



Institute of Physical Chemistry

Polish Academy of Sciences

Charge Transfer Processes in Hydrodynamic Systems
Dr hab. Martin Jönsson-Niedziółka
Associate professor

Kasprzaka 44/52, 01-224 Warsaw, Poland
Tel.+(48 22) 343 33 06
Fax +(48 22) 343 33 33
E-mail: martinj@ichf.edu.pl

Warsaw, 13 August 2020

Review of the PhD thesis written by mgr Anna Cirocka entitled “Modyfikowane transparentne warstwy przewodzące jako nowe materiały elektrodowe”

The reviewed PhD thesis, written by mgr. Anna Cirocka describes the electrochemical characterisation of mostly transparent electrodes functionalised mainly by silanisation. The work behind the thesis has been performed in the Department of Analytical Chemistry at the Faculty of Chemistry at the University of Gdańsk under the supervision of Prof. Tadeusz Ossowski and the auxiliary supervisor Dr Iwona Dąbkowska. The work is performed together with a broad group of collaborators from materials chemistry to analysis, in Poland and abroad. Parts of the work has been published in articles in renowned international scientific journals, where the PhD candidate is the first author of one such article. The candidate has presented her work at numerous conferences and meetings, both national and international.

The thesis has a traditional form that starts with a brief introduction, followed by a literature background, a presentation of the goals of the thesis, an overview of the experimental techniques used, experimental results and discussion, and a short concluding remark. As the goal of the thesis, the author states that it is to synthesise organic films at conducting electrode materials and characterise them electrochemically. The long-term goal is the possibility of a combination of electrochemical and optoelectronic techniques for future sensors. Understandably most of the work presented in the thesis is focussed on transparent electrode materials. Consequently, the literature background contains a chapter about semiconductors, different electrode materials, surface modification procedures, and characterisation methods.

The first of the background chapters gives a primer on the most important aspects of the electronic properties of semiconductors. This introduction is well written but, given the topic of the thesis, it should have included some aspects of electrochemical properties of semiconductors. From that introduction, it feels natural to move on to the description of the transparent electrode materials that are the main protagonists of the thesis. Here we are presented with a reasonably detailed introduction to the physics of doping of the fascinating oxides and how that affects their electronic properties. In this section also I miss any mention of electrochemical usage of FTO and ITO electrodes. A short literature overview that describes their electrochemical properties and how they

have been used in the past would have given a useful background to the work presented later in the thesis. The section about carbon electrode materials provides succinct summaries of their main attributes. In the part on boron-doped diamonds, I find the omission of any mention of surface termination curious, especially in a thesis focussed on the electrochemistry of functionalised electrodes. The surface termination, principally H or OH, has a substantial influence on the electrochemical behaviour and surface chemistry of BDD-electrodes.

The section on surface modification is a good example of clear, pedagogical explanations of the most important processes relevant to the thesis. The candidate gives an overview of silane chemistry and how silanisation is used to functionalise electrode surfaces. A small mistake appears in Fig. 10, where there is no Si in the silane structure.

The description of the different electrochemical techniques used in the thesis is mainly well-written, but I think that, given how much of the thesis is discussing the meaning of peak-separation, this should have been included in the presentation of cyclic voltammetry. Furthermore, I wonder why the author has chosen to use the American standard for presenting voltammograms and not following the more modern IUPAC recommendations. The candidate also uses the word “*depolarizator*” for “substancja elektroaktywna” even though the former is considered obsolete by IUPAC. In the section on impedance spectroscopy the author, describing the parameter n in the constant phase element (CFE), writes that “*Im ta wartość jest mniejsza, tym w większym stopniu układ przyjmuje charakter izolatora*”. In his classic book “Impedance spectroscopy”, JR Macdonald provides several phenomena that can give rise to CPE behaviour (and thus influence n), such as the surface roughness, a distribution of reaction rates at various sites, or inhomogeneities in the electrode composition or thickness. The CPE is a complex element to describe, and the short-cut taken by the author here is a little too simplistic.

The complete literature background comprises about one-third of the entire text of the thesis and is based on well over a hundred cited works. The chapter serves as a theoretical basis for the work to be described in the experimental part, and the techniques used in those investigations. The emphasis is on the materials aspects of electrodes and compounds under study. What is missing is a literature survey that could serve as a backdrop against which the present studies could be described and contrasted.

The experimental chapter is written in a consistent style, and the descriptions of the experiments performed are concise, logical and easy to follow.

The results and discussion chapter is, of course, the most significant part of the thesis. Here, the author should explain their work and weave together a consistent narrative. The structure of the chapter follows a clear, logical path where first the unmodified electrode layer is characterised, later the chosen FTO electrodes are functionalised with silanes. The best electrodes are then chosen for further functionalisation with quinone-derivatives or polymers. However, despite this logical progression, I feel that the different sections are treated as separate entities, and there is maybe too little connection between the results presented in the individual sections in the text.

In the initial section, the candidate presents measurements of the electrochemical windows and the basic electrochemical behaviour of the bare electrodes that will be used for functionalisation later. The measurement of redox cycling of ferricyanide on BDD can serve as an illustration of a problem that appears several times throughout the chapter. The voltammogram shows an unusually large peak-to-peak separation of almost 500 mV. Why is this so? In the literature, well-prepared BDD electrodes typically show almost reversible voltammetry of this redox probe (see e.g. J. Electrochem. Soc., 146, 4551 (1999), for an early example). However, the author does not mention this anomalous behaviour, nor does she attempt to explain why the separation is so wide. This is a general feature in the thesis – experimental data are presented but rarely compared to relevant publications in the literature.

In the description of the contact angle measurements presented in Fig. 33 the authors writes that “*całkowita swobodna energia powierzchni jest niższa dla materiałów o większym stosunku [B]/[C]*”, but looking at the error bars and the heights of the bars in fig 33B, I do not think that this generalisation is warranted. The values for 2k and 5k are practically the same, as are the ones for 7,5k and 10k. It is difficult to see this as a general trend. The same goes for the statement on the next page “*Zaś elektrody o domieszce 2000 ppm wykazują odwrotną tendencję zmian, wartość ΔE jest niższaprzy wyższej hydrofilowości powierzchni*” where I find it hard to talk about a trend when there is only one data point. Pooling the results from Si and glass supports might not be relevant given their different characteristics. I also do not think connecting the WCA data points with a line between samples is appropriate – there are no values between samples and no trend to follow.

The next section, on creation self-assembled silane-layers the candidate has developed a method for reproducible deposition of high-quality coatings. She compares the properties of the layers after different deposition times and multi-layer deposition with APTMS and OTMS in different orders, as well as co-deposition of the two. The experiments concerning silanisation of the FTO surfaces with APTMS and OTMS clearly show that the latter is blocking the electrode, while the former promotes electron transfer. I do have some questions concerning the interpretation of the results. The first is the statement by the candidate that “*Wydawać by się mogło, że niezależnie od kolejności osadzanych alkoksylanów, otrzymane warstwy będą charakteryzować się niemal identyczną strukturą powierzchni, a w konsekwencji opór przeniesienia ładunku na granicy faz elektroda/roztwór będzie na tym samym poziomie*”. I don't see any reason for such an assumption. Rather, since the author says that the deposited layer is complete with few defects, the order should make a crucial difference, as is indeed shown by the author. However, when the author states that “*na powierzchni elektrody FTO powstaje mieszana warstwa silanów*”, I wonder if this is necessarily so. It seems that the results for subsequent depositions could be well explained by the second layer at least partially replacing the first. I wonder if the author has investigated this possibility. If not, does she have any ideas of how this could be done?

In the section on further modification with electroactive compounds, I must ask the question in which sense they are electroactive? While they are quinone-derivatives, they seem to show no electroactivity within the relevant potential window. If that is so, is it still relevant to call them electroactive? Did the author measure any electroactivity of these compounds beyond what is presented in the thesis? In all cases the addition of these layers seem to make the electrodes less efficient for electron transfer, especially at neutral and alkalic pH. Importantly, the electrodes are not completely blocked and could therefore still potentially be used in electrochemical sensing.

My main concern in this section is the very strange data for the measurement of ferricyanide electrochemistry on FTO. Why is the curve in Fig. 40 so different from the one in Fig. 30? And why the strong pH dependence in Fig. 42? Ferricyanide is a redox probe which is usually relatively insensitive to pH. I cannot agree with the explanation by the author that “*Wiadomo, że w przypadku układu $[Fe(CN)_6]^{3-/4-}$ silnie alkaliczne roztwory powodują jego nieodwracalny rozkład. Potwierdzeniem tego zachowania jest obniżenie odpowiedzi elektrochemicznej dla tego układu redoks wraz ze wzrostem pH roztworu [163]*”. In no way can pH 6.16 be called strongly alkalic! This interpretation is also not supported in the cited reference, where cycling at pH 14 led to a decrease of the signal of only 0.24% per cycle and a peak-to-peak separation of ~ 100 mV. Furthermore, the measurements in Fig. 30 are made in Na_2SO_4 , i.e. at pH close to neutral. Despite the assurance by the author on page 108 that ferri-/ferrocyanide “*uwazane są za pary redoks wrażliwe na pH*”, this generally not the case. pH sensitivity of the response of this redox probe on film electrodes is usually related to the electrode - not the probe. This is either through morphological or chemical changes of the film, or through electrostatic interaction with the film. The author seems to realise as much on page 109, concerning a different system, but that insight is absent in this section. Those untypical and unexplained results for FTO also throws doubt on the data from the further modifications. Are those data due to processes with the film, or some unknown process at the oxide surface?

Strange pH-dependence is also seen in the voltammetry of hydroquinone/quinone. Here, a strong pH-dependence would be expected given the two protons involved in the reaction. However, only at the reduction wave is a peak-shift seen, both for FTO and FTO/APTMS. Is this related to the anomalous voltammetry of seen with ferricyanide?

The behaviour described above is repeated in the case of FTO/PPAAm, where a discrepancy is seen between measurements in Na_2SO_4 and phosphate buffer (cf. Fig. 47 and 49). The author explains that the reason is the pH-sensitivity of the amine group in the polymer, which sounds reasonable. But what is the explanation for FTO? This, however, does not change the conclusions of the section, where the author shows that deposition of PPAAm is a balance between plasma deposition and etching.

In Fig. 45, using an electrode functionalised with ammonia groups, the author describes an additional peak “*przy potencjale około -0,5 V*” and attributes it to oxygen reduction. The

peak is closer to 0.75V, a significant difference. I am also not convinced that the explanation is simply oxygen reduction since it is not seen for other redox systems. It is difficult to imagine some process that can be seen only when it “interferes” only with outer-sphere processes. Interpretation of such data can be difficult and without further investigations it is prudent to be more cautious with assigning a mechanism.

A few additional minor points: On page 69 it is written “*W odniesieniu do klasycznej elektrody GC, odwracalność elektrochemiczna dla tego procesu na powierzchni elektrody Si/CNW zwiększyła się o 63 mV.*”, and I must point out that reversibility (odwracalność) is not synonymous with peak-separation and cannot be expressed in millivolts. On page 98 the candidate writes about “*odwracalny proces redoks układu $[Fe(CN)_6]^{3-/4-}$ obserwowany był tylko w pH poniżej 4*”. There are several definitions of reversibility, but none of the electrodes under discussion shows typical electrochemical reversibility, i.e. ΔE close to 59mV. On p. 108 the author writes “*Wartość ΔE w tym pH jest mniejsza o 21 mV w porównaniu do wyjściowej elektrody FTO*”, while it should say *większa*.

In summary, the thesis presents a range of experiments to modify and characterise electrode surfaces with several silanes, quinone-derivatives and polymers. The functionalisation and materials characterisation are concisely described, while the interpretation of electrochemical data in several cases do not seem very well-founded. Evidently a lot of work has gone into the development of the modification processes, and I know from experience that achieving reproducible chemical layer deposition is a difficult task indeed. The goal of the thesis was to synthesise organic films on conducting electrodes, and this main goal was achieved. For this the student should be commended. A more scrupulous electrochemical characterisation would have placed the conclusions about the film-properties on firmer ground. Taking all of this into account it is my opinion that the thesis by mgr Anna Cirocka entitled “*Modyfikowane transparentne warstwy przewodzące jako nowe materiały elektrodowe*” fulfils the criteria mentioned in art. 31 of the act from 14 March 2003 regulating scientific titles (Dz. U. Nr 65/2003 poz. 595 with later changes).

Martin Jönsson-Niedziółka