

REVIEW

by Dr. Daniela Bogdanova Karashanova, professor at the Institute of Optical Materials and Technologies "Acad. Yordan Malinovski" – BAS

on the materials submitted for participation in a competition for the academic position "Associate Professor", Professional direction 4.2. Chemical Sciences (Solid State Chemistry), announced at the Faculty of Chemistry and Pharmacy, SU "St. Kl. Ohridski".

I. General presentation

By order No. PD-38-132 of 24.03.2023 of the Sofia University "St. Kl. Ohridski" Rector Prof. Anastas Gerdzhikov, I have been appointed as a member of the scientific jury of a competition for the academic position of "Associate Professor" at the Faculty of Chemistry and Pharmacy, SU "St. Kl. Ohridski".

In the competition for "Associate Professor", announced in the State Gazette, no. 24 of 17.03.2023, as the only candidate applied **Chief Assistant Professor Dr. Lyuben Mihailov** from the department of "Applied Inorganic Chemistry" of the same faculty.

II. Brief biographical data of the applicant

Chief Assistant Professor Dr. Lyuben Mihailov completed his secondary education at the Technical College of Electrical Engineering in the town of Gotse Delchev, and his higher education at the Mining Technology Faculty of the University of Mining and Geology "St. Ivan Rilski", Sofia as a mining engineer in 2006. He also received a master's degree in chemistry from the Faculty of Chemistry and Pharmacy of SU "St. Kl. Ohridski" in 2009 after studying at the Interuniversity Center for Microelectronics (IMEC), Belgium. He prepared and defended his PhD thesis on the electrocatalytic activity of amorphous and nanocrystalline alloys for hydrogen evolution in the period 2010-2013 at the Faculty of Chemistry and Pharmacy, where he was then successively appointed as the chief specialist in chemical sciences (2015) and as Chief Assistant Professor (2021).

The main areas of scientific and research interest of Dr. Lyuben Mihailov are in the field of electrochemistry, characterization of the microstructure, morphology and chemical composition of materials with Transmission and Scanning Electron Microscopy and Energy-Dispersive Spectroscopy. He conducts courses for students at the Faculty of Chemistry and Pharmacy in "Applied Electrochemistry", "Processes and Apparatus" and "Inorganic Chemical Technologies".

III. Research activity

The results of the research activity of Dr. Lyuben Mihailov, with whom he participated in the announced competition for the academic position of "Associate Professor", were developed within 10 scientific projects, of which 2 were financed under the 7th framework program and RP "Horizon 2020" of European Commission, 2 are for the foundation of centers of excellence and competence, 2 are for the foundation of a center for new materials and the national road map and 3 are with national funding. They are summarized and described in 17 scientific publications, 16 of which are in journals with ISI "impact factor" and 1 is only with "impact-rank". Among them are the renowned ones in the field of catalysis, environmental protection and materials science: Applied Catalysis B: Environmental (IF 2020: 19.11), Applied Materials&Interfaces (IF 2016: 7.80), Acta Materialia (IF 2016: 5.74), The Journal of Physical Chemistry (IF 2017: 4.69) etc., and the total "impact factor" of the journals is 79.819, and 13 of them possess Q1 quartile.

The publications, received citations, participation in conferences, projects and other activities of Dr. Lyuben Mihailov provides the necessary score, corresponding to the minimum national requirements, reflected in the Regulations for the implementation of ZRASRB, as well

as in the Regulations of Sofia University and the Faculty of Chemistry and Pharmacy, and in some of the indicators they exceed them many times - e.g. with regard to the indicators in group D (citations), the minimum threshold is 70 points, and 790 points are presented, and in group G, with a minimum of 70 points, 258 points are presented.

Part of the research activity of Dr. Mihailov, published in 6 of the scientific articles in journals, referenced and indexed in the world databases with scientific information, according to Art. 24, para. 1, item 3 of the ZRASRB is the basis of the **Habilitation thesis**, the topic of which is dedicated to porous materials with application in electrocatalysis and ion batteries. Undoubtedly, this topic is extremely relevant in the research space, due to its connection with priority areas for the European Union, and globally, such as ecology and environmental protection, new energy sources, circular economy. It also has an important practical focus and is related to improving the quality of life.

The candidate's contributions on this topic are related, on the one hand, to the synthesis of the materials, and also to their overall morphological and microstructural characterization and determination of their chemical composition and some physicochemical properties. As he himself notes in the Author's Reference, "he actively participated in the preparation of the alloys, in the electrochemical analyses, the sample preparation, the analyzes with TEM, STEM - EDX, SEM and in the interpretation of the results, discussion and preparation of the publications".

In thematic terms, the publications presented in the competition could generally be divided into the following 3 areas, where the relevant contributions of a fundamental and applied character of the candidate are formed, as he himself presents them in the reference for his contributions:

A. Synthesis, morphological and microstructural characterization of porous materials with application in electrocatalysis and ionic batteries.

The publications included in this topic are also the basis of the candidate's Habilitation Thesis.

Experimental work in this topic begins with the synthesis of alloys with different composition and microstructure, which are subjected to various procedures in order to transform them into porous materials. For example, in publication [1], amorphous alloys based on Zr (Zr-Cu-Ni-Al) were obtained, which were subjected to temperature treatment. Part of the samples were heated at a temperature above the glass transition point T_g , and another part at a temperature above that of crystallization T_x in order to change their microstructure, and hence the subsequent dissolution process. The relationship between the processing temperature, the degree of dissolution and the quality of the resulting porous structure was established. It was also observed that the electrochemical potential did not significantly affect the porosity. The samples were examined using TEM and diffraction methods (SAED, HRTEM) and energy dispersive analysis (EDX-STEM) showed that the less noble metals such as Al and Zr form insoluble compounds (ZrF_4 , Na_3AlF_6 and Na_3ZrF_6), which precipitate in the electrolyte and on the surface of the electrode.

Zr-based alloys ($Zr_{65}Ni_{30}Pd_5$ and $Zr_{55}Ni_{30}Al_{10}Pd_5$) in 0.01M HF to obtain nanoporous metallic materials is the applied approach in article [3]. Ligaments formed during dissolution were found to be mainly composed of Pd and ZrNi nanocrystals with sizes of 3 - 5 nm. The role of Al, which is component a in one alloy, was also revealed. Due to its faster dissolution, it leads to the formation of larger free volumes in the dissolving electrode, necessary for an easier reorganization of the remaining more noble metal atoms (Ni, Pd), forming the nanocrystalline bonds. In this way, it has been proven that the presence of a metal or metals, which dissolve much more easily than the rest of the alloy constituents, has a significant impact on the dynamics of atomic transport and crystallization processes and directly affects the final microstructure of the porous material.

An amorphous alloy based on Au ($\text{Au}_{40}\text{Cu}_{28}\text{Ag}_7\text{Pd}_5\text{Si}_{20}$) has served to create a nanoporous gold material with the potential for application in catalysis (publication [2]). Immersion of the alloy in an electrolyte led to its penetration through defects in the natural surface oxide layer, which served to melt it and form an intermediate layer about 50 nm thick, formed by ligaments about 10 nm wide, voids and remnants of the amorphous phase, in which Au nanocrystals are included. It has been established that temperature is also a key factor in the growth of ligaments. They, in turn, are formed by the collision of Au nanocrystals originating at the boundary with the amorphous phase, which also ensures the presence of pores and cavities between the ligaments.

Nanoporous metal structures were obtained [4] by chemically and electrochemically selective dissolution of the less noble elements from the initial amorphous precursors – Pd-Ni-Si alloys in different ratios. The average pore size and its dependence on alloy composition and selective dissolution method were determined. The smallest pore size of about 45 nm was obtained with $\text{Pd}_{30}\text{Ni}_{50}\text{Si}_{20}$ composition, which provides the more developed surface of this alloy and, accordingly, higher catalytic activity towards the oxidation of ethanol.

The experience of the candidate in the synthesis procedures of alloys of different composition and properties, and especially in the characterization of their morphology and microstructure by means of transmission and scanning electron microscopy, were also applied in the research on the creation of innovative electrode materials in Li- and Na-ion batteries (articles [5] and [6]). For this purpose, a microcrystalline $\text{Cu}_{60}\text{Ag}_{30}\text{Al}_{10}$ alloy, obtained by rapid quenching from a melt, is subjected to additional melting by electrochemical selective dissolution to achieve three-dimensional nanoporous metal structure. An almost complete extraction of Cu from $\text{Cu}_{60}\text{Ag}_{30}\text{Al}_{10}$ was achieved after 120 min of potentiostatic treatment at 350 mV (vs. SHE) in 0.1 M aqueous HClO_4 . The molten sample shows well-defined and homogeneous porosity over the entire surface with ligament size between 100 nm and 200 nm and pore and channel sizes from 100 nm to 2000 nm. The thus created porous structure was used as a carrier and impregnated with active compounds for Li^+ intercalation, especially LiMnPO_4 [5] and with a solution of S in toluene (C_7H_6) [6]. In the first case, subsequent thermal treatment at 500°C gives a LiMnPO_4 phase with an olivine-type structure that inherits the morphology and microstructure of the metal matrix. Good adhesion between the phosphoolivine and the metal alloy was achieved at a deposition density of up to 0.009 g/cm^2 . The achieved electrochemical capacity is about 120 mAhg^{-1} and remains stable during cycling. The as-deposited LiMnPO_4 film shows a slightly lower specific capacitance and better cycling stability compared to its powder counterpart used in conventional electrodes together with carbon and bonding additives. After prolonged charging and discharging, the integrity of the electrode remains unchanged, which is its great advantage. Furthermore, the olivine particles incorporated into the metal pores remain resistant to stresses and strains induced during repeated intercalation and deintercalation of Li^+ . In the second case, after impregnation and heat treatment at 200°C , the electrochemically active coating $\text{Ag}_2\text{S-Cu}_x\text{S}$ is obtained, in which, during the operation of the electrode, silver and copper can be replaced by Li^+ , forming a series of intermediate compounds Li_2S_n , preventing sputtering of the electrode. This provides a reversible specific capacity of $\sim 230 \text{ mAhg}^{-1}$ at a current density of $0.4 \mu\text{A cm}^{-2}$ and stable operation for 1000 cycles at current densities of 1 and 2 Ag^{-1} . Thus, the proposed 3D porous collector allows avoiding the use of excess Li, provides high current density, reducing its local density and the formation of Li dendrites.

B. Investigating the morphology and structure of oxides and phosphates as innovative electrode materials for lithium/sodium-ion batteries

A series of Ni-Mn oxides containing a variable amount of Na ($\text{Na}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$) as well as those containing cobalt ($\text{Na}_x\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$, $0.38 \leq x \leq 0.75$) have been synthesized, studied in detail, with the aim of their application as new, cheap electrode materials in modern Li/Na-ion batteries. The results are described in publications [7,9,10 and 11]. Due to their layered

structure, these oxides can intercalate Li and Na ions, and their intercalation ability depends on their crystal structure and the arrangement of the layers in a certain type of lattice. Therefore, TEM analyzes of the morphology, microstructure and phase composition of the samples, both freshly obtained and after intercalation cycles, are an important part of their characterization.

The TEM images in [7] show that after the electrochemical reaction Ni-Mn oxide consists of thin flat particles with sizes varying in a wide range from 20 to 160 nm. Compared to the primary oxide, the particle size and size distribution remain unchanged. The distributions of nickel and manganese in the particles determined using EDS analysis and STEM images are uniform. The results of the diffraction analysis show that the P3-type structure is preserved during reversible Na⁺ intercalation. For particles with sizes larger than 100 nm, a trigonal superstructure is observed, as is the case with the starting composition. This finding supports the stability of the superstructure arrangement after the electrochemical reaction. TEM experiments provide no evidence for the formation of P2 or O3 type structures during the electrochemical reaction of Na⁺ with P3-Na_xNi_{0.5}Mn_{0.5}O₂.

A detailed structural study of sodium-deficient cobalt-nickel-manganese oxides (Na_xCo_{1/3}Ni_{1/3}Mn_{1/3}O₂) was also carried out [9], obtained by thermal decomposition of mixed acetate-oxalate precursors, followed by thermal annealing between 700 and 800°C. The stability of the layered structure during cycling was proven by ex-situ TEM analyses. The primary fully lithiated Na_{0.67}Co_{1/3}Ni_{1/3}Mn_{1/3}O₂ oxide consists of well-formed fine particles with sizes between 20 and 100 nm that remain unchanged after the electrochemical reaction performed with both Na-rich and with poor Na oxides. The polycrystalline electron diffraction pattern of primary and cycled oxides shows a mixture between layered and NiO-like phases. The difference between the primary and the oxides after cycling originates from the lattice parameters of the layered phase: the lattice parameters for the primary P3-Na_{0.67}Co_{1/3}Ni_{1/3}Mn_{1/3}O₂ oxide are $a = 2.837 \text{ \AA}$ and $c = 16.735 \text{ \AA}$, and after the electrochemical charge/discharge, they become $a = 2.84 \text{ \AA}$ and $c = 14.44 \text{ \AA}$. The observed decrease in the c -parameter reveals a strong contraction of the layer (i.e., from 5.7 to 4.8 Å), while the small variation of the a -parameter is associated with a slight change in the distance between the metal ions inside the layers. In contrast to the layered, the NiO-like phase has unchanged lattice parameters, proving that only the layered is involved in the electrochemical reaction, while the NiO-like phase is electrochemically inert.

The design and construction of a new type of hybrid sodium-lithium-ion cell, by using a unique combination of electrodes (Li₄Ti₅O₁₂ spinel as the negative electrode and deposited Na_{3/4}Co_{1/3}Ni_{1/3}Mn_{1/3}O₂ oxide as the positive electrode) in a conventional lithium electrolyte (LiPF₆ salt dissolved in EC/DMC) is the subject of the research presented in [10]. The coexistence of two intercalation phases of lithium and sodium is also proven by ex-situ TEM analysis. The cycled oxide consists of well-formed particles with sizes of about 500 - 700 nm. The lattice parameter estimated by SAED along the [011] direction is $a=8.43 \text{ \AA}$, which coincides with that determined by ex-situ XRD analysis of Na intercalated in Li_{4/3}Ti_{5/3}O₄ oxide ($a=8.4359 \text{ \AA}$). HRTEM images of selected particles show the presence of closely interconnected nanodomains with different lattice parameters. Based on the calculations along the [011] direction, local regions with at least four different lattice parameters were distinguished and the phases were identified: the primary Li_{4/3}Ti_{5/3}O₄ and the pure sodium phase Na_{6/3}Li_{1/3}Ti_{5/3}O₄. This result is clear evidence for the formation of both lithium- and sodium-intercalation phases during extended cycling. Both types of phases are assumed to be involved in charge-discharge reactions.

TEM analyzes provide further evidence for Na⁺ and Li⁺ intercalation in the positive electrode oxide. STEM-EDS images and spectra were taken and the corresponding polycrystalline electron diffraction of the oxide cycled 10 times between 1.0 and 3.5 V. The diffraction pattern was shown to consist of a mixture of two layered phases. The first phase can be assigned to the R $\bar{3}m$ space group with lattice parameters $a = 0.284 \text{ nm}$ and $c = 1.44 \text{ nm}$ and an interplanar spacing of 0.48 nm. For comparison, the lithium analogue LiCo_{1/3}Ni_{1/3}Mn_{1/3}O₂ is characterized by the same O3-type structure, but with slightly different lattice parameters: a

= 2.8541 Å and $c = 14.2130$ Å. This proves once again the transformation of the primary P3- to O3-phase during lithium intercalation. The second phase also has a layered structure, but shows a larger space between the layers. The most significant result is obtained from the HRTEM analyses. The images show variable interplanar distances where at least three different ones can be distinguished - 0.48, 0.52 and 0.88 nm. Although the first two values are related to the interplanar distances of the Li- and Na-containing phases, the latter is significantly higher (by more than 50%) and cannot be explained on the basis of the electrostatic repulsion between the charged metal layers. Large expansion of the interstitial space has been reported only when H₂O molecules are inserted into the interstitial space of sodium-deficient transition metal oxides, leading to the formation of hydrate phases with the general composition Na_xMO₂.nH₂O.

Manganese oxide Mn₅O₈ also with a layered structure was applied for the first time for the intercalation of Li⁺ and Mg²⁺ in non-aqueous electrolytes [12]. TEM images show elongated particles with an average length of about 40 nm and a cross section of up to 10 nm. Diffraction analyzes revealed that these particles correspond to the layered structure of the Mn₅O₈ phase and that they remain constant in shape and size after cycling (charging and discharging) in both lithium and magnesium electrolytes. Interpretation of the HRTEM images revealed that the layered structure of Mn₅O₈ was completely transformed into a spinel-type structure after cycling.

New data on the reversible intercalation of lithium and sodium ions in sodium-manganese phosphoolivine NaMnPO₄ when used as a cathode in modern lithium-ion batteries have been provided [8]. The TEM results confirm the stability of the olivine-type structure after ball-milling. The important discovery is that the olivine particles are coated with carbon additives (binding substances). The coating thickness varies between 2 and 10 nm. In addition, some individual carbon particles with dimensions of about 20 nm are also observed. The TEM study proves that ball milling and subsequent annealing at 400°C is an effective way to ensure good interfacial contact between the olivine particles and the carbon additives. The distribution of Na, Mn, P, O and C elements determined using STEM-ED X images and spectra clearly prove that the nanoparticles are of NaMnPO₄ composition, which is homogeneously covered with carbon. TEM analysis allows to get an idea about the structural stability of phospho-olivines cell operating time. After the intercalation/deintercalation cycle, the morphology of NMP/C is preserved.

Monometallic and bimetallic Rh - Ni catalysts supported on γ -alumina (Al) and modified with yttria aluminum oxide (Y-Al) are the subject of research in [13]. The structure of nanoparticles on the surface of a reduced RhNi/Al catalyst was investigated by TEM. High-resolution images show that the particles are crystalline and for reduced RhNi/Al catalyst correspond to Ni (111) and Rh (111). The average particle size of selected reduced and spent Ni/Al, Ni/Y-Al and RhNi/Al catalysts was also determined from the TEM images. A more homogeneous distribution of metal nanoparticles on the surface of reduced Ni/Y-Al and RhNi/Al catalysts was found with respect to that observed for Ni catalyst on pure alumina. Agglomeration of the particles was observed in all catalysts after operation, which was more pronounced in the spent Ni/Al. The Ni/Al catalyst shows the largest average size of 5.95 nm and a more heterogeneous distribution of particles up to 18 nm in size. However, the spent Ni catalyst supported on Y-modified alumina showed smaller particles and a more homogeneous size distribution as those below 5 nm dominated, followed by the bimetallic RhNi catalyst. The spent RhNi/Al catalyst was characterized by an increase in the size of the metal particles from 3.62 nm to 4.99 nm, as well as by the detection of traces of carbon fibers, which are produced in the catalysis of hydrocarbons.

C. Characterization of the morphology and structure of gold nanoparticles obtained by different methods

This topic unites the study of the morphology and microstructure of metal nanoparticles synthesized by different methods. Three of the publications ([14, 15,16]) deal with the synthesis

and characterization of gold nanoparticles, and the last one ([17]) concerns the preparation of Pt(II) nanocapsules and their application to two types of cancer cells.

By means of TEM, the shape and sizes of the synthesized Au nanoparticles were determined, and the dependences of their average sizes and the distribution intervals of their diameters on the relevant experimental conditions, the type of reducing agents, etc. were established. Using the high resolution mode, the interplanar distances in the crystal lattice of the nanoparticles were visualized and their phase composition was confirmed. It was found that in most cases they are spherical in shape. In the study in [14], it was shown that nanoparticles are made up of multiple twin domains.

Using EDS-STEM, the distribution of platinum in different types of cancer cells was tracked and the areas of its accumulation were visualized. A relationship was established between the manifested cytotoxicity of the studied platinum agents and their structural characteristics important for their cellular uptake.

IV. Critical notes and recommendations

In general, **I have no critical comments** on the presented materials. I would only note that in the list of citations there are some citations from co-authors of the candidate in their publications, outside the scope of the competition. This should remove them from the list of independent citations (eg. “Kalapsazova, M. L., Zhecheva, E. N., Tyuliev, G. T., Nihtianova, D. D., Mihaylov, L., & Stoyanova, R. K. (2017). Effects of the particle size distribution and of the electrolyte salt on the intercalation properties of P3-Na₂/3Ni₁/2Mn₁/2O₂. Journal of Physical Chemistry C, 121(11), 5931-5940. doi:10.1021/acs.jpcc.6b12887” is cited in „Kalapsazova, M., Kostov, K., Zhecheva, E., & Stoyanova, R. (2020). Hybrid Li/Na ion batteries: Temperature-induced reactivity of three-layered oxide (P3-Na₂/3Ni₁/3Mg₁/6Mn₁/2O₂) toward lithium ionic liquid electrolytes. Frontiers in Chemistry, 8 doi:10.3389/fchem.2020.600140“ etc.)). Due to the huge number of citations presented by the applicant, this finding does not in any way change the fact that the applicant also meets the minimum requirements of the ZRASRB and the current regulations for its application in terms of group D indicators.

In topic **C. Characterization of the morphology and structure of gold nanoparticles obtained by different methods**, one publication ([17]) is presented, which refers to Pt nanoparticles, and this should be reflected in the formulation of the topic.

V. CONCLUSION

Those presented by the candidate in the competition, Chief Assistant Professor Dr. Lyuben Mihailov documents and materials fully meet the requirements of the Law on the Development of the Academic Staff in the Republic of Bulgaria, the Regulations for its implementation and the relevant Regulations of the Faculty of Chemistry and Pharmacy of SU "St. Kl. Ohridski" and the topic of the announced competition for the academic position of "associate professor". The results included in the competition are original, with a large volume and significance and in topical thematic areas.

That is why I am fully convinced that I give a positive assessment to the works and activities presented in the competition and I recommend to the honorable members of the Scientific Jury to vote positively for the Faculty Council of the Faculty of Chemistry and Pharmacy to choose Chief Assistant Professor Lyuben Mihailov for the academic position of "Associate Professor" at the Faculty of Chemistry and Pharmacy, SU "St. Kl. Ohridski" in the field of higher education 4.2. Chemical sciences, Scientific field Solid State Chemistry.

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Prepared the review:

Prof. Dr. Daniela Karashanova