REVIEW

of the materials submitted for participation in the competition for the academic position "Associate Professor" in the professional field 4.2 "Chemical Sciences" (Solid State Chemistry) announced by the Institute of General and Inorganic Chemistry – BAS in State Gazette 46 / 26.05.2023 г.

Candidate: chief assist. prof. PhD Alexander Svetoslavov Tsanev

Member of Scientific Jury: Prof. DSc Martin Slavchev Bojinov, UCTM

1 General remarks and biographical information

Chief assist. prof. PhD Alexander Tsanev has submitted all necessary documents to apply for the academic position of associate professor at the Institute of General and Inorganic Chemistry – BAS. The reference table presented shows that his results exceed the minimum national requirements for that position.

1.1 Biographical data

Alexander Tsanev was born on 18.09.1977 in Plovdiv. In 2001 he graduated as a Master of Science in Inorganic and Analytical Chemistry at the Faculty of Chemistry, Sofia University. Since 2004 he has been working at IGIC-BAS as a chemist, assistant professor and chief assistant. He sustained a Ph.D. thesis on *Synthesis and characterization of mixed oxide films of Zr with rare earth elements Ce and Y for catalytic applications in* 2017.

1.2 Participation in scientific projects

Dr. Tsanev is a team member of the project "National Center for Advanced Materials" (UNION) of NSF (2009-2013). In addition, he is a participant in a number of other projects funded by NSF: NFNI-T01/6 "Innovation approach for obtaining structured catalysts for the disposal of methane emissions", KP-06-H27/2 "Study of the influence of outer space on the physico-chemical properties of glassy carbon coatings after long exposure at the International Space Station", as well as in the Distributed Infrastructure "Production and Research of New Materials for Technical Applications, as well as Conservation, Access and E-Storage of Artifacts (INFRAMAT)".

2 Description of presented documents

The scientific production of Dr. A. Tsanev consists of 29 papers, of which 21 have been published in international journals. In addition, he has presented over 10 times at international and national scientific conferences. Prior to the participation in the present competition, Alexander Tsanev has defended a dissertation for obtaining the educational and scientific degree of Doctor (2017). In that respect, only the part of the scientific works that relate to the competition for associate professor will be reviewed (the 2 publications on which the PhD thesis is based will be omitted). In general, the publications of Dr. Tsanev are in reputable specialized international journals, such as Applied Surface Science, Mater. Sci. Eng. B, J. Electrochem. Soc., Materials Chemistry and Physics (2), J. Mater. Sci. Mater

Electron., Solid State Sciences, Catalysts, Materials, etc. He presents a large number of papers in Bulgarian scientific journals, such as Compt. Rend. Bulg. Acad. Sci., Bulgarian Chemical Communications, as well as in Proceedings of International Conferences (J. Physics: Conf. Ser.). As a rule, Chief Assist. Tsanev works within a team of Bulgarian and foreign researchers. Given the complexity of the systems studied and the wide range of methods used, a relatively large number of authors often participate in publications. The general review of the works unequivocally shows that in the majority of the presented scientific articles Chief Assist. Tsanev has a significant involvement.

3 General overview of the scientific activities of the candidate

Dr. A. Tsanev's basic and applied research is in a dynamically developing interdisciplinary field – synthesis and characterization of thin oxide films with applications as catalysts, electrocatalysts, sensors, functional and protective coatings. In the following sections, the main results obtained, the ideas and interpretations generated will be briefly discussed.

3.1 Investigations of the corrosion resistance of oxide systems

The chemical composition of cerium-containing conversion layers on aluminum alloy has been studied by XPS. The conversion films obtained consist of Al_2O_3, a mixture of Ce^{3+} and Ce^{4+} (in a 2:3 ratio) and Cu^{+}, Cu^{2+}. It is demonstrated that the presence of Cu^{2+} leads to an increase in the content of Ce^{4+} thus increasing the corrosion resistance. The effects of the pretreatment with NaOH and HNO3 and the subsequent treatment of aluminum alloy with cerium and phosphate conversion layers on chemical composition and oxidation state of elements have also been studied. Anodized Al alloys, electrochemically modified with Cu, Ni and Cu/Ni have been also characterized. The aluminum oxide-Cu layers contained mainly Cu(0), as well as Cu^{+}, Cu^{2+} ions. In the case of aluminum oxide-Ni –films, the incorporated metal is in three oxidation states – Ni(0), Ni^{2+}, Ni^{3+}, including Ni_3S_2. As a result of XPS investigations of anodized Zn, the presence of $ZnC_2O_4.2H_2O$ at the surface that increases the corrosion resistance of Zn-based functional layers in optically active sensor elements has been demonstrated. Analogously, Zn anodizing in borate electrolytes leads to the formation of zinc borates at the electrode surface. XPS analyses indicate that during anodization of Zn in alkaline electrolytes, the surface layer consists mainly of crystalline ZnO. That determines their good corrosion resistance when used as anode materials for batteries. The role of thermal treatment of combined zinc/cerium primers, formed on low carbon steel for oxide protective coatings was also investigated.

3.2 Catalytic materials

Glassy carbon electrodes, modified with nano-sized coatings of ZrO_2 or $ZrO_2 + Ce_2O_3 + Y_2O_3$, applicable as cathodes for the release of active chlorine, were electrochemically synthesized and characterized by XPS. It is shown that the layers present lead to an increase of the rate of hydrogen evolution and suppress the chlorine reduction processes. It was suggested that the modification of the glassy carbon surface with nanosized oxides of Zr and Zr + Ce + Y may be a good alternative to Cr^{6+} based compounds. TiO_2/Bi_2O_3 layers obtained by plasma anodization were investigated with XPS, and it was shown that the bismuth oxide particles incorporated in TiO_2 determined the photo-catalytic activity of the coatings. The effect of chemical composition on photo-catalytic oxidation rates of methyl orange deposited by plasma electrolyte oxidation in the presence of transition metals (Mn, Ni, Co) was studied with titanium oxide films. It has been demonstrated that the photo-catalytic activity of the layers depends largely on the concentration of transition metals in the electrolyte, as well as on the type of metal employed.

3.3 Chemically synthesized compounds

The processes of preparation of nano crystalline boron nitride by ion sputtering and subsequent thermal treatment have been investigated by XPS. It is demonstrated that as a result of the conversion of boron-containing thin organic films and subsequent thermal treatment at 450–850ºC in a nitrogen atmosphere, a nano crystalline phase of boron nitride is obtained. It is shown that as the posttreatment temperature increases, so does the amount of boron nitride phase produced.

4 Main scientific contributions

The analysis of the scientific production of Alexander Tsanev makes it possible to make a summary of the basic and applied scientific contributions, as follows:

4.1 Enrichment of existing knowledge and theories

4.1.1 Studies of the pretreatment of aluminum alloys in alkaline and acidic environments have shown that different pretreatment procedures result in the formation of surface oxide layers with variable thickness and composition depending on the treatment. These differences were also found to be a prerequisite for a different rate of formation and homogeneity of the cerium oxide conversion layers, which exhibited an essential role in the corrosion resistance of anodized aluminum samples.

4.1.2 The results of the study of the influence of anodizing and surface treatment processes of the aluminum alloy with cerium chloride show an oxidation reaction of an aluminum oxide molecule from the water to two molecules of AlO(OH) in which the resulting oxide-hydroxide fills the pores of the resulting conversion layers. It was found that during the deposition of cerium chloride, $Ce(OH)_3$ was formed on the surface. It is shown that the products of the reactions that have taken place co-precipitate in the pores of the anodic films films and block them, thus sealing the oxide layer more effectively in comparison to hot water.

4.1.3 The effect of cerium ions on the corrosion protectivity of anodized aluminum alloys coated with conversion layers of cerium oxides/hydroxides has been established. In this case, it is shown that the cerium oxide conversion layer practically does not affect the corrosive impact of the aggressive environment. It is also shown that the changes that have occurred as a result of corrosion processes on aluminum are expressed in increasing the concentration of the formed corrosion products of AlOOH and $Al(OH)_3$. Due to the low solubility of these products, the corrosion resistance of the system increases.

4.1.4 It was found that conversion layers obtained by successive treatment of the aluminum alloys in NaOH and HNO_3 solutions and coated with CeO_x and $CuCl_2$ were of considerably greater thickness than those treated with sodium hydroxide alone. This is related to the occurrence of a larger number of active cathode sections (Al_3Fe intermetallides) after additional treatment with HNO_3. The thickness of the conversion coatings was also estimated. As a result of the analyses, the deposition mechanism of these layers was established. These studies allow the optimization of the processing processes of aluminum alloys in order to obtain maximum surface protecting cerium conversion coatings.

4.1.5 The role of silver ion incorporation on the surface properties of aluminum alloys, as well as the relationship of these properties to the corrosion resistance of these alloys, has been established. It was found that oxides in which silver ions were not incorporated, aluminum consisted entirely of Al_2O_3, while in those containing silver ions, the oxide was accompanied by $Al(OH)_3$ and AlOOH. It was also found that silver is incorporated into the pores of aluminum alloys is in the form of Ag^+, suggesting the presence of an oxidation process prior to its intrusion. As a result, the mechanism of its incorporation has been established – oxidation of Ag probably proceeds with the inward migration of O^{2-} ions from the electrolyte through the surface to the pore walls and bottoms of aluminum oxide.

4.2 Applied scientific contributions

4.2.1 It was shown that when depositing phosphate coatings from solutions of Na_3PO_4 or NH_4 H_2PO_4 onto conversion layers, the surface of those layers is completely covered with sparingly soluble and/or insoluble PO_3^- and P_2O_5/P_4O_{10}. Based on the XPS data, a substantial influence of phosphate posttreatments on the chemical composition and oxidation state of the elements on the surface of the systems studied was found.

4.2.2 As a result of phosphate treatment, the concentrations of Al_2O_3 and Ce_2O_3+ CeO_2 in cerium conversion coatings are substantially reduced at the expense of the formation of $AlPO_4$ AlOOH and $CePO_4$, as well as compounds of the type PO_3^- and P_2O_5/P_4O_{10}.This was demonstrated to lead to a decrease of diffusion rate of chloride ions in such layers and suppression of pit formation.

5 International significance of the scientific papers of the candidate

The scientific activities of Dr. Tsanev and the research teams in which he participates is well known to investigators in the field of simple and mixed oxides with catalytic properties, surface treatment of metals for corrosion protection and preparation of multifunctional oxide thin layers and nanocomposites. Up to present, 64 citations of the works of Dr. Tsanev are noted (according to the Scopus database), almost entirely from foreign authors, most part stemming from papers included in the competition documents. Some of the works have been cited several times, such as Materials Chemistry and Physics (2019) – 8 times, International Journal of Electrochemical Science (2018) – 7 times, Journal of Physics: Conference Series (2016) – 6 times, etc. The Hirsch index of Dr. Tsanev according to Scopus is 6, after excluding self-citations of all co-authors - 5.

CONCLUSION

● The domain in which the main basic and applied research results of Chief Assist. Tsanev is situated is leading and promising for science and technology. The synthesis and characterization of thin metal and oxide films with optimal properties for a number of important applications open wide opportunities (some of which are unique) for fundamental and applied research, and in the last few decades this scientific field has emerged as a rapidly developing area of inorganic materials science.
● The scientific development of Chief Assist. Tsanev is harmonious. He successively passes through scientific degrees and titles, which allowed him to emerge as an effective and self-sufficient scientist.
● Chief Assist. Tsanev and the research teams in which he participates have made a thorough analysis of a number of problems in the studied field and have systematically focused on solving those problems. In the process of their research, the teams generate new methodologies and ideas, the role of Dr. Tsanev being very important.
● The scientific contributions of Alexander Tsanev are significant and have received a good international evaluation. These results have been achieved via a large amount of multi-method studies conducted on complex systems and phenomena at a very high level. His scientific indicators are high, which is a criterion for the level of research conducted and the results obtained, and they fully meet the requirements of the Regulations on the Terms and Conditions for occupying academic positions at the Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences.

That is why I would strongly like to recommend to the honorable Scientific Jury to award the academic position of Associate Professor in the field 4.2 Chemical Sciences (Solid State Chemistry) to Chief Assist. Dr. Alexander Svetoslavov Tsanev.

Sofia, 17.09.2023 Reviewer:

(Prof. Martin Bojinov, DSc)