

**Application form for research topics
in the field of engineering and technology
for candidates to the Doctoral School
in the academic year 2024/2025**

Proposed subject matter of a doctorate
Surface modification of electrodes for green hydrogen generation by electrolytic water splitting
Scientific discipline (<i>delete as appropriate</i>)
AUTOMATION, ELECTRONICS, ELECTROTECHNICS AND SPACE TECHNOLOGIES CIVIL ENGINEERING, GEODESY AND TRANSPORT MECHANICAL ENGINEERING
Proposed doctoral thesis supervisor
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Brief description of the research topics with an indication of the scientific issues (max. 350 words)
<p>Civilisation's need to replace carbon-bearing fossil fuels with environmentally friendly ones increased interest in hydrogen production by the electrochemical decomposition of water. Consequently, there is a need to develop new electrode materials for this process replacing those made of noble, critical raw metals.</p> <p>The main goal of the project is the surface modification of solid, metallic electrodes for hydrogen production by the nanostructured thin films based on ternary metal-carbon systems. The magnetron sputtering in the HiPIMS (High Power Pulse Magnetron Sputtering) mode will be used to deposit high-quality coatings.</p> <p>The project aims to acquire new knowledge on the synthesis of ordered ternary carbide coatings by physical vapour deposition (PVD) methods and their characterization (structure, transport properties, corrosion resistance in acidic and alkaline environment) in terms of the use as electrocatalytic materials for hydrogen production.</p> <p>In the laboratories of the Faculty, we dispose of the modern technology and research equipment, which fully enables carrying out such works in a laboratory scale.</p> <p>State of the art</p> <p>In recent years, research on electrode materials for hydrogen production by water electrolysis through hydrogen evolution reaction (HER) has focused on searching for material solutions based on readily available elements, excluding expensive noble metals, which will ensure high reaction efficiency with the simultaneous long-term durability of electrodes operating at high current densities. These electrodes are developed for use in acid or alkaline environments while focusing on universal solutions that provide good results regardless of the pH of the electrolyte.</p>

Several catalytic activity descriptors were developed during the work on selecting electrode materials for HER, which to some extent support the material selection process. The most important of them is the free energy of hydrogen adsorption (ΔG_H), which was used to create the so-called volcano plot [1,2], as well as electronic descriptors represented by a d-band centre and structural descriptors [3,4]. In addition to pure metals with a sufficiently low free energy of hydrogen adsorption (ΔG_H) value, such as Mo, W, Co, Ni and their alloys [5-8], a wide range of their compounds were tested, such as chalcogenides, phosphides, oxides, as well as nitrides and carbides [9-11]. Much work has been done on carbon-based composite materials [12].

The intensively studied group consisted of composites based on amorphous carbon with nanometric metallic (Ni, Co) or carbide precipitates (MoC, WC, NbC) [13-15], deposited in the form of thin films. In the case of the latter, the presence of the carbon matrix, on the one hand, protected the catalytically active metallic or carbide precipitates against corrosion.

The research team has long-standing experience in research on thin films of Me/MeC-DLC/aC:H nanocomposite materials containing metals (Ti, Mo, W, Co) or their carbides embedded in an amorphous, hydrogenated or hydrogen-free carbon matrix, deposited by PVD (Physical Vapour Deposition) methods. Our research on manufacturing processes, structure, mechanical, and tribological properties included binary TiC-aC:H [16], WC-aC:H [17], as well as multi-component systems such as FeCrNi-C [18], NiCr-C [20] and CoCrMo-C [19,21].

References

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- [18] T. Suszko et al., *Scr. Mater.* 136 (2017) 24-28.
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- [20] T. Suszko et al., *Appl. Surf. Sci.* 591 (2022) 153134
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Justification of the purposefulness of taking up the research topics (max. 150 words)

There is a significant need to develop new electrode materials for hydrogen production from the water-splitting processes, to replace noble metallic elements, which are too expensive for large-scale production. The idea behind the project is to use common industrial metals such as Ni, Co, W or Mo and their carbon-based nanocomposites. The knowledge gained will allow us to fulfil the condition of minimising the use of critical raw materials.

Proposed topics of doctoral theses within the proposed research subject matter (up to 3 topics)
<ol style="list-style-type: none"> 1. Structure, transport properties and corrosion-resistance of ternary metal carbide coatings in alkaline and acidic media. 2. Surface modification of electrodes for hydrogen generation by electrolytic water splitting.
The sources of financing of the research topics (the subject matter of currently implemented research grants financed from external sources or as part of subsidies)
<p>PK internal project</p> <p>2. Research conducted in the framework of currently submitted projects:</p> <ol style="list-style-type: none"> a) M-ERA Net 2024 “Nano-structural coatings for hydrogen generation electrodes” b) NCN project OPUS 49 (2023) “Self-organised coatings on 3D substrates for Hydrogen Evolution Reaction – synthesis, nanostructure and properties”
Confirmation of the possibility of ensuring access to scientific apparatus and software necessary for the realization of the proposed research topics (<i>delete as appropriate</i>)
FULLY/ PARTIALLY
If the answer is PARTIALLY or NONE please indicate a type of missing scientific apparatus and/or software and the sources of financing an access to them
<p>Access to XPS, Conductive AFM and HRTEM is provided by our partners on a collaboration basis:</p> <ol style="list-style-type: none"> 1. Linköping University, Thin Films Group at the Department of Physics, Chemistry and Biology, Sweden 2. Institute of Metallurgy and Materials Sciences, Polish Academy of Sciences, Cracov, PL 3. Nanobiomedical Centre, Adam Mickiewicz University, Poznań, PL
List of the supervisor's scientific achievements in the field of indicated scientific problems
A list of up to 5 major supervisor’s publications related to the proposed research topics, published in journals indexed in the Web of Science or Scopus for the period of the last 3 years (taking into account the IF Impact Factor and the MNiSW score)
<p>T. Suszko, W. Gulbiński at al. Amorphous FeCrNi/a-C:H coatings with self-organised nanotubular structure, Scripta Materialia 136 (2017) 24-28/IF 4,559/200p</p> <p>T. Suszko, W. Gulbiński, E. Dobruchowska at al., Quasi-amorphous, nanostructural CoCrMoC/a-C:H coatings deposited by reactive magnetron sputtering, Surface and Coatings Technology 378 (2019) 124919/IF: 3,192/100p</p> <p>T. Suszko, W. Gulbiński, K. Załęski, G. Greczynski, J. Morgiel, V. Lapitskaya, Nanocolumnar, self-organised NiCrC/a-C:H thin films deposited by magnetron sputtering, Applied Surface Science 591 (2022) 153134</p>
A list of research grants financed by the National Science Centre, the National Centre of Research and Development and the European Research Council for the period of the last 5 years
New, advanced composite wear-resistant coatings on stainless steel, Project No NCN: OPUS - UMO2011/03/B/ST8/06130 (2012-2015) – project coordinator
A list of research services provided for industry related to the proposed research topics for the period of the last 5 years
1. Research service entitled "Development and production of anti-wear coatings on mandrel tools", as part of the R&D Project of FANAR S.A. Ciechanów no. POIR.01.01.01-00-0531 "Development of

tools and micro shank tools with particular emphasis on nano-structured PVD coatings". Project implemented as part of Measure 1.1 of the Intelligent Development Operational Program 2014-2020, financing institution: NCBiR, implementation period: January 15, 2016 - July 31, 2018, value of the research service: PLN 1,420,000.00 net (PLN 1,746,600.00 gross) role in the project: contractor.

2. Research service entitled "Designing deposition processes and testing the properties of tool coatings for difficult-to-machine materials", as part of the R&D Project of FANAR S.A. Ciechanów no. POIR.01.01.01-00-0274 / 17 pt. "Development of a series of taps and drills coated with nano-structured coatings for working with difficult-to-machine materials". Project implemented under Measure 1.1 of the Intelligent Development Operational Program 2014-2020, financing institution: NCBiR, implementation period: 01/01/2018 - 30/06/2020, the value of the research service: PLN 830,000.00 net (PLN 1,020,900 gross), role in the project: contractor