Wrocław University
of Science and Technology

Department of Process Engineering and Technology of Polymer and Carbon Materials

Wroclaw, 09.11.2023

Evaluation of the PhD thesis of MSc Eng. Krzysztof Sielicki, entitled: "Study on application of carbon materials and its hybrids in electrochemistry"

The thesis of Mr Krzysztof Sielicki was submitted on September 5, 2023 to the Scientific Council of the Discipline of Materials Engineering at the West Pomeranian University of Technology in the procedure for promotion to Doctor of Philosophy degree in the field of Engineering and Technology. The thesis was prepared under the supervision of prof. dr hab. Ewa Mijowska together with prof. ZUT, dr hab. Xuecheng Chen who served as assistant supervisor.

Substance of the work

The dissertation addresses a very important and current problem of hydrogen production in the process of water electrolysis. The work was focused on the preparation and physicochemical characterization of several variants of Metal-Organic Framework derived (MOF-derived) electrode materials, acting as HER (Hydrogen Evolution Reaction) and OER (Oxygen Evolution Reaction) catalyst. The author puts forward an ambitious hypothesis that carbon materials functionalized with non-metals (nitrogen, phosphorus) or non-noble metals (aluminum, nickel, cobalt) may have catalytic properties towards electrochemical water splitting, which are comparable to commonly used rare metals (e.g. platinum and rhodium). The origin MOF materials were synthesized by the author using a well-known and easy-to-implement solvothermal method (at atmospheric pressure) followed by a number of labor-intensive, independently developed physicochemical modification. Structural changes of the material were reported by number of analytical techniques (X-ray diffraction - XRD, transmission electron microscopy - TEM, X-ray photoelectron spectroscopy - XPS). The catalytic properties were verified by dedicated electrochemical techniques.

Some of the reported electrochemical results have high application value and may contribute to the manufacturing of low-cost devices for water splitting in the near future.

HR EXCELLENCE IN RESEARCH

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Moreover, the mechanism of OER catalysis of Al/Co/P-doped CMOF (Carbonized MOF)) proposed in the final chapter seems to be a good guideline for further scientific research on the described issue.

Formal aspects of the PhD dissertation

The work has been written in the form of a traditional dissertation divided into a literature part, a discussion of the results with a short summary. The manuscript contains 102 pages, which is divided into 6 main chapters. The thesis includes also 2-page abstract in English and Polish, table of contents, list of abbreviations, list of used 102 references and, finally, list of 16 original publications in which Mr. Sielicki is a co-author. The layout of the dissertation is clear, coherent and with logical order of the presentation. The thesis starts with the introduction in Chapter 1, giving general understanding scientific issue and scope of the work. It also briefly introduces content of the next chapters. Chapter 2 describes actual technology of hydrogen production and utilization with stress on water electrolysis and energy recovery in a fuel cell. Chapter 3 gives very concise overview about different techniques MOF preparation and the applications of these materials as a catalyst in HER and OER. Chapters 4 and 5 consist original research part of the thesis describing experimental methods and results. The work is closed with an extended summary (4 pages) containing conclusions and directions for further research.

Unfortunately, the author made some editorial mistakes. The table of contents is missing paragraph 2.1.1 from page 72 and paragraph 1.1.1 from page 42. Moreover, the numbering of paragraph 2.2.1 in chapter 2 is duplicated - both in the manuscript and in the table of contents. This was probably due to the rush in editing the work. Fortunately, the above defects do not affect the readability and coherence of the dissertation.

Comments and questions to PhD student

I found several shortcomings and potential errors in the work that should be discussed during the public defense.

<u>Review of the literature:</u>

1. Only figures 9 and 13 have referred origin indicated in the caption or in the text of the manuscript. Does it mean that the remaining graphics were created by the author of the dissertation?
2. Page 9: HER and OER (alkaline electrolytes) reactions are unbalanced.
3. Fig. 11 (right-top corner): The presented molecule is a carboxylic acid and not an aldehyde.

<u>Experimental methods:</u>

4. Page 46: What does it mean that “The measurements were compensated at 85%”?
5. Page 48: The author declared the intentional use of a wide voltage range from -10V to 10V. Meanwhile, in all reported electrochemical measurement the measured potential does not exceed the range from -2.5 to 2.5V. What was the reason for this procedure? It should be

noted that wider voltage range involved an automatic reduction in the resolution of the recorded potentials from 100 to ~305 μV.

6. Page 49: The use of galvanostatic electrochemical impedance spectroscopy (GEIS) at applied constant current of ±10 mA and amplitude perturbation (Va = 10 mV) was stated. Meanwhile, this technique uses current perturbation. Is it a unit error or maybe the PEIS technique was used with a potential perturbation imposed on the constant voltage?
7. Page 50 (end of page): Chronopotentiometry is galvanostatic technique – not "potentiostatic".

Results and Discussion:

8. Fig. 25: XRD spectra appears to be inconsistent with Raman spectra. The results of the Raman analysis indicate a systematic ordering of the carbon phases up to temperature of 950°C, as the author confirmed on page 56. Meanwhile, the diffractogram for the material obtained at 950°C is almost flat without a visible d_{002} peak (interlayer spacing), which suggests the absence of the carbon phase or its amorphic nature. Please comment on this fact.
9. Fig. 34: It is a mistake to assume that the percentage residue in a TGA analysis is the content of elemental aluminum and cobalt in the tested material. Under the analysis conditions (air), the residue is in the form of oxides. The real metal content in MOF should be much lower.
10. Thanks to XPS analysis, the author proved the complex physicochemical structure of the synthesized materials (different oxidation states, alloy formation, etc.). However, there is a lack of basic information about the general elemental composition in the dissertation. Can the author quote the content of individual elements (at%), especially Al, Co, Ni, N and P, in selected materials analyzed using the XPS technique?
11. Fig. 40: Comparing catalytic properties on substrates of such highly different morphology is risky. How was the surface area of the carbon foam calculated? Was it just a 1 cm x 1 cm square, like in the case of graphite foil? Due to the highly porous nature of the foam, its real contact surface with the electrolyte is much larger and cause the shape of LSV curve.
12. Fig. 41 and 44: The impact of different nickel and platinum salts on HER performance has been discussed too briefly. Does the author have any hypothesis that could explain how changing the anion in the salt added at the early stage of MOF synthesis may affect the electrochemical properties of the final electrode material?

General comment:

13. In my opinion, the title of the thesis is a bit imprecise. The author considers in his research only the process of electrochemical water splitting, which is only a small part of "electrochemistry".

Final remarks

Despite the numerous comments mentioned above, the scientific and technological value of the work should be assessed quite high. In chapter 5, paragraph 2.2, the author showed that the P-CMOF(Al) material is characterized by catalytic activity in OER comparable to reference RuO_2

and with even better durability in prolonged water splitting. However, all prepared catalysts had HER activity much lower than the reference, commercially available platinum on a carbon substrate. For this reason, the hypothesis announced in the dissertation can be considered partially confirmed.

There are two significant achievements of the work:

1) Development the electrode material not-containing noble metals of catalytic activity in OER comparable to RuO_2.
2) Explanation of mechanism of OER catalysis by carbons derived from Co- and P-doped Al-MOF.

In the years 2019 to 2023, Mr. Sielicki was a co-author of 16 publications in reputable journals, such as “Applied Catalyst B: Environmental” (IF=24.2) or “ACS Applied Materials & Interfaces” (IF=10.4). However, it should be noted that only 2 papers are *stricte* related to the doctoral thesis. One work was published in "Materials & Design" (IF=9.4) and the second one in “Journal of Alloys and Compounds” (IF=6.2).

In my opinion the PhD work of Mr. Sielicki contributes significantly to the development of scientific discipline of Materials Engineering and demonstrates the necessary knowledge and skills to obtain degree of doctor.

In conclusion, I therefore state that doctoral dissertation of Mr. Krzysztof Sielicki meets all statutory criteria for doctoral theses (art. 187 ustawy z dnia 20 lipca 2018 r. Prawo o szkolnictwie wyższym i nauce (Dz. U. 2018 poz. 1668 z późn. zm.)).

Therefore, I submit to the High Council of the Discipline of Materials Engineering at the West Pomeranian University of Technology a request for acceptance the thesis and I support the application to confer on Mr. Krzysztof Sielicki the PhD degree in the field of Engineering and Technology, in the discipline of Materials Engineering.

Finally, taking into account the high scientific value of the presented results, confirmed by publications, I suggest honoring the dissertation.

(prof. PWr, dr hab. Krzysztof Kierzek)