

UNIVERSITY OF PÉCS
Doctoral School for Chemistry

Novel layers for optical ammonia sensors

PhD Thesis

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1. Introduction

The interaction of light and matter offers several techniques for the interrogation of optical chemical sensors. Devices based on the measurement of absorption, refractive index change, fluorescence or polarization, are fabricated generally. The sensors discussed in this work are reflection based devices; they are interrogated using reflection measurements in the visible range. These sensors can provide important advantages compared with other chemical sensors. As the principle of detection relies on the straight interaction of light and material; this setup can be used in many situations when the measurement with other devices can hardly be performed. Electromagnetic noise or the incidental radioactivity of the sample does not have any effect on the performance of these sensors. Another advantage of them is the inexpensive manufacturing (in most of the cases) and the possibility of miniaturization.

An optical chemical sensor usually consists of a support and a chemical layer, which contains plasticized polymers in many cases. The sensing compounds are immobilized in this polymer, which also provides the medium or chemical environment for the reaction. As the chemical structure of the polymer changes, the chemical equilibrium shifts, and a change in the calibration parameters of the sensor can be measured. After a certain time, like in case of other chemical sensors, the change of the device becomes necessary.

Sensors were prepared by immobilizing triphenyl-methane type acid-base indicators on different support materials. Instead of using plasticized polymers, other novel substances were applied to extend the lifetime and minimalize the drift in the calibration parameters of the sensors.

The indicator molecules were immobilized on electrochemically prepared porous aluminium-oxid surfaces. Properties of the surfaces were modified by adding ionic liquids or applying sol-gel coatings. In the first part of the thesis the scientific literature and the theoretical background of this field is discussed. The importance of ammonia detection, the many possible ways of determination, including electrochemical, semiconductor based methods and some other unique techniques are described in these chapters. The most often used chemical layers are summarized in a separate chapter. In the experimental part of this work the exact circumstances of the experiments are described, while the results and conclusions can be found in the last section.

2. Research Aims

In this thesis a research for novel sensor materials is described. The main objective of the work was to avoid the use of plasticized polymers and find a better medium for the immobilization of the indicators. The following aims were laid down:

- By knowing the excellent adsorption capabilities of electrochemically fabricated oxide layers, the first aim was to determine if these layers could be used as sensor supports. In the small pores of the surface the indicator molecules are not in dissolved form, which raises questions about the equilibrium constant and the reversibility of the chemical reaction used for the detection. I proposed to get information on the relationship between the fabrication process and the analytical parameters of the sensors, at the same time.
- It seemed to be reasonable to determine, how non-water-soluble apolar solvents (ionic liquids) – used as additives – influence the analytical and time dependent parameters of the sensors
- Several references were found on the immobilization of indicators in ormosil layers. As the formation of Al-O-Si bond is possible, it was obvious to examine, whether the sol-gel based sensing layer can be deposited on the surface of anodized aluminium. A higher adhesion was expected, which can be advantageous for the preparation of long lifetime chemical sensors.

3. Materials and Methods

For the fabrication of anodized aluminum commercially available aluminum foils and bands were used. In the first experiments the sol-gel layers were immobilized on 18×24 mm microscope cover glasses, later anodized aluminum plates were also used.

The chemicals used at the electrolysis and sol-gel preparation were all analytical grade purchased from Fluka and Riedel de Haen. For the preparation of aqueous solutions ultrapure water was used, with a conductivity lower than 0,5 $\mu\text{S}/\text{cm}$.

The triphenyl-methane indicators used for the preparation of the sensing layer were Reanal chemicals (bromophenolblue – BPB, bromocresolgreen – BCG, bromocresolpurple – BCP). The cresol red indicator was purchased from Fluka. Chemicals used for covering the pores such as o-nitrophenyl-octyether (o-NPOE), hexamethyl-tetracosane (Squalane), dioctyl-sebacate (DOS) were Fluka products, while the OV-17 silicon was obtained from Merck.

Precursors for the sol-gel cocktails were purchased from Sigma-Aldrich Co. Methyl-triethoxysilane (MTEOS), tetraethoxysilane (TEOS), dimethyl-dimethoxysilane (DiMe-DiMOS), phenyl-triethoxysilane (Ph-TriEOS) and aminopropyl-triethoxysilane (APTES) were used.

In some experiments a small amount of 1-butyl-3-methylimidazolium-hexafluorophosphate ([BMIM][PF₆]) ionic liquid, produced by Sigma-Aldrich, was added to the sensing layer.

The measurements were mainly performed on an Avantes Avaspec 2048 fiberoptic CCD spectrophotometer and an Avantes reflection setup. The reflection probe was connected to a home-built flow through measuring cell.

The ammonia calibrating gas was purchased in flasks from Linde Gas Co., with 100 ppm nominal concentration. To reach the proper concentration, this gas was diluted with air on a setup of three Cole-Parmer flowmeters. The highest flow-rate was 150 ml/min, the measured values had to be corrected, according to the quality of the gas, by using a correction chart. The concentration could be changed in the range of 0-94 ppm, with ca. 1,5 ppm resolution.

4. Results

- I. Investigation of anodized aluminium supports
 - a) During the investigation of anodized aluminium - as a possible support for optical chemical sensors - excellent adsorption capacity and outstanding reflectivity of the surfaces was measured.
 - b) By taking electronmicroscopic images it was stated, that the size of the pores is increasing while the pore density is decreasing in the 6-24V voltage range, using sulphuric acid based DC anodizing method. I observed, that above 24V the self-ordering of the pores occurs.
 - c) I observed, that a longer electrolysis results in a thicker oxide layer. After ten minutes of electrolysis a 10-12 μm layer was found on the surface of the aluminium.
 - d) Triphenyl-methane type indicators were immobilized in the porous oxide layers, and the adsorption isotherms of the electrochemically modified surfaces were taken.
- II. The investigation of sensors prepared on anodized aluminium
 - a) The immobilized indicator molecules were protonated with the dilute solution of dodecylbenzenesulphonic acid, this way ammonia sensors were fabricated. The most important properties of the sensors were investigated; the spectral changes in the presence of ammonia were measured, calibration curves were plotted, sensitivity and time dependent parameters were determined. In the selected concentration range the highest reflectance change was provided by the sensor prepared by 18V cell voltage, however the shortest response time belonged to the 12V layer.

- b) The results show, that the dynamic range shifts towards the higher concentrations and gets narrower with the increasing temperature of the environment.
- c) The sensors underwent a leaching probe. Additional apolar layers were used to decrease the dissolution of the indicator, and to extend the lifetime of the sensors. Although the response times were found to be longer, due to the additional coatings.
- d) The repeatability of sensor fabrication was also investigated. The standard deviation of the preparation was found to be smaller than 4%.

III. The use of ionic liquids

- a) Ionic liquid was added to the solution of the indicator before the adsorption process. The main objective of this step was to keep the water content of the layer on a constant level and this way a longer lifetime of the sensors was expected. Although the ionic liquid [BMIM][PF₆] takes up water and keeps it in the pores of the oxide layer, which is advantageous regarding the lifetime, the indicator gets deprotonated due to the shift in the chemical equilibrium and a narrower dynamic range can be observed.
- b) Experiments were performed by replacing the indicator with others and by changing the concentration of the ionic liquid systematically. It had to be stated, that the use of the ionic liquid [BMIM][PF₆] does not have advantages in case of these ammonia sensors.

IV. Sol-gel based sensors

- a) Sol-gel layers were prepared on glass supports, using ormosil precursors. The phenyl-trietoxysilane matrix provided the best results; favourable response times were measured, compared with other ormosils.
- b) Layers were prepared by the immobilization of two different but spectrally similar indicators at the same time. These results showed that by changing the ratio of the

two indicators, the sensitivity and reflectance change of the sensors can be tuned. Using indicator mixtures this way, enables the preparation of sensors designed for certain tasks.

V. Sol-gel layers prepared on anodized aluminium

- a) Sensors were prepared by the combination of aluminium-oxide and sol-gel techniques. The anodized aluminium support was coated with the sol-gel by simple spin-coating. The porous oxide layer provided an excellent mechanical stability for the sensing layer, compared with the widely used glass surfaces. This way a weak point of the sol-gel sensors, the peel off of the layer, could be avoided. The chemical composition of this immobilized layer can be modified in a wide range without any effect on the adhesion.
- b) Calibration curves of the sensors were taken, and the time-dependent parameters were determined. The analytical properties of the sensors barely change, while the response and regeneration times are two times longer than in case of the glass supports.

VI. Development of a sensing device

- a) A simple interrogating unit was developed in our laboratory, which is capable of making difference between the protonated and deprotonated state of the sensor. The result of the measurement can be displayed in a simple way.
- b) The optical part of the instrument was designed and prepared by me. Switching level of the device was set, and the hysteresis of the switching was determined.

5. Thesis Points

- I. It was investigated, how the conditions of the anodic oxidation of aluminium plates, influences the structure of the oxide layer generated in the process. Using electronmicroscopic images it was stated, that the size and number of pores can be controlled with the parameters mentioned above. Thickness of the layer and the adsorption capacity – related to indicator molecules – was determined.
- II. I was the first to prepare aluminium-oxide based ammonia sensors by immobilizing triphenyl-methane type indicators in the porous layers. It was stated, that the spectral changes and time-dependent parameters of the sensors can be controlled by the structure of the layer, so by the circumstances of the electrolysis accordingly.
- III. The possibility of using ionic liquid was investigated in the case of different indicators. It was stated, that the use of ionic liquids – in contrast with carbon-dioxide sensors – is not preferable for ammonia sensors.
- IV. Sol-gel layers were prepared on glass supports, using ormosil precursors with different polarities. Calibration curves were taken which showed, that the sensitivity of the sensors depended on the organic modification. Novel layers were also prepared by the immobilization of two different but spectrally similar indicators at the same time. The sensitivity of these layers can be tuned by the ratio of the indicators.
- V. Anodized aluminium was also applied as a support for sol-gel layers, instead of the generally used microscope cover glasses. It was stated, that these novel sensors had an outstanding mechanical stability. Their analytical parameters barely changed, but the response times were found to be longer, compared with the glass based sensors.
- VI. An interrogation unit for the sensors was developed. The optical unit of the instrument was designed and prepared by me. Tuning of the device was performed, and hysteresis of the switching was measured.

6. List of Publications

I. Publications related to this thesis

1. **Ákos Markovics**, Géza Nagy, Barna Kovács
“Reflection based sensor for gaseous ammonia”
Sensors and Actuators B 139 (2009) 252–257 **IF: 3,083**
2. **Ákos Markovics**, Barna Kovács
“Fabrication of optical chemical ammonia sensors using anodized alumina supports and sol-gel method”
Talanta 109 (2013) 101-106 **IF: 3,794**

Manuscripts under review:

3. **Ákos Markovics**, Barna Kovács
“Development of optical ammonia sensors with tuneable dynamic range for environmental applications and a related read-out device with yes-no output”
Microchimica Acta, Submitted: 23/04/2013

II. Other referred publications

1. I.Kasík, J.Mrazek, O.Podrazky, M.Seidl, P.Tobiska, V.Matejec, B. Kovacs, **A. Markovics**, M.Szili, K.Vlckova, „Preparation and characterization of thin transducer layers sensitive to free chlorine in water” ,Material Science and Engineering C 28 (2008) 842-847.
IF: 1,812
2. I.Kasík, J.Mrazek, O.Podrazky, M.Seidl, P.Tobiska, V.Matejec, B. Kovacs, **A. Markovics**, M.Szili, K.Vlckova, „Preparation and characterization of transducer layers for opto-electrochemical detection of chlorine in water”, Proc. SPIE 6585, 65850Z (2007)
3. I. Kasik, J. Mrazek, O. Podrazky, M. Seidl, J. Aubrecht, Petr Tobiska, M. Pospisilova, V. Matejec, B. Kovacs, **A. Markovics**, M. Szili, „Fiber-optic detection of chlorine in water” Sensors and Actuators B: Chemical, Volume 139, 1 (2009) 139-142
IF: 3,083
4. C.Gouveia, **A.Markovics**, J.M. Baptista, B. Kovacs, P.A.S. Jorge,
„Measurement of CO₂ using refractometric fiber optic sensors” ADVANCES in SENSORS, SIGNALS and MATERIALS, ISBN: 978-960-474-248-6 (2010) WSEAS Press

III. Non-referred publications related to this thesis

1. B.Kovács, **Á.Markovics**, G. Nagy
„Anodized alumina as support for reflection based optical ammonia sensor” (poster),
7th Symposium on Instrumental Analysis, p.83 (2003)
2. **Markovics Ákos**, Nagy Géza, Kovács Barna
„Alumínium oxidon kialakított reflexiós szenzor ammónia gázra” (*lecture*)
Analitikai Vegyészkonferencia 2004 (78.o) (2004)
3. **Markovics Ákos**
„Alumínium oxid felületén kialakított reflexiós szenzor ammónia gázra” (*lecture*)
XXVII. Országos Tudományos Diákköri Konferencia, Kémiai és Vegyipari Szekció
(2.helyezés) (2005)
4. **Markovics Á**, Nagy G., Kovács B
„Alumínium oxidon kialakított reflexiós szenzor ammónia gázra”. (*poster*)
Műszaki Kémiai Napok '05, 310.o. (2005)
5. **Ákos Markovics**, Barna Kovács, Imre Sánta, Géza Nagy
„Electrochemical preparation and characterization of nanoporous alumina films”
(*poster*), 8th Symposium on Instrumental Analysis P55 (94.o) (2005)
6. **Markovics Ákos**, Kovács Barna, Nagy Géza
„Alumínium-oxid réteg szerkezetének hatása optikai ammónia szenzor tulajdonságaira”
(*lecture*) Kémiai Szensorok Kutatásának Eredményei Workshop II. (2006)
7. **Markovics Ákos**, Nagy Géza, Kovács Barna
„Gyors válaszidejű optikai ammónia szenzor” (poster)
Centenárium Vegyészkonferencia 2007, ISBN 978-963-9319-68-4, p.168. (2007)
8. **Ákos Markovics**, Barna Kovács, Géza Nagy
„Sol-gel coated anodized alumina for sensor applications”
(poster) 9th International *Symposium* on Instrumental Analysis, Pécs (2008)
9. **Ákos Markovics**, Barna Kovács, Géza Nagy
„Reflection based sensor for gaseous ammonia”
(poster) Eurotrode IX, Dublin (2008)
10. **Markovics Ákos**, Kovács Barna, Nagy Géza „Új közegek optikai kémiai ammónia
szensorok fejlesztéséhez” (*lecture*)
Kémiai Előadói Napok 2009 (2009)
11. **Markovics Ákos**, Kovács Barna, Nagy Géza „Optikai kémiai ammónia szenzor
alkalmazása szellőző rendszer vezérlésére” (*lecture*)
Kémiai Szensorok Kutatásának Eredményei Workshop (2009)

12. **Ákos Markovics**, Barna Kovács, Géza Nagy
Fabrication of optical chemical ammonia sensors using anodized alumina supports and sol-gel method (*poster*)
Eurotrode X, Book of abstracts, P129 (187.o.) (2010)

IV. Other non-referred publications

1. Hajós Rebeka, **Markovics Ákos**, Papp Tamás, Kovács Barna
“Optikai szenzor különösen kis oxigén koncentrációk mérésére (poszter)”
Centenárium Vegyészkonferencia 2007, ISBN 978-963-9319-68-4, p.167.
2. Kozima Szaláncz, **Ákos Markovics**, Barna Kovács
„Polyurethane – ionic liquid matrix for optical CO₂ sensing”
Eurotrode X, Book of abstracts, P131 (189.o.) (2010)
3. Barna Kovács, Aleksandar Széchenyi, **Ákos Markovics**
„Optical CO₂ sensors based on hydrogencarbonate ion detection”
Eurotrode X, Book of abstracts, P35 (93.o.) (2010)
4. C. Gouveia, P. Caldas, **A. Markovics**, P. A. S. Jorge, J.M. Baptista, B. Kovacs
“LPG-based interferometric sensor for measurement of dissolved CO₂”
SEON 2009 - Symposium on Enabling Optical Networks and Sensors 2007, Lisbon, Portugal
5. K. Balogh, J.M. Jesus, C. Gouveia, J.O. Domingues, **A. Markovics**, J.M. Baptista, B. Kovacs, Carlos M. Pereira, Maria-Teresa Borges, P.A.S. Jorge
“Optical technology for measurement of dissolved CO₂ in aquaculture
SEON 2012 - Symposium on Enabling Optical Networks and Sensors 2009, Lisbon, Portugal.
6. K. Balogh, **A. Markovics**, C. Gouveia, J.M. Baptista, P.A.S. Jorge, B. Kovacs
“Phenol derivative based carbon dioxide sensor for environmental monitoring”
Eurotrode 2012, Barcelona (poster)

Patents, utility models

1. U 10 00023 (utility model) „Átfolyó mérőcella és optikai elrendezés kémiai minta lumineszcens optikai érzékelővel történő méréséhez” 2010.01.28 (co-author)
2. 20121000027080 (patent, Portugal) „Sistema óptico sensor para determinação de parâmetros químicos baseado em novos materiais sensíveis e medição do índice de refração” 2012 (co-author, NIF: 841751411)