

Ammonium- and Nitrate-Selective All-Solid-State Microelectrodes Based on AgI-Ag₂O-V₂O₅ Glass Transducer

by Renata Mamińska¹, Marta Kucharek¹, Paweł Jozwiak², Jerzy Garbarczyk²,
Artur Dybko¹ and Wojciech Wróblewski^{1*}

¹ Faculty of Chemistry, Warsaw University of Technology,
ul. Noakowskiego 3, 00-664 Warsaw, Poland

² Faculty of Physics, Warsaw University of Technology,
ul. Koszykowa 75, 00-662 Warsaw, Poland

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AgI-Ag₂O-V₂O₅ glasses of mixed ionic and electronic conductivity were used as planar transducers for construction of all-solid-state NH₄⁺- and NO₃⁻-selective microelectrodes. The sensors were prepared by direct deposition of the PVC-based membrane of an appropriate composition onto the transducer surface. Working parameters of the obtained internal solution-free miniaturized ion-selective electrodes were tested under flow conditions. The designed electrodes exhibited good long-term stability and high selectivity towards primary ions, comparable to the selectivity of conventional ion-selective electrodes based on PVC membranes containing nonactine and quaternary ammonium salts. The results have proven that AgI-Ag₂O-V₂O₅ glass material can be used for preparation of cheap, simple in structure all-solid-state ion-sensitive microelectrodes.

Kompozyt AgI-Ag₂O-V₂O₅, wykazujący mieszane przewodnictwo jonowo-elektronowe, zastosowano jako planarny przetwornik w elektrodach na stałym podłożu, selektywnych na jony NH₄⁺ oraz NO₃⁻. Miniaturowe elektrody jonoselektywne otrzymano przez nałożenie membran z plastifikowanego poli(chloru winylu) bezpośrednio na powierzchnię przetwornika. Parametry pracy tak skonstruowanych elektrod wyznaczono w układzie przepływowym. Charakteryzowały się one wysoką selektywnością na jony główne, porównywalną z selektywnością klasycznych elektrod jonoselektywnych wykorzystujących nonaktyne oraz czwartorzędowe sole amoniowe, oraz dobrą stabilnością długoterminową. Otrzymane wyniki wykazały, że szklisty kompozyt AgI-Ag₂O-V₂O₅ może być stosowany w konstrukcji prostych i tanich jonoselektywnych mikroelektrod na stałym podłożu.

* Corresponding author. E-mail: wuwu@ch.pw.edu.pl; Fax: +48-22 234 5631

Traditional glasses exhibit network-like architecture comprising main network-forming component (*e.g.* SiO_2 , Al_2O_3) and a network modifier (*e.g.* Na_2O , Li_2O), which makes the structure of a glass more open and lowers its transition temperature. Chalcogenide glasses are the most important and popular in potentiometry. These are inorganic materials containing one or more chalcogen elements: S, Se, or Te, but not O, in conjunction with more electropositive elements (most commonly As and Ge) [1–4]. Chalcogenide glasses are less robust and weaker bonded materials than oxide glasses. Nevertheless, potentiometric sensors with chalcogenide glass membranes are in many cases superior to crystalline membrane electrodes, *e.g.* they exhibit higher durability in acidic and redox media than crystalline electrodes. A very important feature of chalcogenide glasses is the possibility of ion sensitivity control by changing the glass structure at the molecular level (*e.g.* $\text{CdS-Ag}_2\text{S-As}_2\text{S}_3$ glass is sensitive to Cd^{2+} ions, while $\text{PbI}_2\text{-Ag}_2\text{S-As}_2\text{S}_3$ glass is sensitive to Pb^{2+} ions). Since the synthesis of such material is carried out from pure elements in quartz ampoules under the pressure of 0.1–0.01 Pa, it is easy to obtain a glass of required composition and sensitivity. This feature was exploited extensively by the group of Vlasov, who developed solid-state electrodes sensitive to many ions (*e.g.* Pb^{2+} , Ag^+ , Cu^{2+} , Fe^{3+}) based on chalcogenide glass membranes of different composition [1, 5–8]. Chalcogenide glasses were firstly used as bulk membranes [1], but pulsed laser deposition and sputtering techniques allowed obtaining thin glassy films useful for fabrication of ion-selective electrode microstructures [9–11]. Preparation of microsensors based on thin films of chalcogenide glass for detection of Hg^{2+} and Cd^{2+} ions has been already reported [10, 11]. Thin layer (15–30 nm) of Cu-As-Se glass has been also applied as a Cu^{2+} -sensitive membrane of a microsensor for flow-through and flow-injection analysis [12].

Further studies on ionic glasses led to the conclusion that the best conducting glass should contain high concentration of silver iodide [13]. High mobility of silver ion and relatively simple structure of glass network make these materials useful for the fast ion transport studies in the glassy phase. Ionically conducting glasses may be used also as solid electrolytes or membranes sensitive to specific ions (*e.g.* Na^+ , Li^+). Such glasses are highly resistance to acidic solutions, similarly to chalcogenide glasses. Moreover, the application of vitreous materials involves the possibility of constructing multilayered sensing systems by stacking several thin glass layers. Multilayered sensing system for detection of Na^+ ions based on $\text{NaI-Ag}_2\text{O-B}_2\text{O}_3\text{-P}_2\text{O}_5$ glass has been proposed by Guessous *et al.* [14]. The system consisted of several thin films stacked together: chromium/silver/ionic bridge/sensitive membrane (Na^+ -sensitive aluminosilicate glass). However, despite favorable electrochemical properties of Ag^+ -doped glasses, only few examples of their application as ion-sensitive membranes in potentiometric electrodes have been described in the literature.

In this paper, AgI-Ag₂O-V₂O₅ glass composite (40% AgI, 30% Ag₂O, 30% V₂O₅) of mixed ionic and electronic conductivity has been applied as a planar transducer in all-solid-state microelectrodes based on polymeric membranes. The presence of a glass modifier (Ag₂O) and a dopant (AgI) in this material provides ionic conduction *via* Ag⁺ ions, whereas electronic conduction is preserved due to the presence of V⁴⁺ and V⁵⁺ ions acting as electron hopping centers *via* oxygen bridge between vanadate polyhedra [15]. Within the composite structure, silver ions participate in several types of interactions: some Ag⁺ ions form strong bonds or interact weakly with the glassy network, while some others are surrounded by I⁻ ions. It has been proposed that Ag⁺ surrounded by I⁻ exhibit higher mobility than other Ag⁺ ions, giving rise to high ionic conductivity. Coupled conductivity of the whole material allows one to eliminate the internal electrolyte phase and to place the plasticized PVC membranes directly onto the glass surface.

For our investigations, we have chosen NH₄⁺- and NO₃⁻-selective membranes since fast and accurate determination of these ions is of special interest in biology, medicine, soil science, and environmental protection. Concentration of these ions is an important indicator of natural water quality and sewage purification efficiency; also monitoring of the level of nitrogen-based species in ground-, surface-, and wastewater, as well as in wastewater treatment process control is crucial. Since most methods used for determination of ammonium and nitrate ions are expensive and time-consuming, the development of simple and cheap sensors for the real-time ion monitoring seems to be very desirable.

EXPERIMENTAL

Chemicals

All inorganic salts were of analytical grade and were obtained from Fluka. 0.1 mol L⁻¹ standard stock solutions were prepared in redistilled water. Working solutions were obtained after appropriate dilution of stock solutions. Ammonium-sensitive ionophore – nonactine, quaternary ammonium salt (anion exchanger) – tetradodecylammonium nitrate (TDDAN), lipophilic salt – potassium tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (KTFPB), high molecular mass poly(vinylchloride) (PVC), plasticizers: bis(2-ethylhexyl) sebacate (DOS) and o-nitrophenyl octyl ether (o-NPOE) were purchased from Fluka. Freshly distilled tetrahydrofuran (THF) from Fluka was used as a solvent for membrane components.

Fabrication of AgI-Ag₂O-V₂O₅ glass

The rapid quenching technique (melt quenching) was used for the fabrication of AgI-Ag₂O-V₂O₅ glass material. Details of the glass preparation method are described elsewhere [16]. Appropriate amounts of pre-dried AgI, AgNO₃ (POCH, Poland) and V₂O₅ (ABCR) were thoroughly mixed in a mortar. Alumina crucibles filled with the mixture were placed in electric furnace (600°C for 10 min and 700°C for 5 min in air).

The molten mixture was rapidly poured out onto a stainless-steel plate and immediately covered with another stainless-steel plate. The obtained composite layer (0.5 mm in thickness) containing 40% of AgI, 30% of Ag₂O, and 30% of V₂O₅ was cut into squares (5 mm × 5 mm) to obtain transducer samples. Dimensions of the transducers matched the previously constructed flow-through cell [17].

AC impedance spectroscopy (IS) was applied to determine total electrical conductivity of glass transducers. Gold electrodes were sputtered onto opposite sides of polished glass samples. The measurements were performed at the room temperature using a Solartron 1260 Analyzer and applying a small AC voltage signal and recording the current response. The spectra were measured in the 100 mHz–10 MHz frequency range and the amplitude of AC signal was set to 30 mV RMS in a two-electrode mode. Ionic (1.80×10^{-3} – 1.85×10^{-2} S cm⁻¹) and electronic (1.11×10^{-3} – 3.91×10^{-3} S cm⁻¹) conductivities were determined based on the numeric analysis of the spectra (equivalent circuit approach). Mean values of electronic and ionic transference number equaled 0.30 ± 0.15 and 0.70 ± 0.15 , respectively [18].

Preparation of microelectrodes

AgI–Ag₂O–V₂O₅ was used as a planar transducer for the construction of all-solid-state microelectrodes. Plasticized PVC membranes selective to NH₄⁺ and NO₃⁻ were deposited directly onto the glass surface. Basic membrane solution contained 1% (m/m) of nonactine or tetradodecylammonium nitrate, 50 mol% with respect to ionophore of KTFPB (NH₄⁺-selective membrane), 32–33% (m/m) of PVC, 65–66% (m/m) of DOS (NH₄⁺-selective membrane) or o-NPOE (NO₃⁻-selective membrane). The components (~ 100 mg) were dissolved in 0.5 mL of freshly distilled THF. The resulting membrane solutions (7 μL) were deposited onto the transducer surface previously cleaned with distilled water and methanol. After evaporation of the solvent, miniaturized sensors were mounted in a flow-through cell [17] and conditioned for 3 days in 0.01 mol L⁻¹ NH₄NO₃ aqueous solution. Five ion-sensitive microelectrodes of each membrane composition were prepared.

Measurements

Potentiometric measurements were carried out in an automated measuring system, which consisted of a peristaltic pump (Minipuls 3, Gilson), a burette (Dosimat 665, Metrohm), and a data acquisition PC-based system (with 16-channel amplifier: EMF-16) with LabView application [19]. Calibration plots of the studied microelectrodes were determined in a flow-through cell in the solution of NH₄⁺ and NO₃⁻ ions in the concentration range 10⁻⁶–10⁻⁵ mol L⁻¹ in the presence of 0.1 mol L⁻¹ interfering ions (0.01 mol L⁻¹ in case of K⁺), pH = 5–6. Response characteristics were measured by increasing stepwise the activity of primary ion by 0.5 pX. Calibration plots and selectivity coefficients were studied within 3 months in order to evaluate long-term stability of the prepared microelectrodes. A customized Ag/AgCl electrode with a double junction containing 1 mol L⁻¹ CH₃COOLi was used as a reference electrode. The measurements were carried out at 20°C.

A non-linear least squares fitting of the Nikolski–Eisenman equation to the experimental data was applied to calculate the values of selectivity coefficients: logK (NH₄⁺, M⁺) and logK (NO₃⁻, X⁻) (theoretical slope was assumed) [20]. Ion activities in aqueous solutions were calculated according to the Debye–Huckel approximation. Non-linear regression method was based on the Levenberg–Marquardt algorithm and was carried out using Origin 6.0 (Microcal Origin).

RESULTS AND DISCUSSION

Potentiometric properties of AgI-Ag₂O-V₂O₅ glasses have been investigated in our previous paper [18]. Due to their composition, glass structures exhibited selectivity and sensitivity similar to these of AgI crystalline membrane electrodes. For this reason, unmodified glass material could be used for construction of silver- and halide-sensitive all-solid-state microelectrodes. Despite their satisfactory characteristics, AgI-Ag₂O-V₂O₅ microelectrodes showed poor reproducibility of the standard potential – for five structures E° varied in the range ± 50 mV.

Due to the mixed electronic-ionic conductivity, AgI-Ag₂O-V₂O₅ glass can also be applied as ion-to-electron transducer in polymeric membrane all-solid-state microelectrodes, in which the internal electrolyte (or any other layer mediating charge transfer at the membrane/transducer interface) is eliminated. In such an arrangement, ion-sensitive layer is placed on the transducer surface and ion-to-electron signal transduction takes place within the glass structure. Preliminary results concerning internal solution-free microelectrodes based on model valinomycin-based PVC membranes [18] have initialized further studies described in this paper.

PVC membranes containing nonactine as a neutral carrier and tetradodecylammonium nitrate as a conventional anion exchanger have been proposed to develop all-solid-state NH₄⁺- and NO₃⁻-selective microelectrodes for environmental flow-cell analysis. Calibration plots obtained for these microelectrodes were determined in the flow-through cell in 0.1 mol L⁻¹ and 0.01 mol L⁻¹ solutions of different interfering ions. Figures 1 and 2 present calibration curves of NH₄⁺- and NO₃⁻-selective microelectrodes measured in 0.1 mol L⁻¹ NaCl and 0.1 mol L⁻¹ Na₂SO₄ solutions, respectively. In both cases, experimental data were in good agreement with theoretical Nikolski–Eisenman equation, similarly as it was observed for K⁺-selective microelectrodes based on AgI-Ag₂O-V₂O₅ transducers [18].

Mean values of selectivity coefficients determined using the non-linear least squares fitting against several interfering ions are presented in Table 1. Theoretical responses and selectivity pattern of the designed microsensors, comparable to classical ion-selective electrodes based on the same membrane composition, have proven their proper fabrication procedure. It was assumed that Ag⁺ and/or K⁺ exchange is responsible for the charge transfer at the glass/polymeric membrane interface. The only drawback of NH₄⁺- and NO₃⁻-selective microelectrodes was their limited reproducibility in terms of ion selectivity (in certain cases selectivity coefficients varied in the range ±0.40, see Tab. 1). However, the constructed microsensors were characterized by quite good reproducibility of the standard potential, *i.e.* the differences in measured E° values of four NH₄⁺- and NO₃⁻-selective microelectrodes did not exceed ±40 mV and ±25 mV, respectively. Reproducibility of the standard potential was

significantly better than in case of glass-based K^+ -selective microelectrodes (± 85 mV for 5 microsensors) [18].

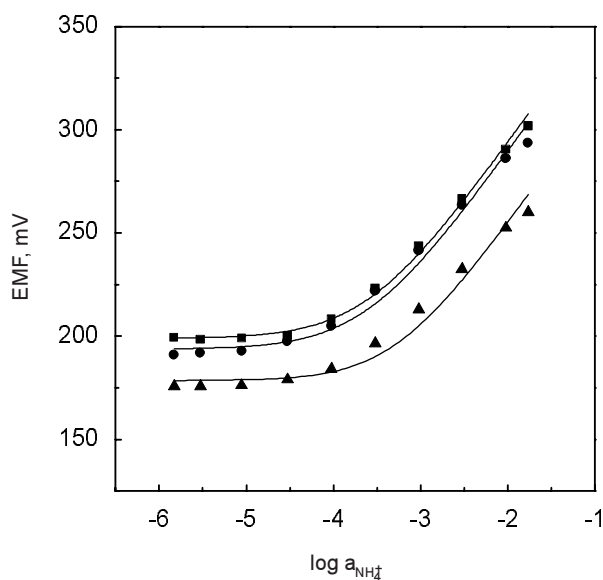


Figure 1. Calibration plots of three NH_4^+ -selective microelectrodes with $AgI-Ag_2O-V_2O_5$ transducer determined in $0.1 \text{ mol L}^{-1} NaCl$

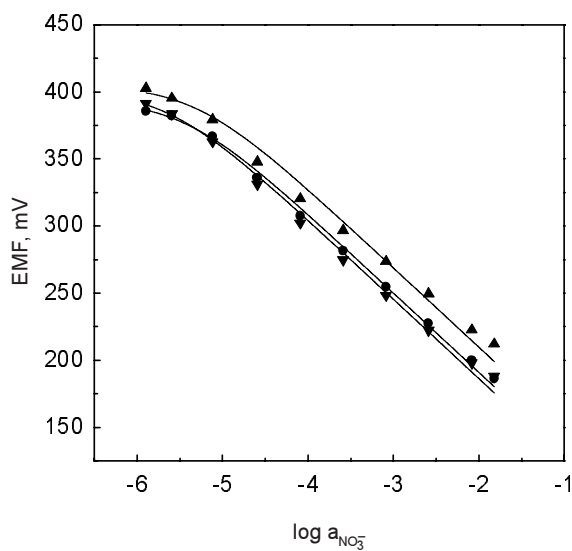


Figure 2. Calibration plots of three NO_3^- -selective microelectrodes with $AgI-Ag_2O-V_2O_5$ transducer determined in $0.1 \text{ mol L}^{-1} Na_2SO_4$

Table 1. Selectivity coefficients: a) $\log K(\text{NH}_4^+, \text{M}^+)$ of NH_4^+ -selective microelectrodes based on $\text{AgI-Ag}_2\text{O-V}_2\text{O}_5$ transducers (mean values calculated for 4 sensors); b) $\log K(\text{NO}_3^-, \text{X}^-)$ of NO_3^- -selective microelectrodes based on $\text{AgI-Ag}_2\text{O-V}_2\text{O}_5$ transducers (mean values calculated for 4 sensors)

a)

Interfering ion M^+	$\log K(\text{NH}_4^+, \text{M}^+)$
K^+	-0.35 ± 0.20
Na^+	-2.30 ± 0.20
Li^+	-3.30 ± 0.40
Ca^{2+}	-3.50 ± 0.40

b)

Interfering ion X^-	$\log K(\text{NO}_3^-, \text{X}^-)$
Br^-	-1.30 ± 0.20
Cl^-	-2.30 ± 0.25
HCO_3^-	-4.50 ± 0.40
SO_4^{2-}	-4.30 ± 0.20

Stability of the potential of microelectrodes was examined within 24 h under continuous flow conditions in $0.01 \text{ mol L}^{-1} \text{NH}_4\text{NO}_3$ solution. During this time, potential drift of all-solid-state microsensors did not exceed 5–20 mV. However, for some microelectrodes of both types the potential increased by 30–40 mV during the first 2 h of the experiment.

Long-term stability is one of the most important parameter of a sensor, which determines its analytical applicability. Long-term stability of $\text{AgI-Ag}_2\text{O-V}_2\text{O}_5$ -based microelectrodes was investigated by measuring their responses towards primary ions in $0.1 \text{ mol L}^{-1} \text{NaCl}$ solution during 3 months. Calibration lines were plotted every week. They are shown in Figures 3 and 4 (for clarity, only the characteristics of exemplary microelectrodes determined every two weeks are depicted). Selectivity coefficients of both types of microelectrodes were satisfactorily stable. They varied in the ranges $\log K(\text{NH}_4^+, \text{Na}^+) = -2.35 \pm 0.20$ and $\log K(\text{NO}_3^-, \text{Cl}^-) = -2.40 \pm 0.25$ confirming that the electrodes did not lose their selectivity. Good repeatability of the sensor response, *i.e.* good stability of the standard potential in time ($\pm 10\text{mV}$) was also measured during 7 weeks for NH_4^+ -selective microelectrodes.

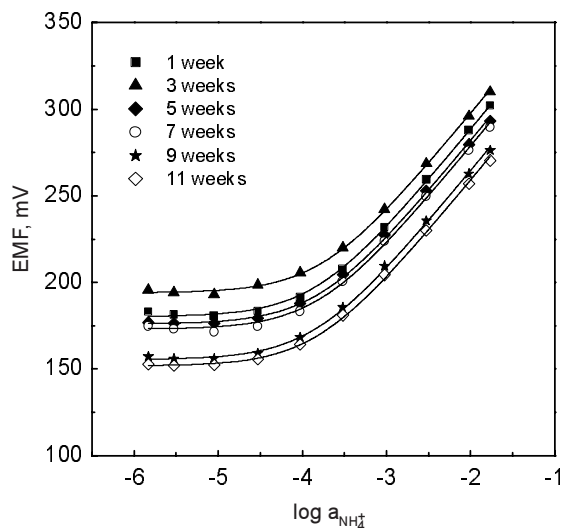


Figure 3. Calibration plots of NH_4^+ -selective microelectrode with $\text{AgI-Ag}_2\text{O-V}_2\text{O}_5$ transducer measured within 3 months in $0.1 \text{ mol L}^{-1} \text{ NaCl}$

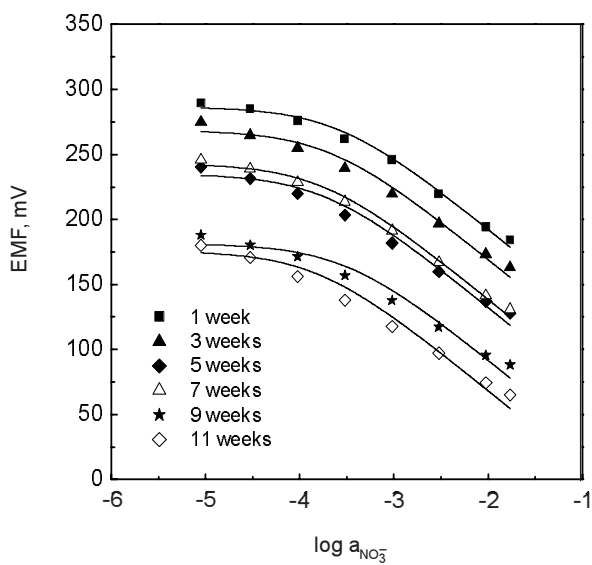


Figure 4. Calibration plots of NO_3^- -selective microelectrode with $\text{AgI-Ag}_2\text{O-V}_2\text{O}_5$ transducer measured within 3 months in $0.1 \text{ mol L}^{-1} \text{ NaCl}$

Long-term potential stability of NO_3^- -selective membranes was worse as the variations of E° in the range ± 25 mV were noticed during 7 weeks. However, it is important to emphasize that the calibration plots of the investigated microsensors tended to shift towards lower potential values, which was especially pronounced for the responses determined 9 and 11 weeks after preparation of the electrodes (this effect was also noticed for glass-based K^+ -selective microelectrodes [18]). The obtained results led to the conclusion that reliable lifetime of NH_4^+ - and NO_3^- -selective all-solid state microelectrodes is limited to 2 months and practical application of such microsensors requires frequent calibration cycles.

CONCLUSIONS

The studies presented in this paper have proven that $\text{AgI-Ag}_2\text{O-V}_2\text{O}_5$ glass can be used as an ion-to-electron transducer in all-solid-state polymeric membrane microelectrodes for flow-cell analysis. The applied glass material exhibited mixed electronic-ionic conductivity and due to this fact architecture of the sensor could be simplified by eliminating the internal electrolyte layer. The developed NH_4^+ - and NO_3^- -selective microelectrodes showed model selectivity pattern, favorable long-term stability, and their responses towards primary ions agreed excellently with the theoretical ones. A systematic decrease of the electrode potential in time was probably related to the formation of a solution layer between the glass surface and the polymeric membrane. This phenomenon will be investigated in our further studies. However, the problem of limited time stability of the signal can be overcome in practice by frequent calibration of the microsensors.

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REFERENCES

1. Vlasov Y.G. and Bychkov E.A., *Ion-selective Electr. Rev.*, **9**, 5 (1987).
2. Vlasov Y.G., Bychkov E.A. and Legin A.V., *Talanta*, **41**, 1059 (1994).
3. Seddon A.B., *Journal of Non-Crystalline Solids*, **184**, 44 (1995).
4. Guessous A., Sarradin J., Pradel A. and Ribes M., *Solid State Ionics*, **70/71**, 368 (1994).
5. Vlasov Y.G., Bychkov E.A. and Medvedev A.M., *Anal. Chim. Acta*, **185**, 137 (1986).
6. Vlasov Y.G., Bychkov E.A. and Selsenev B.L., *Sens. Actuators B*, **2**, 23 (1990).
7. Legin A.V., Bychkov E.A., Selsenev B.L. and Vlasov Y.G., *Sens. Actuators B*, **26/27**, 377 (1995).
8. Legin A.V., Vlasov Y.G., Rudnitskaya A.M. and Bychkov E.A., *Sens. Actuators B*, **34**, 456 (1996).

9. Mourzina Y.G., Schubert J., Zander W., Legin A., Vlasov Y.G., Luth H. and Schoning M.J., *Electrochim. Acta*, **47**, 251 (2001).
10. Guessous A., Papet P., Sarradin J. and Ribes M., *Sens. Actuators B*, **24/25**, 296 (1995).
11. Guessous A., Sarradin J., Papet P., Elkacemi K., Belcadi S., Pradel A. and Ribes M., *Sens. Actuators B*, **53**, 13 (1998).
12. Bychkov E.A., Bruns M., Klewe-Nebenius H., Pfennig G., Raptis K., Hoffmann W. and Ache H.J., *Sens. Actuators B*, **26/27**, 384 (1995).
13. El-Damravi G., Hassan A.K. and Doweidar H., *Physica B*, **291**, 34 (2000).
14. Guessous A., Sarradin J., Papet P., Pradel A. and Ribes M., *Sens. Actuators B*, **26/27**, 360 (1995).
15. Garbarczyk J.E., Machowski P., Wasiucionek M. and Jakubowski W., *Solid State Ionics*, **157**, 269 (2003).
16. Wasiucionek M., Garbarczyk J.E., Wnetrzewski B., Machowski P. and Jakubowski W., *Solid State Ionics*, **92**, 155 (1996).
17. Chudy M., Dybko A., Wróblewski W. and Brzózka Z., *Anal. Chim. Acta*, **429**, 347 (2001).
18. Mamińska R., Józwiak P., Garbarczyk J., Dybko A. and Wróblewski W., *Microchim. Acta*, in press.
19. Dybko A., *Metrol. Meas. Syst.*, **VIII**, 263 (2001).
20. Wróblewski W., Chudy M. and Dybko A., *Anal. Chim. Acta*, **416**, 97 (2000).

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