Talanta 109 (2013) 101–106

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Fabrication of optical chemical ammonia sensors using anodized alumina supports and sol–gel method

Ákos Markovics, Barna Kovács*

University of Pécs, Department of General and Physical Chemistry, Ifjúság útja 6, H-7624 Pécs, Hungary

ARTICLE INFO

Article history:
Received 3 September 2012
Received in revised form
21 January 2013
Accepted 28 January 2013
Available online 8 February 2013

Keywords:
Optical ammonia sensor
Anodized alumina
Sol–gel
Ormosil

ABSTRACT

In this comparative study, the fabrication and the sensing properties of various reflectometric optical ammonia gas sensors are described. In the first set of experiments the role of the support material was investigated on four different sensor membranes. Two of them were prepared by the adsorption of bromocresol green indicator on anodized aluminum plates. The applied anodizing voltages were 12 V and 24 V, which resulted in different dynamic ranges and response times for gaseous ammonia.

The sol–gel method was used for the preparation of the other batch of sensors. These layers were coated on anodized aluminum plates (24 V) and on standard microscope cover glasses. In spite of the identical sensing chemistry, slightly different response times were measured merely because of the aluminum surface porosity. Gas molecules can remain entrapped in the pores, which results in delayed recovery time. On the other hand, the porous oxide film provides excellent adhesion, making the anodized aluminum an attractive support for the sol–gel layer.

1. Introduction

The electrochemical modification of aluminum has been widely used in mechanical engineering, primarily to form protective coatings on mechanical parts. Different anodizing methods are known; the process of the electrochemical surface treatment can be performed using AC or DC power, in solutions of inorganic or organic acids [1].

Although the porous surface morphology of the anodized alumina was described many years ago, only recent developments in nanotechnology leads one to take a closer look at the pores, to investigate the correlation between the parameters of the electrolysis and the size or density of these nanostructures [2,3]. In the last 15 years several studies have been published, describing these relations [4–8]. It was found that, at higher anodizing voltage, temperature or electrolyte concentration, larger pores and different porosity could be observed [9]. An interesting phenomenon, the self-ordering character of the pore formation, was also reported, that made this electrochemical process a useful tool in the hands of chemists dealing with nanometer sized reactors, sensors and other applications [10–12].

The porous aluminum-oxide surface can be used as a sensing layer of capacitive sensors [13,14]. Optical chemical sensors for measuring gas phase or dissolved oxygen and oxygen partial pressure have also been prepared on anodized aluminum-oxide (AAO) substrates, as in Refs. [15–17]. Recently, an optical ammonia sensor prepared on AAO has been reported in our previous study. In that work, the adsorption capacity and surface morphology of anodized aluminum sensor supports were investigated [18]. It was found that the properties of the optical sensors, such as response time and dynamic measuring range, could be influenced by changing the conditions of electrolysis used for surface layer preparation on aluminum tapes. Excellent reflection properties and good reproducibility of manufacturing are the greatest advantages of the use of electrochemically modified aluminum as a support. However, these nanoporous films showed relatively long regeneration times. Furthermore, water evaporates from the pores slowly, shifting the chemical equilibrium of the immobilized indicator and the optical signal. As a result of that change, a decrease in the reproducibility of the sensor function was measured. With additional hydrophobic coatings, the desiccation of the oxide layer can be prevented and the cross-sensitivity to water vapor can be reduced, although a further increase in response times is expected.

More recently, Chang et. al. [19] used bromocresol green indicator adsorbed on mesoporous Al–MCM-41 silica surfaces for the detection of gaseous ammonia. Interestingly, they found that a sensor design similar to the one in Ref. [18] resulted in a more sensitive device. Their sub-ppm detection limit (0.185 ppmv) cannot be explained by the nature of the indicator (it was the same: bromocresol green in both cases), but rather by the interaction between the indicator and the supporting material. Interestingly, the response and recovery times reported in Refs. [18,19] have been found to be similar.

Similar to our previous work, in this study, aluminum plates with electrochemically prepared porous oxide layers were used as

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* Corresponding author. Tel.: +36 72 503600 24680; fax: +36 72 503635.
E-mail address: kovacs1@gamma.ttk.pte.hu (B. Kovács).

0039-9140/$ - see front matter
http://dx.doi.org/10.1016/j.talanta.2013.01.054

supports for optical chemical ammonia sensors; however, two completely different immobilization techniques were compared (Fig. 1).

In the first method, the sensitive dye was entrapped in the pores of the anodized layer by adsorption from solution of the chosen triphenyl-methane type compound. Aluminum parts are often painted with a similar technology in the industry, although for those surfaces the pores are usually sealed to prevent leaching.

Entrapment in ormosil films was the second immobilization method used. It is well known from literature that indicators entrapped in organically modified silica have excellent sensing properties [20]. These transparent sol–gel layers are usually applied on glass supports; on microscope slides, cover glasses or optical fibers, and therefore an additional reflective background is required when reflectance spectroscopy is used for signal transduction. To overcome the problem of insufficient surface reflection, two different supports were tested. In a set of experiments the ormosil films were coated on microscope cover glasses, while an external mirror was used in the optical measuring cell. Measurements were also performed on identical sol–gel layers applied on highly adhesive and reflective anodized aluminum plates. The different types of sensors were compared by their spectral response to gaseous ammonia in the 0–100 ppm concentration range, and the recovery times from ammonia to air. Mechanical stability of the layers was also investigated.

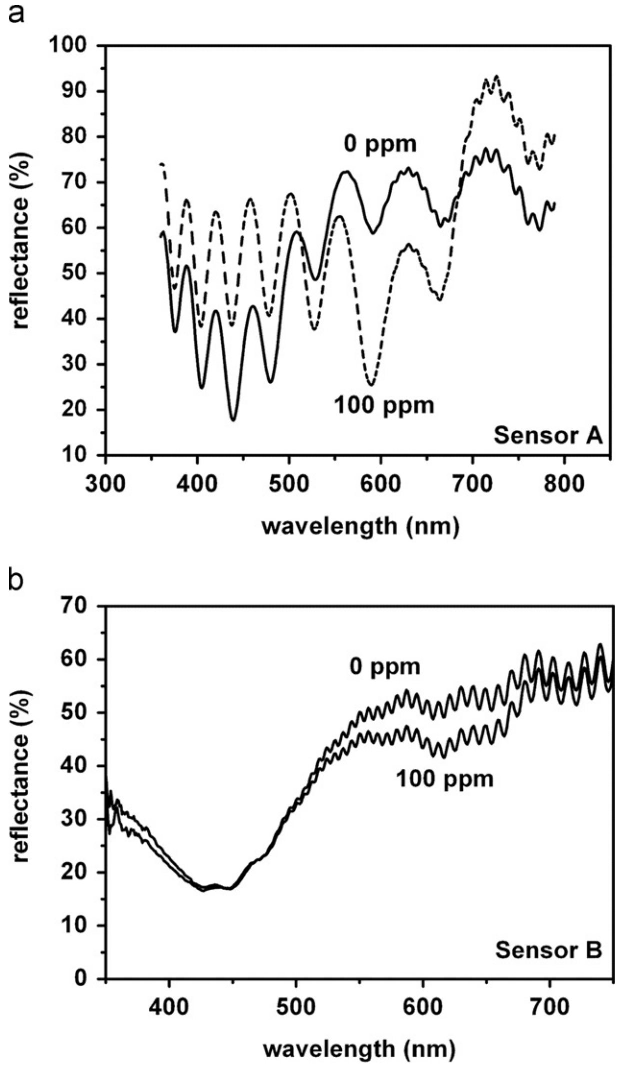

Fig. 1. (a) Reflectivity spectra of sensor A at 0 ppm and 100 ppm equlibrial ammonia gas concentrations. (b) Reflectivity spectra of sensor B at 0 ppm and 100 ppm equlibrial ammonia gas concentrations.

2. Materials and methods

The 99.5% pure 0.5 mm thick aluminum tape was purchased from Köbal Ltd. (Budapest, Hungary) and cut to the proper size in the mechanical workshop of this laboratory. The bromocresol green (BCG) and bromphenol blue (BPB) triphenyl-methane dyes were obtained from Reanal Ltd. (Budapest, Hungary). Dodecylbenzenesulphonic-acid (H-DBS) was purchased from Fluka (Buchs Switzerland). Inorganic acids and salts used for the preparation of the anodizing bath were Riedel de Haen products. All the chemicals were analytical grade and used as received. Solutions were prepared with ultrapure, deionized water. Calibrating gas with a nominal 100 ppm concentration (93.7 ppm NH_3 in nitrogen) was purchased from Linde (Répcelak, Hungary). The sol–gel precursors, phenyl-triethoxysilane (Ph-TriEOS), methyl-trimethoxysilane (MTEOS), dimethyl-dimethoxysilane (DiMe-DiM-OS) and aminopropyl-triethoxysilane (APTES), were purchased from Fluka.

2.1. Sensor fabrication

2.1.1. Preparation of nanoporous aluminum-oxide based sensors

Aluminum plates (1.5 cm × 6 cm) were cleaned with ethanol and electropolished in a 4:1 mixture of ethanol (96%) and perchloric acid (60%), for 3 min with a 3.3 A current. The power was supplied by a CAI 20-1084 stabilized current/voltage source. Only 1.5 cm of the plates was immersed in the solution; in this way, 146 A/dm^2 current density was applied. After polishing, the plates were thoroughly rinsed with deionized water and immersed in the anodizing bath (5% v/v sulfuric acid). The prepared substrate was connected as anode, and a U shaped aluminum block was used as cathode in the circuit. During the 10 min of electrolysis, the cell voltage was kept constant at 12 V or 24 V. The electrolysis was followed by 1 min of washing and another minute in the ultrasonic bath. Finally, the plates were dried and prepared for the immobilization of the dye.

The immobilization was carried out by simply immersing the plates in a 0.1% (m/v) solution of the indicator. After 10 min of soaking, the plates were carefully washed with distilled water to remove excess indicators from the pores, dried at room temperature and immersed into a solution of 10% (m/m) H-DBS for protonation for 5 s. As the indicator molecules became protonated and the color of the surface clearly changed, the sensors were taken out of the solution and dried.

2.1.2. Preparation of ormosil based sensors

The sol–gel cocktails were prepared in 1.5 ml poly(ethylene) containers. After weighing 6 mg of the indicator dye, 400 μl Ph-TriEOS was pipetted into the vessels. Since the indicator cannot be dissolved at this concentration in the Ph-TriEOS, 1% (4 μl) of APTES was added to increase the solubility. The mixture was then shaken for 3 min. According to our previous experiences, this additive minimizes mechanical problems, inhomogenities and cracking of the layer. After 1 min of shaking, 120 μl of a solution containing 10 g H-DBS, 20 g water and 24 g 96% ethanol was added to the solution. The optimal water to ethanol ratio (slightly over 2:1) was determined in previous experiments. H-DBS acts as a catalyst and protonating agent, and also promotes the solubilization of the dye. Usually, diluted hydrochloric acid is used for this purpose.

Gelation started immediately after shaking the mixture (1 min by hand and 1 min in an ultrasonic bath) and the wall of the container became significantly warm (40–60 °C). Within 10 min the sol–gel cooled down to room temperature. The layers were prepared immediately on glass supports (Bürker microscope cover glass) or freshly anodized aluminum plates, with a spin-coater device (300 rpm), by spreading 50 µl of cocktail on the surface. The sensor layers were cured at 80 °C for 1 h.

2.2. Instrumentation

The instrumentation used for the characterization of the sensors is described in our previous work [18]. Briefly, it consisted of a three-flowmeter gas mixer setup which was suited for the control of the ammonia gas concentration in the 0–100 ppm range, with 1.5 ppm resolution. The home-built flow-trough measuring cell contained an aluminum base to fix the fiber optic probe, a rubber gasket with gas inlets and outlets and an acrylic cover. The sensors were placed between a sealing rubber layer and the acrylic cover, pressed face down against a standard bifurcated fiber optic probe and fixed by screws. One end of the Y-shaped fiber optic cable was connected to an Avantes Ava–Hal light source, while the other lead to the Avantes 2048-2 spectrophotometer. For reflectance measurements a built-in mirror was used as reference.

3. Results and discussion

3.1. Investigation of the effect of the support material on the sensor response

The effect of the support material on the calibration and the response of the sensors were investigated by the comparison of four distinct types of sensor membranes. The main composition and preparation method of these membranes are detailed in Table 1. The first two sensors (A and B) were prepared on nanoporous aluminum-oxide surfaces by simple adsorption, the third one (C) was fabricated with the sol–gel method on a planar glass substrate, while the fourth (D) was made with the combined aluminum support—sol–gel layer composition. For the C and D sensors spin coating was used for layer preparation.

In case of all the four sensors, the same dye (BCG) was used, only the sensor matrices were different. Sensors A and B were prepared by distinct potentials (12 V and 24 V), while the sol–gel based sensors differed only in the material of the support. After preparation, calibration curves were taken, and recovery time studies were performed. Analytical properties of the different sensing layers were compared (Table 2).

A comparison with other similar ammonia sensors – regarding the indicator and the adsorption based immobilization – was also performed. As the results (summarized in Table 3) show, the sensitivities, response times and recovery times of BCG and BPB based sensors depend strongly on the structure of the support matrix.

3.2. The effect of the applied cell voltage on the sensor response

Different reflectance spectra were measured in the case of electrochemically prepared (A and B) sensors. In our previous studies, SEM images of the differently prepared surfaces were taken and compared [18]. Those images show how the surface morphology, porosity, and pore-diameter of anodized aluminum varies with conditions of the electrolysis.

Table 1
Preparation method of the sensors.

Sensor	Support	Anodizing	Immobilization	Dye
A	Aluminum	12V, 10 min	Adsorption	BCG
B	Aluminum	24V, 10 min	Adsorption	BCG
C	Glass	–	Sol–gel	BCG
D	Aluminum	12V, 10 min	Sol–gel	BCG

Table 2
Analytical properties of the BCG based sensing layers.

Sensor	Dynamic range (ppm)	Concentration of 50% response (ppm)	Total reflection change[a] (%)
A	6–60	30	18
B	0–10	5	8
C	0–80	34	10
D	0–80	36	5

[a] Measured at 620 nm; electropolished aluminum was used as reference.

Change of reflectance corresponding to 100 ppm ammonia gas concentration was found to be 17.6% for sensor A and 8.1% for sensor B at 620 nm wavelength. In case of sensor A, a periodic noise distorted the spectrum of the immobilized dye. The high amplitude noise was not present in the case of sensor B (Fig. 1a and b). The low frequency and high amplitude component disappears at higher voltage (sensor B), while a high frequency low intensity component can still be observed.

This phenomenon has interferometric origin resulting from reflections at the air/alumina and alumina/aluminum interfaces. In our previous experiments [18], the thickness of the oxide layers – estimated from SEM images – was found to be 10–20 µm, depending on the anodizing voltage and on the duration of the electrolysis. Theoretical calculations [24], taking the short period interference fringes (10 and 9 nm period in the 600–700 nm range on Fig. 1a and b, respectively) confirmed the experimental results (11 and 13 µm). Nevertheless, the long period fringes (60–70 nm period in the 600–700 nm range) could not be explained by this simple model which indicates, that the period of the interference depends also on the pore size and pore distribution of the layer.

Calibrations, made in 15 equidistant concentration steps between 0 and 100 ppm, resulted in different calibration curves (Fig. 2). The graphs were created by plotting the reflectance changes at 620 nm (the absorption peak of the basic form of the indicator) that were normalized to the maximal values measured over the saturation concentration. For a better comparison the results of all four sensor types were plotted on the same graph. As it can be seen, the conditions of electrochemical surface treatment have strong influence on sensing characteristics. The detection limit of sensor A was found to be below 6 ppm, while the dynamic range was between 6 and 60 ppm. At 80 ppm the sensor got saturated. Sensor B showed higher sensitivity, for 6 ppm of gaseous ammonia concentration a 70% response was found. Between 6 and 60 ppm a slow saturation was measured. The concentrations corresponding to the 50% responses are: 30 ppm for sensor A, and 5 ppm for sensor B.

In order to study the recovery characteristics of the different sensors, the equilibrial response for 100 ppm ammonia gas concentration was measured. After the stabilization of the optical signal, the concentration was rapidly changed to zero by flushing the measuring cell with air. The relative reflectance changes (sensor responses) were measured and plotted versus time. The obtained reflectance–time curves are shown in Fig. 3. As can be seen, the regeneration of sensor A was slightly faster. This can be a result of the differences in the porosity and thickness of the aluminum-oxide films.

The recovery times for both sensors are long; the total time of regeneration was more than 1 h. Our previous experiences proved that this process could be accelerated by heating the measuring cell.

Table 3
Properties of the sensors compared with other ammonia gas sensors in the literature.

Dye	Matrix	Dynamic range[a]	Response time	Recovery time	Ref.
BCG[b]	Silica microspheres	1,4 ppb–2 ppm	n.a.	n.a.	[21]
BCG	Al–MCM-41 silica	0,25–2 ppm	2.5 min	24 h	[19]
BPB	PMMA, PVB, EC	n.a.	1 h	hours	[22]
BCG	Cellulose acetate	0–15 ppm	5 min (t_{90})	n.a.	[23]
BCG	Sensor A	10–54 ppm	8 min (t_{90})	2 min (t_{50})	this work
BCG	Sensor B	1–26 ppm	6 min (t_{90})	4 min (t_{50})	this work
BCG	Sensor C	10–66 ppm	< 10 min (t_{90})	8 min (t_{50})	this work
BCG	Sensor D	10–66 ppm	12 min (t_{90})	30 min (t_{50})	this work

[a] The dynamic range is defined as the range between 10% and 90% sensor response.
[b] The analytes were aliphatic amines in this case.

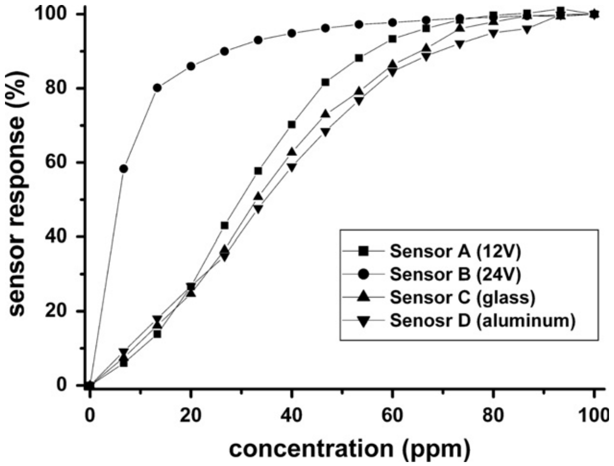

Fig. 2. Normalized calibration curves of the sensors for gaseous ammonia in the 0–100 ppm concentration range.

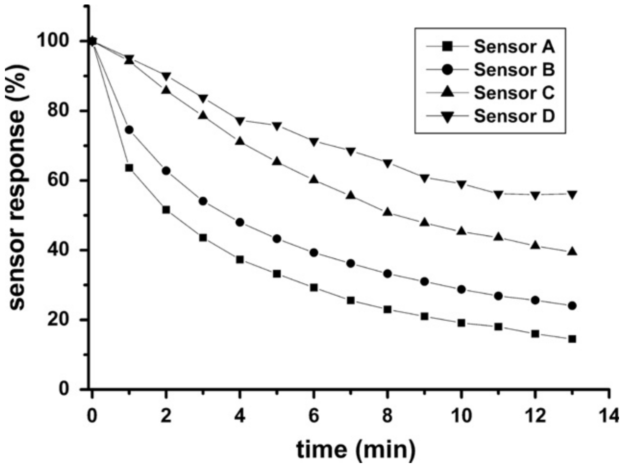

Fig. 3. Normalized recovery curves of the sensors when changing the ammonia concentration from 100 ppm to 0 ppm at $t=0$ s, measured at 620 nm.

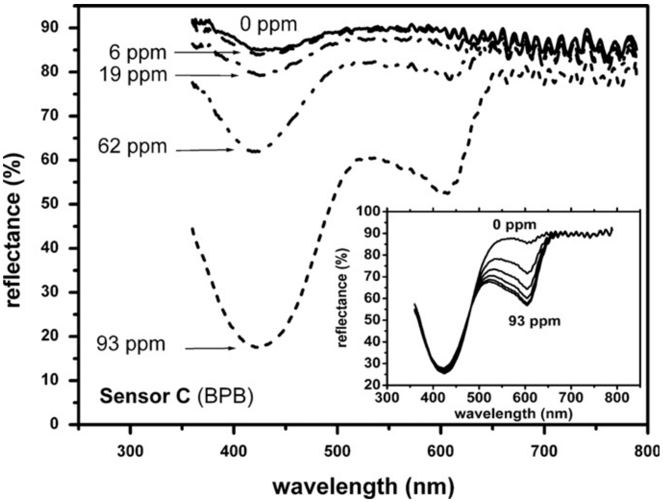

Fig. 4. Spectral changes of sensor C during conditioning with increasing ammonia concentration. Inset: Spectra recorded during calibration of an already conditioned sensor.

3.3. *Properties of the sol–gel sensors*

The sensor layers prepared of ormosils were treated at 80 °C for one hour to complete the gelation, as it was described in Section 2. During the curing, the resulting sensing layers became completely transparent and they had almost no color (pale yellow) when observed with the naked eye. Therefore, a short conditioning process was necessary before performing the first measurement or calibration: the layers were simply exposed with 100 ppm ammonia for 10 min and than flushed with air for 30 min to recover the base line. The conditioning process was followed spectrophotometrically on a Ph-TrEOS layer. A freshly prepared and pretreated sensing layer was cooled down to room temperature, fixed into the flow through cell, ammonia–air mixtures were pumped through, and the reflection spectra were recorded (Fig. 4). It can be clearly seen in Fig. 4 that at the beginning of the measurement (upper curve) the reflectance is very high, varying between 85–90%, depending on the wavelength. The sol–gel layer was almost transparent at this point, the absorbance of the indicator was minimal, and the light was reflected from the built-in mirror of the measuring cell. A small decrease in the reflectance (80–90%) was observed when increasing the ammonia concentration to about 20 ppm within 15 min. Above that concentration (93%) the reflectance dropped at the spectral bands corresponding to the acidic form (380–450 nm, from 85% to 15% reflectance) and to the basic form (550–630 nm, from 90% to 50% reflectance) of the indicator. After 30 min incubation time, the signal became stable. After regeneration (60 min in air), the sensing layer was ready for further measurements. A calibration was performed on the same sensor, while recording the spectra on the whole visible range. After plotting the results a clear isobestic point (at 480 nm) appeared on the graphs, indicating a pure acid–base reaction of the indicator.

The reflection shift obtained during the conditioning was measured in case of freshly prepared layers only. On further calibrations the phenomenon was not present. We note that the curves plotted in Fig. 4. were recorded using Bromophenol blue (BPB) indicator, as this sensing material gives a higher spectral response to ammonia and this way the effect can be observed in an easier way.

Similar effect has been reported previously by Malins et al. [25] for bromocresol purple indicator embedded in methyltrietoxysilane ormosils, and more recently by Chang et al. for BCG covered mesoporous silica adsorbent [19]. In this latter work, freshly prepared sensing membranes were cyclic exposed to ammonia containing sample. In the first cycle a different response was measured compared with the subsequent cycles. The effect was explained by a strong binding of the analyte to the sensing material. According to our results, the explanation of the unusual effect and thus the necessity of conditioning can be extended. It seems, that closing of the sulphono-lactone ring of the indicator can occur during the thermal treatment. On the other hand our ormosils were prepared with acid catalyst, so during the process, the indicators molecules were transformed into their completely protonated form, i.e. their sulfonate groups were also protonated. The pKa of the sulfonate group is around 3, that is lower than of the –OH group (pKa 4–6, depending on the indicator). Thus the sulfonate group is consuming ammonia faster before the –OH group is deprotonated, and the ammonium ions can form an ion-pair with the sulfonate anion. In any case Fig. 4(b) indicates that after the conditioning the sensing layer is responding reversibly to ammonia.

3.4. The difference between glass and aluminum supports

Slight differences were found between sol–gel sensors prepared on glass substrates (C) and anodized aluminum surfaces (D). Although the calibration spectra are similar, the absolute changes are smaller in the case of the latter (Fig. 5). The self-reflectance of the sol–gel coated anodized aluminum is only 35% of the reflectance of the reference mirror of the measuring cell, and moderate interference can be observed on the spectra. Note that for sensors C and D, where the dye was entrapped in a sol–gel film, no reflectance change was measured at 430 nm.

The normalized calibration curves taken from the spectral data are almost coincident, a quasi-linear range was found in both cases between 0 and 80 ppm of ammonia concentration (Fig. 2) Saturation of the sensors occurs over 90 ppm. The concentrations corresponding to the 50% responses are: 34 ppm for sensor C and 36 ppm for sensor D.

The recovery response curve of the aluminum based sensor (D) shows slower regeneration (Fig. 3). Presumably, the ammonia molecules can be entrapped in the pores of the oxide layer, which results in a longer diffusion time. Although the response is slower, excellent mechanical stability was observed in case of this sensor. The sol–gel layer did not peel-off, even no cracking was observed during the experiments as the result of the excellent adhesion between the sol–gel and the nanoporous surface.

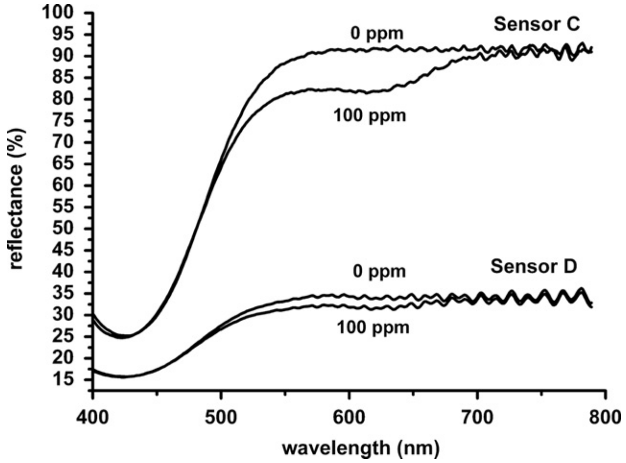

Fig. 5. Reflectivity spectra of sensors C and D for 0 and 100 ppm ammonia concentrations.

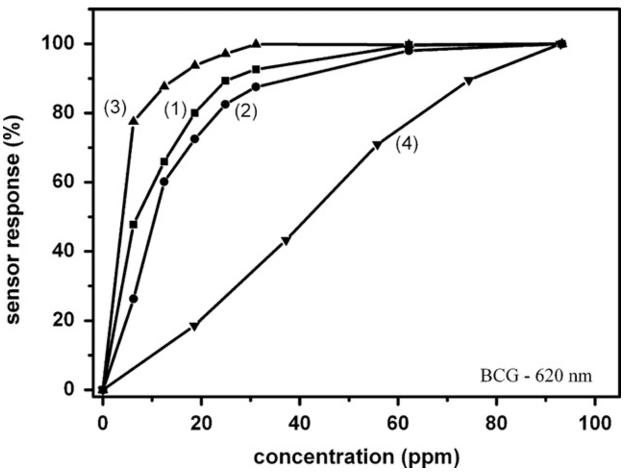

Fig. 6. Normalized calibration curves of sensors prepared with different ormosil precursors. As a comparison, the calibration curve of a sensor identical to sensor A is also shown. We note that no APTES was added to the sensors. (1) Sensor A, (2) MTEOS, (3) DiMe-DiMOS, and (4) Ph-TriEOS.

The effect of the precursor's polarity on the sensing characteristics was also investigated. Methyl-triethoxysilane (MTEOS), dimethly-dimethoxysilane (DiMe-DiMOS) and phenyl-trietoxysilane (Ph-TriEOS) layers were prepared on glass surfaces, and a reference aluminum-oxide based sensor was fabricated at the same time. The aluminum-oxide based sensor was identical to sensor A, while the Ph-TriEOS sensor was identical to sensor C. Calibration curves of all the sensors were taken in the 0–100 ppm nominal ammonia concentration range, and the results were plotted in Fig. 6. It can be stated, that the sensitivity of the sensors is increasing in the phenyl–methyl–dimethyl order. The calibration curve of the aluminum-oxide based sensor lies between the MTEOS and DiMe-DiMOS curves. This curve is slightly different from the one presented in Fig. 2, although the same type of sensor was examined in both experiments. The same difference can be seen in the case of the Ph-TriEOS sensor and sensor C in Fig. 2. This seeming inconsistence informs us about the repeatability of the sensor fabrication, which was found to be lower than 4% in terms of reflectance, measured batch to batch.

4. Conclusion

Anodic oxidation of aluminum ensures a cheap and highly reproducible method for sensor support preparation. The sensitivity, response time and dynamic range can be controlled by the conditions of the electrolysis. The applied voltage has a major contribution on the surface morphology and thus on the sensing properties; at higher anodizing voltage a more sensitive sensor can be prepared.

The porous oxide layer also provides an excellent adhesive surface for sol–gel layers. Due to the self-reflectance of the support, no external mirror is needed for reflectometric measurements. The sensing parameters, such as dynamic range, detection limit or sensitivity, are almost identical with the glass supported sensors. Only the response times are slightly prolonged, due to the gas adsorbing nature of the porous surface of the support.

We note that the response characteristics of these sensors fit the requirements of many agricultural applications, such as ammonia monitoring in stock-yards, breeding farms and composting facilities.

Acknowledgment

The work was partly supported by “Developing Competitiveness of Universities in the South Transdanubian Region” (Grant no. SROP-4.2.1.B-10/2/KONV-2010–0002).

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