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Recenzja rozprawy doktorskiej mgr Libu Manjakkala

Tytuł rozprawy: „Badanie potencjometrycznych i konduktometrycznych czujników pH opartych na tlenkach metali, wytwarzanych technologią grubowarstwową i LTCC oraz ich zastosowanie w bezprzewodowych systemach monitorujących"

Rozprawa została przygotowana w języku angielskim, zatem w celu ułatwienia Doktorantowi zapoznanie się z recenzją została ona również napisana w języku angielskim.

Review of the Ph.D. thesis

"*Investigation of Potentiometric and Conductimetric Metal Oxide Based pH Sensors Fabricated in Thick Film and LTCC Technology and Their Application in Wireless Monitoring Systems*"
by Mr Libu Manjakkal, M.Sc.
Institute of Electron Technology in Warsaw Division in Kraków

IMPORTANCE OF THE TOPIC AND RELEVANCE

Miniaturization of chemical sensors started in early 1970s, when prof. Piet Bergveld invented ion sensitive field effect transistor (ISFET). This led to intensive use of silicon technology and compatible materials, mainly inorganic gate insulators as sensing materials deposited by means of variety of thin-film techniques. The very first, and still used, pH-sensitive materials are the following: silicon dioxide - introduced by P. Bergveld in 1970, silicon nitride and alumina – introduced by H. Abe & T. Matsuo in 1979, alumina with improved stability – H. van den Vlekkert (1988), titanium pentaoxide – by T. Matsuo (1981) and then improved by J. Voorthuyzen & P. Bergveld (1990), iridium oxide – by T. Katsube (1982) and W. Olthuis (1990), Pt, Ir and Ta oxides – K. Kinoshita & M. Madou (1984) and ruthenium oxide - by C. Iwakura (1977), *etc*. Although a vast part of researches on electrochemical sensors including novel

sensing materials have been already conducted for decades, nevertheless this has been still a hot topic, especially in conjunction with emerging technologies.

Mr. Manjakkal – a PhD candidate, joined the research on metal oxide based pH sensors choosing cheaper and possibly more flexible technologies, such as thick-film technique and low temperature cofired ceramic (LTCC). The later one has another advantage – easy integration of the sensor with electronic module and for example designing of wireless sensors. In general, subject of the considered thesis comprises several important and interesting problems related to development and investigation of pH sensing materials based on single and binary metal oxides as well as formation of reference electrode for potentiometric measurements. In particular, the main objective of the PhD thesis was to propose a potentiometric and conductometric metal oxide based pH sensors fabricated in thick film and LTCC technology. The PhD project were realized at Institute of Electron Technology, who has already possessed a long experience in design and fabrication of electrochemical sensors, mainly silicon based.

THESIS STRUCTURE

The thesis form is the monograph, in which Mr. Manjakkal presents his research in the classical book format, consisting of 7 main chapters and summary of the thesis (in total 139 pages). The thesis objectives and outline (Chapter 1) was preceded by a short introduction, which allows establish background for clearly defined research aims. Chapter 2 is related to general overview of sensing mechanism and properties of metal oxide based pH sensors. The aims of the thesis were clearly defined. In consecutive chapters 3 to 6, experimental procedures, fabrication and characterization methods of the sensors as well as results – properties of single and binary oxide based pH sensors and pH-sensor LTCC-chip for wireless monitoring are described. Each of the four chapters include short introduction with a relevant literature review. Content of each chapter is in a form of a manuscript almost ready for publication as a journal paper. This is a very convenient approach leading to clearly and logically viewed objective of the thesis.

Research and resulting scientific publication including PhD thesis have to follow some formal rules. In general scientific formalism of the thesis is adequate and satisfactory. The language of the PhD thesis is written as well as typographical standard are good and very few misprints are found in the body text.

A subject-related literature review includes 146 references where over 53% comprises most up-to-date items of the last decade. This may also render that the subject of the thesis concerns up-to-date and relevant research.

THESIS CONTENT

As it was mentioned before, PhD candidate proposed a method of preparation of pastes for thick-film technology composed as a single- or binary metal oxides mixtures (RuO_2, TiO_2, SnO_2,

Ta_2O_5, or RuO_2-TiO_2, RuO_2-SnO_2, RuO_2-Ta_2O_5, RuO_2-Ta_2O_5-glass). Potentiometric (solid-state coated-wire type) and conductometric (interdigitaed two electrode system) pH-sensors were fabricated using screen-printing on alumina substrates and LTCC technology.

The developed materials for sensing layers and sensors were characterized using methods of structural and composition characterization (such as: X-ray diffraction, Raman spectroscopy, optical and scanning electron microscopy, energy dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy) and methods applied in electrochemistry (including: potentiometric methods and impedance spectroscopy). The materials and sensors were characterized by properly selected method showing that PhD candidate possesses needful researcher skills allowing an effective investigation necessary for this kind of dissertation and discussion. He also undertook efforts to acquire knowledge on sensing mechanism of oxide layers.

NOVELTY AND ORIGINALITY

The thesis research generates significant new knowledge in a scientific area. Variety of single and binary metal oxides based sensors were developed and extensively investigated. Almost all developed pH sensors exhibit Nernstian response. The potentiometric pH-sensors screen-printed on the alumina substrate with RuO_2-Ta_2O_5 (containing 70% ruthenium oxide by weight) and RuO_2-Ta_2O_5-glass exhibit the best performances, namely high sensitivity- slope equals to 56.4 mV/pH and 58 mV/pH, respectively. Also the pH sensors fabricated with home-made pastes shown better performances then commercial ruthenium oxide rich (ESL) ones (response time ca. 60 s, poor linear correlation coefficient and selectivity, higher drift effect).

The analysis of impedance spectra of the interdigitated pH sensors based on a binary oxide revealed mixed electronic and ionic conduction which may underlie to complex sensing mechanism of RuO_2-based pH sensors.

The most significant achievement is development of miniaturized silver/silver chloride reference electrode with KCl-glass top layer. Development of a small, reliable and stable reference electrode for potentiometric measurements has been a very crucial problem limiting many applications, especially long-term monitoring. Extension of the investigation on the miniaturized KCl-glass layer based Ag/AgCl reference electrode may lead to wide implementation of the solution proposed by the PhD candidate. It should be considered if the solution could be a object of a patent.

Based on the described results it is clear that the developed sensing material and sensors and particular miniaturized electrodes are potentially applicable for determination and discrete monitoring of pH. However more extended evaluation of applicability of the sensors is limited due to not included information on frequency of recalibration.

REMARKS TO THE THESIS

Some remarks related to the PhD thesis:

1. Terminological inexactitude, namely PhD candidate gives some information on evaluated parameters (page 32/33), the definitions do not correspond to recommended definitions by IUPAC (*Pure & Appl. Chem.,* 66/12, pp. 2527-36, 1994), *e.g.* response time. The IUPAC recommendations outline also experimental procedures for measuring the response time. As a result also methods/protocols for measurement of time drift and other measurements are not clear. Also composition of the test solutions and other measurement conditions should be presented.

2. Reproducibility (repeatability) – there is no information on number of investigated sensors as well as deviation of the sensors response. The comparison between two sensors lots presented in Fig. 4.16b is not satisfactory. It is advisable to show standard deviation at least in results concerning applicability of the sensors.

3. There is also not defined method of selectivity measurements. The methods of measurement and evaluation of selectivity coefficient are also defined by IUPAC, *e.g.* fixed interference method (FIM, separated solutions method (SSM) and others. In the PhD thesis, there is only a statement (page 63): "*the interfering effect of Li^+, Na^+ and K^+ ions was investigated by measuring of the change in potentiometric sensitivity of the developed sensor. (…) in test solutions with different pH values where compared in the solutions containing additionally 0.01 M LiCl, NaCl, KCl salts.*" This might be considered as an examination somehow similar to FIM, however a type of the test solution nor its composition was mentioned then, selectivity coefficient could not be evaluated. In addition in the inset in Fig. 4.17b, value of the slope for all cations should have the same sign.

4. Presentation of the results in Table 8.1 is very clear and useful. Nevertheless some of the parameters presented there should be expressed quantitatively instead of quantitative description *e.g.:* "*drift effect*" should be replaced by time drift coefficient expressed in mV/h, "*reproducibility*" – standard deviation of selected parameters for measured group of sensors, selectivity coefficients instead of "*interference to other ions*", and long-term stability should also be expressed as a change of selected parameters (sensitivity – slope, drift coefficient, response time, *etc.*) in time. In this case quantitative description should be only used as additional.

5. In the case of impedance spectroscopy measurements (Chapter 4), for better interpretation it would be recommended to introduce an equivalent circuit RC model. The RC model was introduced for single metal oxides based sensors (Chapter 5).

6. The long-term storage of the sensors in distilled water, six and 12-month, influenced potential difference between conventional reference electrode and thick-film glassy-KCl one (page 49). Since, as it was aptly suggested in the thesis, it may results form KCl leakage out from the glassy-KCl layer, then it is a loss that another storage solution, such as 0.1 M KCl aq. was not tested. This might diminish of diffusion out of the salt partials from the glassy-KCl layer due to reduction of the concentration gradient.
7. Since the titanium pentaoxide is known as a material exhibiting relatively high light effect, analyzing the results an insufficiency appears concerning light effect in the sensors, especially these with sensing layer containing Ta_2O_5.
8. In Chapter 2.2, three non-ideal characteristics are described, this part should be extended.
9. In Chapter 2.4, there is a long list of different metal oxides used for pH sensors however, there are no cited references. There is also some imprecise information in literature review (Chapter 2.4), in particular page 23 where information on presented condition of some experiments does not allow correct assessment.

As a last comment it is also worth to add that ion-selective field effect transistors belong to potentiometric type sensors, which was missed in introduction or misleadingly described in Introduction (page 8).

Some editorial shortcomings:

1. Equation (2.3) is not properly written. It should be square brackets in numerator and denominator since $[MO_x(OH)_y]$ and $[MO_{x-\delta}(OH)_{y+\delta}]$ stands for concentration of the species.
2. For mathematical notations are conventionally presented with use of italic fonts.
3. Missed RTG abbreviation.

Questions:

1. There is a question concerning temperature of operation dependence of the sensors response?
2. Since there are other chemical and electrochemical methods of silver chloride formation then it could be mentioned advantage of the method applied in experimental part based on use of hypochloride oxides.

Summarizing, PhD candidate demonstrated a solid understanding of the state-of-the-art in the research area and the knowledge of the most important and current literature. The methodology was sound and described scientifically however in some parts in over-brief form.

It can also be stated that the results are presented clearly, however there is a deficiency due to lack of information on reproducibility of sensors performances (standard deviation, number of measured sensors, *etc.*). In my opinion, by PhD candidate did not discuss extensively enough own results in context of those obtained by others researchers. Although the results are only briefly discussed in relation to the research of others, the thesis demonstrates a good understanding of the implications of the work in a broader scientific context.

PhD candidate showed his creative abilities. Applicability of the developed pH sensors increased significantly thanks to development of stable and miniaturized reference electrode for potentiometric sensors.

Finally, Mr Manjakkal's publication achievements should be highlighted, which are 5 publications in journals indexed in JCR Thomson-Reuters base, such as: *Sensors and Actuators B. Chem*. (IF^{2015}=4.087), *Electroanalysis* (IF^{2015}=2.13) – 2 papers, *Electrochim. Acta* (IF^{2015}=1.450), *Microelectronic Int.* (IF^{2015}=0.659)). His current total impact factor is 10.482.

CONCLUSIONS

Overall, this PhD thesis has very good level. Mr. Libu Manjakkal acquired all necessary practical skills, theoretical knowledge and high motivation for research work. The PhD thesis satisfies requirements of Polish Law on Academic Degrees and Title and Degrees and Title in the Arts (*Official Journal of Laws of 2003, No. 65, item 595, as amended,* Dz.U. 2003 Nr 65 poz. 595).

Quality of this thesis is fully in agreement with requirements for PhD thesis in the field of Electronics. Therefore, I recommend admitting Mr. L. Manjakkal to further stages in his doctoral assessment process.