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Review

of the doctoral thesis entitled **Modified carbon fibre cloth as a material for high performance self –supported electrocatalytic water splitting electrodes** prepared by **Karolina Kordek-Khalil, MSc** to receive a doctor's degree from Wrocław University of Science and Technology, Faculty of Chemistry.

The basis for the preparation of the review was the invitation letter signed by prof. Marek Bryjak, the President of the Commission for Academic Degrees in the Discipline of Chemical Engineering of Wrocław University of Science and Technology.

The doctoral thesis of Ms Karolina Kordek –Khalil has been prepared under the scientific supervision of Piotr Rutkowski, PhD DSc and co-supervision of Ewa Lorenc-Grabowska, PhD DSc.

The thematic scope of the dissertation is focused on the development of methods for the preparation of fibrous carbon-based materials as electrodes or supporting carbon materials for metallic electrodes and their characterization and evaluation of electrocatalytic properties.

Although the application areas of conventional carbon fibers are already well recognized and such materials are today widely used in structural composites technology, mainly due to their superior mechanical properties, many laboratories are working on the development of fibrous carbon materials due to their unique physico-chemical properties.

Micro and nanoforms of fibrous carbon are today the subject of extensive research into applications in the fields of energy storage and new energy sources, electrodes, components for modern electronics and in environmental systems. A number of prospective applications of carbon-based fibrous materials have also been proposed in the field of medical diagnosis

and therapy. Therefore, the choice of the topic of Ms Karolina Kordek-Khalil's doctoral thesis, its importance and novelty is accurate and fully justified.

The dissertation is a collection of four thematically consistent publications, entitled "*Modified carbon fibre cloth as a material for high performance self-supported electrocatalytic water splitting electrodes",* with additional comments and unpublished supplementary data. Thus, the doctoral thesis contains four copies of publications with a guide to these works.

The work consists of six main chapters. The first chapter introduces the reader to the main goal of the research and its objectives and contains the literature review. In this chapter, the author presents a brief theoretical introduction to the state of the art in the field of carbon fibres and related materials, methods of their modification designed for manufacturing carbon-based electrode materials, noble metal-based and noble metal-free electrodes for hydrogen and oxygen evolution reactions (HER, OER) with an emphasis on the self-supported electrocatalysis. This analysis was supported by literature reports covering 191 references. This proves the broad scientific knowledge of the doctorant and her appropriate theoretical preparation to undertake experiments described in the doctoral dissertation. In item 3 of this chapter the doctorant reports that the synthetic and electrochemical characterization parts of the work were performed by the author at various research centers including Centre for Clean Environment and Energy, Griffith University, Gold Coat, Australia, Department of Polymer and Carbonaceous Materials, Wrocław University of Science and Technology and Catalan Institute of Nanoscience and Nanotechnology, Barcelona**.**

Chapters 2,3,4 and 5 contain the copies of four published papers with comments preceding each paper.

First paper in Chapter 2, entitled " **Cobalt- based composite films on electrochemically activated carbon cloths as high performance overall water splitting electrodes" (International Journal of Hydrogen Energy, IF=4,939, (2019**), contains the results of electrochemical activation of fibrous carbon in the form of cloth, prior to electrodeposition of cobalt-derived layer, evaluation of the physicochemical and electrocatalytic properties of the produced carbon /metal composite electrode.

Chapter 3 discusses the results of the paper entitled "**Tailoring the composition of on step electrodeposited CU, Ni/Co,Ni(OH)2 composite coating for highly active hydrogen evolution electrode". The articles was edited in Sustainable Energy and Fuels Journal (IF=5,503) in 2019.** The authors presented the results of the manufacture of carbon

electrodes covered with a film consisting of two metals namely, cobalt and nickel. Electrocatalytic properties of those electrodes have also been shown.

The third paper, **"Influence of pulsed laser ablation on structure, morphology and electrocatalytic properties of cobalt-based films deposited on carbon cloths" discussed in Chapter IV, has been published in Applied Surface Science (IF=6,182) in 2020.** The experiments showed in this paper were focused on the application of electrochemically activated carbon cloth to be coated with a cobalt –based film by means of physical method, i.e, pulsed laser ablation. The article compares electrochemical and physical methods of activation fibrous carbon electrode materials in relation to their electrocatalytic properties.

In chapter 5 the author discusses a paper titled **"Two–step activated carbon cloth with oxygen –rich functional groups as a high-performance additive-free air electrode for flexible zinc –air batteries. The work has been published in 2018, in Advanced Energy Materials, the journal with an extremely high IF= 22,040**. The paper presents an approach to the manufacture of metal-free carbon –based electrode and its electrocatalytic potential. In this Chapter additional supporting information for the paper is also included. It is particularly interesting work in terms of the practical verifying the experimental results, due to the fact that the electrode material based on a pure carbon. This material, intended for a flexible electrode, was obtained by a two-stage oxidative treatment of the surface of carbon cloth.

The last chapter 6 contains summary, conclusions and abbreviations and acronyms used in the papers and guide. The doctorant presents the perspectives and ideas for further development of the fibrous carbon –derived electrodes. This part of the attachments of the doctoral thesis also contains declarations in which Ms Karolina Kordek–Khalil and co-authors declare their contribution to preparation of the articles. The declarations show the real commitment of the authors in the performance of the publications and reveal that the doctorant has a dominating contribution to their creation. Analysis of these declarations deserves special emphasis, taking into account the fact that two publications were created with the participation of three authors, one four authors, and the last work was created with the participation of 12 authors. The latter publication however, is very extensive work, published in a prestigious journal with a very high IF. Moreover, this publication is enhanced by the extensive additional scientific data available from the Wiley Online Library. This chapter contains information regarding other scientific achievements of the doctorant, i.e. two other publications, not included to the dissertation papers, her participation in research

projects and scientific conferences, her international internships, research visits, scholarships and awards.

The evaluation of a doctoral dissertation prepared in the form of a monothematic series of publications is a difficult challenge for the reviewer. This problem is mainly due to the fact that the presented works have been rigorously evaluated by experts in a given field, before being published. It therefore seems that no further evaluation of these works is necessary.

On the other hand, in addition to the above-mentioned articles, the doctoral dissertation also contains many additional comments, yet unpublished research results supplementing the publications of the doctorant, as part of her scientific activity, closely related to the main area of research. Moreover, the author used the same form of carbon, i.e. microfibrous carbon in all four publications, which allows the reviewer to take a slightly broader look at the area of the research, without the need to re-review individual papers.

All the mentioned above publications appeared in highly ranked scientific journals from the Web of Science/Thompson Reuter's Journal Citation Report. In all publications, Ms Karolina Kordek-Khalil is the first author. The total "Impact Factor" of the publications constituting the doctoral dissertation, according to the Journal Citation Report list from the year of publication is about 38,7. Taking into account the requirements of the journals in which the works were published and the need to adapt to the requirements of these journals in term to the selection and adequacy of bibliographic sources, it should be stated that the doctorant has established knowledge in the field of research. At the same time, the subject matter of the doctorant work fits perfectly into the current research trends.

After reviewing both the scientific achievements of the doctorant and her additional descriptions of the individual sections of the work, I state that the main objectives discussed at the end of chapter 1 have been achieved. The research results published in the articles that form the basis of the doctoral dissertation constitute a thematically consistent scientific material. Publication 4 discussed in Chapter 5 is a particular example of research focused on the practical use of laboratory experimental results.

The most important achievements of the work, in my opinion, can be briefly summarized, as follows:

- in the field of preparation of fibrous carbon materials as electrode materials or substrates for composite electrodes, determination of the processing variables of modification conditions,
- development of CC-AC- electrode materials revealing a hydrogen evolution reaction overpotential about 500 mV with a significantly low oxygen evolution reaction overpotential,

i.e. 360 mV, and with a high oxygen reduction reaction potential (0.72V) what makes the elaborated material among the most active bifunctional metal free OER/ORR electrocatalysts. This material also exhibits superior oxygen electrocatalytic activity and durability.

- proposing an original model of the structure of the near-surface layers of fibrous carbon-based materials subjected to selected physical, chemical and electrochemical modifications as electrode materials

- on a practical level, the well-designed and conducted experiments to develop flexible zinc-air model of battery using CC-AC material as a flexible air electrode under different mechanical folding conditions. The result of this research was to design and obtain a two-electrode battery prototype on a scale allowing for practical application.

The dissertation raises some issues to which the reviewer would like to draw attention, and which require clarification or comments:

-the common denominator of all four publications was the use of fibrous carbon in the form of cloth from two sources, i.e. carbon cloth used as electrode material in fuel cells, assigned in the dissertation as CC-raw, and cloth retrieved from CFRP composites, assigned as CT. The publications do not provide a more complete characteristics of initial carbon fibres in cloth that would allow to define their structural differences. It is well known that the susceptibility to oxidation, strongly depends on the carbon structure i.e. the d002 interplanar spacing and crystallinity. Although the author identified both materials with Raman spectroscopy, this method does not fully allow to determine the carbon structural ordering by analyzing D and G bands.

-chapter 2 (Table S1) can nitrogen in carbon fibre come from the polymer precursor (polyacrylonitrile) or is it only introduced by chemical treatment? It can be seen from this table that unmodified CC sample is nitrogen-free prior to the activation treatment (EACC). Typically, the most common ex-PAN derived low crystalline carbon fibres also contain nitrogen from the polymer precursor.

-why the author decided to use such a complex method for preparing the CT carbon cloth by burning up the polymer matrix? Was it really a composite (CFRP) or just a “prepreg” in the form of lamina for making the composite? Removal of the polymer matrix in air at 500 ° C is a difficult process to control and the fibres may have a heterogeneous surface structure, as

well as partially carbonized debris of organic origin, not structurally bonded to the fibrous carbon material.

- chapter 5 (paper 4); selecting the conditions of step 2 for preparation of the electrode material for zinc-air batteries; the author heated the samples at 500ºC, for 2 hours, in the air atmosphere. As a consequence, fibrous samples with a modified surface structure were obtained. It may be expected that, due to the formation of gaseous oxidation products containing carbon, e.g. CO or CO2, the fibre diameter is reduced ? Such a process can lead to an increase in the brittleness of the carbon cloth and a decrease in its flexibility (reduction in strain to failure). Has the author observed such a phenomenon?

-an interesting experiment is presented in publication 4 in Fig. 4 f,g- galvanostatic discharge-charge cycling curves Zn-air battery using CC-AC electrode under different folding condition; what would happen if the dynamic conditions were inverted, i.e. multiple cyclic mechanical tests (fatigue folding) first, followed by galvanostatic measurements? Will the electrode maintain stable, repeatable parameters**?**

- chapter 5 (paper 4, fig. 6): determination of the electron transfer number (n) by means of the rotating ring electrode disc test (RRDE); the carbon sample was cut into round pieces and pasted into a glassy carbon spot: were these tests repeated for a single sample and if so, what was the accuracy of the measurement (SD)?

The above remarks and questions do not change my high assessment of the work and do not in any way diminish its substantive value. Based on the descriptions and publications presented in the dissertation, I state that the doctorant has an extensive knowledge in the field of chemistry and electrochemistry of carbon materials and the analysis of the processes accompanying the development of electrode materials.

The nice edition of the dissertation documentation draws attention, the graphics, the quality of the figures, images and micrographs, and the text is clarity of the structure of the chapters are well done. The work is well organized, written in clear and concise manner, with appropriate wording regarding the issues raised.

Summing up the presented documentation containing the PhD student's scientific achievements, i.e. a set of four published articles, along with a supplementary information to these publications, I can state that it fully meets the requirements of the doctoral dissertation.. All publications have been published in highly ranked scientific journals, which proves the originality of the research carried out.

Conclusion

Concluding, I state that the doctoral thesis of Ms Karolina Kordek-Khalil "*Modified carbon fibre cloth as a material for high performance self –supported electrocatalytic water splitting electrodes*" fulfils all the requirements for gaining a PhD in accordance with the Art. 13 of the Act of March 14, 2003 on academic degrees and academic title, as well as degrees and title in the field of art (uniform text: Journal of Laws of 2014, item 1852, as amended). Thus, I recommend to the Commission for Academic Degrees in the Discipline of Chemical Engineering of Wrocław University of Science and Technology the admission of Ms Karolina Kordek-Khalil to the public defence.

Appreciating the scope of the presented work, the level of the scientific experiments, the richness of the methods used, along with the interpretation of the experimental results, as well as the application aspects of the conducted research, assuming that this work meets any other required criteria established by the Faculty of Chemistry of Wrocław University of Science and Technology in terms of distinguishing the doctoral theses, I allow myself to request the Commission to distinguish the doctoral thesis.