Significance of contributions to science and practice.

I believe that Section 4 also clarifies the importance of his research work, which is mainly in lithium-ion batteries area. Here again it is appropriate to mention both US patents. In my opinion, the work on catalysts for a methanol cell is of great importance, as this fuel cell is a very good alternative for an electric vehicle.

7. **Critical notes and recommendations on the candidate's scientific work.**

Technical note: There is a difference in the number of papers that qualify for a professorship and those in the minimum requirements.

8. Conclusion.

The scientific metrics and the results of the candidate's activity exceed the requirements of the LDASRB, its Regulations and the Regulations of IPC-BAS, therefore with full conviction I propose the Honorable Scientific Jury to propose to the Scientific Council of IPC to elect Associate Professor Dr. Svetlozar Dimitrov Ivanov to the academic position of "Professor" in the professional field "4.2 Chemical Sciences", scientific specialty "Physicochemistry" for the needs of the section "Phase Formation, Crystalline and Amorphous Materials" of the Institute of Physical Chemistry "Academician Rostislav Kaishev" at BAS.