Iwona Flis-Kabulska, D.Sc., Ph.D., M.Sc., Prof. in UKSW
University of Cardinal Stefan Wyszyński
Warszawa

Warszawa, 20 September 2022

OPINION

on Ph.D. thesis

THE PROCESS OF ALKALINE WATER ELECTROLYSIS FOR THE PRODUCTION OF ULTRA-PURE HYDROGEN AND OXYGEN GASES FOR PEM FUEL CELLS APPLICATIONS

Applied by Mateusz Łuba, M.Sc. the University of Warmia and Mazury in Olsztyn in partial fulfilment of the requirements for the doctoral degree
in the discipline of environmental engineering, mining and power engineering

The Ph.D. thesis by Mateusz Luba, M.Sc., deals with production of hydrogen by water electrolysis. This is a part of so called Hydrogen Economy which tends to use hydrogen as a dominating source of energy. In contrast to fossils, hydrogen can be produced from inexhaustible resources of water and from renewable energy sources. Its combustion product (water) is inert for the environment. At present, hydrogen is produced almost entirely by fossils conversion. Electrolytic hydrogen will be produced on a large scale when renewable energy sources will be better available, environmental requirements more strict, and electrolysers more efficient. The latter issue is the goal of the present thesis. The subject of this thesis is in line with the current trends to develop more effective and cheaper energy sources which would eventually replace the fossils, at least in some branches of life, such as e.g. transportation.

In the Introduction, the Ph.D. Candidate clearly and comprehensibly presents hydrogen as an ideal source of energy, its accumulation, and its production by water electrolysis. Various aspects of this topic have been described based on extensive citation from literature of the subject. On this basis, the objectives of the dissertation were formulated as follows:

“1. Preparation of innovative, highly catalytic and relatively inexpensive Ni foam-based electrode materials for cathodic generation of hydrogen (HER);

2. Preparation of original, cost-effective Ni foam-based electrode materials for anodic generation of oxygen (OER);

3. Construction of stack-innovative, laboratory-scale alkaline water electrolyser unit”.

In this work, electrodes were prepared from commercial Ni foam. Cathodes were activated by deposition of iridium (for single cells) or palladium (for Alkaline Water Electrolyser stack unit), whereas anodes were modified by deposition of platinum, cobalt, molybdenum and by voltametric cycling or potentiostatic oxidation.

Deposition of iridium resulted in a significant enhancement of HER. Beneficial effect of iridium deposition rose with the extension of duration of spontaneous (electroless) deposition or deposition current. Impedance values for HER were presented in Tables, together with relevant values for related

systems obtained by other authors. This presentation showed the superior electrocatalytic activity of the presently prepared iridium treated cathodes.

Treatment of anodes with platinum or by voltametric sweep oxidation did not activate the OER, instead, considerably beneficial effect was achieved by deposition of cobalt, molybdenum or potentiostatic oxidation. Similarly as in the case of cathode, impedance results were displayed in Tables, together with chosen published data by other authors and systems. Again, it showed superiority of the treatment elaborated in this work.

Apart from the research on electroactivity of modified materials, there has been designed and constructed a laboratory-scale electrolyser of high power, reaching about 500 W. A stack unit was composed of nine single cells; at current of about 20 A, it attained a stack voltage of about 20 V. The constructed electrolyser is of considerable practical value, because it can outline the design for efficient small electrolysers which are needed e.g. at filling stations to locally produce hydrogen for hydrogen-powered vehicles. Long-terms tests have shown high durability of the constructed electrolysers, and high effectiveness of untreated Ni foam electrodes, comparable with that of palladium-activated cathodes. This suggests that Ni-foam based electrodes are long-working electrolysers sufficiently efficient even without activation with noble metals.

This dissertation is written in good language and style, and is appropriately concise. It presents valuable results of considerable significance for research and application.

Apart from its positive aspects, it contains some minor drawbacks which, according to my evaluation, are as follows.

1. The Candidate writes in several places about his **"innovative.. original**" treatments applied to the electrodes. I consider the words **"innovative.. original** as inappropriate, because Ni foam and other catalysts are commonly used also by other authors.
2. On p. 26 it is written: "works by Liu et al. [65] and by Gao et al. [66] provided interesting HER results produced on **analogous** materials, namely: NiCo2S4/Ni3S2- and Ni-Se-Cu-modified Ni foam composites". Please notice that unlike Ni foam in this work, the above materials contain S, Co, Se and Cu, hence must not be called **analogous.**
3. In this dissertation, results are presented mostly in Tables in form of multi-digit numbers which may be exact, but hard to compare. Graphical form would help to comprehend the meaning of these numbers and their superposition.
4. The author recognizes that the semicircles are inclined, hence the capacitive element should be described by *CPE*, but not by capacitance *C,* as called in this dissertation. This is inferred by units of *CPE* in Tables, but why the exponent at *s* is written in different ways throughout this work?
5. Page 31, Paper II: The second low-frequency semicircle has been attributed to adsorption. This is correct, however, also mass transfer can give similar semicircles (book by Andrzej Lasia: Electrochemical Impedance Spectroscopy and its Applications"). I hope that the latter would be easier to check, e.g. with rotating disc electrode.
6. Data in Fig. 14 (p.50) show that catalytic effect of Pd was not remarkable: after 168 h, the same stack voltage was attained at currents of 21.0 A and 23.6 A for Pd-free and Pd-activated cathodes, respectively. Activation of cathodes with iridium was shown in this work to be very effective, therefore, why it was not applied in the laboratory stack unit?

The above remarks do not depreciate this thesis. Extended research and construction work have been carried out, delivering new results of significant value to better understand the electrocatalysis and to construct more efficient electrolysers for water splitting. This dissertation is based on the four publications in recognised international journals with good impact factors.

Herein I state that the thesis presented by Mateusz Łuba, M.Sc. fulfil the requirements for the doctoral degree in the discipline of environmental engineering, mining and power engineering, and therefore I recommend this thesis for further stages of the Ph. D. award procedure.