COATED-WIRE TYPE ION SENSITIVE ELECTRODES BASED ON NANOSTRUCTURED ATO THIN FILM

MARIA PAVAI[a], DORU MANCIULEA[b], FIAMMETTA KORMOS[c], IRINA TARSICHE[d]

ABSTRACT. The functional performances of some cation and anion sensitive self-made, coated-wire type ISEs (ion selective electrodes), where the conventional metallic conductor was replaced by nanostructured ATO (antimony doped tin dioxide) thin film are presented. Two different PVC based membranes, cation and anion sensitive, respectively, were coated on ATO films prepared by the sol-gel technique. By using AFM (Atomic Force Microscopy), EIS (Electrochemical Impedance Spectroscopy) and sheet resistance measurements the film nanostructured morphology and the good electrical conductivity, respectively, were established. The cation sensitive ISE shows the best functional characteristics towards K^+: linear response range: 5×10^{-5}-$10^{-1}ML^{-1}$, sensitivity: 56±1 ΔmV/ΔpC, detection limit: 2×10^{-5} $ML^{-1.}$ The anion sensitive ISE shows the best functional characteristics towards NO_3^- : linear response range: 3×10^{-5}-$10^{-1}ML^{-1}$, sensitivity: 55±1ΔmV/ΔpC, detection limit: $1,8\times10^{-5}ML^{-1}$. The life time of the ISEs was 8 days.

Keywords: coated-wire type ISE, ATO, sol-gel.

INTRODUCTION

Nowadays, ISEs are widely used for the quantification of various cationic or anionic species in industry, medicine or environment quality control.

Coated-wire electrodes were first developed in 1971 and refer to a type of ISE in which an electroactive species is incorporated in a thin polymeric (PVC) support film coated directly on a metallic conductor, usually platinum, silver, copper or graphite rods. Electrodes of this type were developed for a wide variety of both organic and inorganic cations and anions [1, 2, 3, 4, 5].

[a] *Chemical Research Center of the Hungarian Academy of Sciences, str. Pusztaszeri 59-67, Budapesta, Ungaria, marcsikam13@yahoo.com*
[b] *Universitatea "Babes-Bolyai", Facultatea de Stiința Mediului, str. Kogălniceanu Nr. 1, RO-40084, Cluj-Napoca, Romania, doru21@yahoo.com*
[c] *Dekra Certifications SRL, str. C. Brâncuşi, nr. 131, RO-400458 Cluj-Napoca, Romania, metti @personal.ro*
[d] *Universitatea "Babeş-Bolyai", Facultatea de Chimie şi Inginerie Chimică, str. Kogălniceanu Nr. 1, Cluj-Napoca, RO-40084, Romania, itarsiche55@yahoo.com*

Literature data show a continuously growing interest in developing new, low cost materials to be used in the construction of electrodes. Among these materials, the ATO thin film plays an important role due to its remarkable electrical and electrochemical properties: good electrical conductivity, large useful potentials range, low double layer capacity and lack of surface phenomena [6].

The paper deals with the study of the functional performances of some self-made coated wire type ISEs obtained by replacing the conventional metallic wire with ATO nanostructured thin film, deposited on glass rod. Two different PVC based membranes, cation and anion sensitive, respectively, were deposited on the ATO thin film. The synthesis route and electrical characteristics of the ATO thin film are also presented.

RESULTS AND DISCUSSIONS

1. Characterization of the ATO nanostructured thin films

The ATO thin films were prepared by the sol-gel technique. In order to establish the electric properties, namely the electric conductivity, of the thin films several parameters were evaluated as follows:

1.1. The number of free charge carriers was evaluated from EIS measurements and by using the Mott-Schottky equation which provides a relationship between the experimentally measured capacitance, the number of free charge carriers and the flat band potential [7, 8]:

$$\frac{1}{C^2} = \frac{2}{\varepsilon\varepsilon^0 eN}(E - E_{fb} - \frac{kT}{e})$$

where: C – differential capacitance, ε - relative static permittivity of the semiconductor, ε^0 – permittivity in vacuum, e- elementary charge, N- number of free charge carriers, E- applied potential, E_{fb}- flat band potential, T- absolute temperature , k- Boltzmann constant.

1.2. The exchange current density was also calculated on the basis of EIS measurements and by using the equation below [8]:

$$i_0 = \frac{RT}{nFR_{ct}A}$$

where: R- the gas constant, T – absolute temperature, n- number of exchanged electrons, F - Faraday constant, R_{ct} - charge transfer resistance, A - electrode surface aria.

1.3. The sheet resistance of the films was evaluated using the four-point method.

The experimental results are summarized in Table 1.

Table 1. Parameters characterizing the electrical conductivity of ATO thin films

Number of charge carriers (N/cm^3)	Sheet resistance (Ω/cm^2)	i_0 (A/cm^2)	R_{ct} (Ω)
$1,5 \times 10^{20}$	42	2×10^{-6}	6500

Considering the experimental data in Table 1, one may see that the ATO thin films prepared according the route described in the experimental section show high number of free charge carriers, relatively large exchange current, low charge transfer resistance, low sheet resistance, meaning an overall good electric conductivity. Therefore the ATO thin film can replace the conventional metallic conductor in the construction of coated-wire type ISEs. On the other hand AFM measurements revealed the nanostructured morphology of the film (particles sizes range between 180-195 nm) (fig. 1) which also contribute to the overall good electrical properties of the thin films.

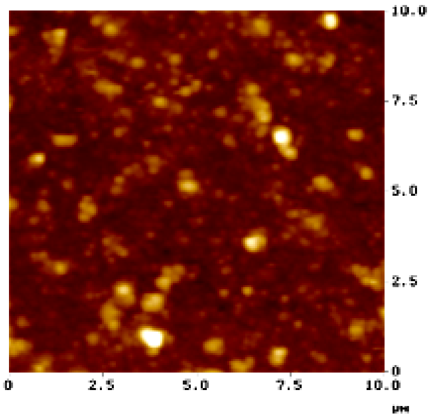

Figure 1. AFM images for the obtained ATO films

2. Functional characteristics of cation and anion ISEs

2.1. Response characteristics of the ISEs

The response of the ISE's obtained by coating the ATO film with the PVC based membrane containing as electroactive compound potassium tetraphenylborate was tested by direct potentiometry towards the following cations: K^+, NH_4^+ and Tl^+. The experimental results representing the mean of two successive measurements performed with two electrodes, under the same experimental conditions are summarized in table 2.

Table 2. Response characteristics of the cation sensitive ISEs

Cation	Dynamic response domain (ML^{-1})	Linear response domain (ML^{-1})	Sensitivity ($\Delta mV/\Delta pC$)	Detection limit (ML^{-1})	Repeatability (mV)
K^+	10^{-5}-10^{-1}	5×10^{-5}-10^{-1}	56±1	2×10^{-5}	±1
NH^+_4	10^{-4}-10^{-1}	2×10^{-4}-5×10^{-2}	53±1	1.1×10^{-4}	
Tl^+	10^{-3}-10^{-1}	5×10^{-3}-8×10^{-2}	52±1	$1,8\times10^{-3}$	

The working pH range was 5-9 and the response time was 30 sec.

According to the experimental data, the ISEs show the best response characteristics towards K^+: wide linear response range, almost Nernstian sensitivity in the linear response range and the lowest detection limit. For this specific ion, measurements were performed from high to low concentration, too. These measurements showed a complete lack of memory effect and a good repeatability. In order to establish the life time of the electrode the measurements were repeated, in the same experimental conditions, for several days. It was found that after 8 days the repeatability and the sensitivity of the electrodes decreased abruptly. Soaking the electrodes in KCl solutions with concentrations ranging between 10^{-4}-10^{-1} ML^{-1} did not improve the electrodes behaviour. It can be assumed that after this period of time a leak of the membrane components occurred and therefore the PVC based membrane must be renewed.

The response of the ISE's prepared by coating the ATO film with the PVC based membrane containing cetylpyridinium chloride as electroactive compound was tested towards the following anions: NO_3^-, ClO_4^-, TFB^- (tetraphenylborate).The experimental results, mean of two successive measurements performed with two electrodes under the same experimental conditions are summarized in table 3.

Table 3. Response characteristics of the anion sensitive ISE

Anion	Dynamic response domain (ML^{-1})	Linear response domain (ML^{-1})	Sensitivity ($\Delta mV/\Delta pC$)	Detection limit (ML^{-1})	Repeatability (mV)
NO^-_3	10^{-5}-10^{-1}	3×10^{-5}-10^{-1}	55±1	$1,8\times10^{-5}$	±1
ClO_4^-	5×10^{-4}-10^{-1}	2×10^{-4}-8×10^{-2}	52±1	1.6×10^{-4}	
TFB^-	10^{-4}-10^{-1}	8×10^{-3}-8×10^{-2}	51±1	$6,8\times10^{-3}$	

As one may see from the data in table 3, the anion sensitive ISEs show the best functional characteristics towards NO_3^-: widest linear response range, lowest detection limit and almost Nernstian sensitivity in the linear response range. The response time was 30 seconds. The measurements performed for this specific ion from high to low concentration showed a slight memory effect especially close to the lower limit of the dynamic response range. Soaking the electrode, between two successive measurements, in a KNO_3 10^{-2}M solution for 30 seconds improved the ISEs response. The life time of the electrodes was 8 days.

2.2. Selectivity

The selectivity study was performed for both cation and anion sensitive ISEs for K^+ and NO_3^- as primary ions by using the fixed interference method. The selectivity coefficients K^{pot} are summarized in table 4.

Table 4. Selectivity study results for the K^+ sensitive ISE

Primary ion	Interferent X	$K^{pot}_{K^+,X}$	Primary ion	Interferent X	$K^{pot}_{NO_3^-,X}$
K^+	NH_4^+	10^{-1}	NO_3^-	Cl^-	10^{-2}
	Na^+	2×10^{-3}		TFB^-	10^{-4}
	Tl^+	2×10^{-3}		ClO_4^-	10^{-1}
	Mg^{2+}	10^{-5}		SCN^-	10^{-2}

The data in table 4 show that both K^+ and NO_3^- sensitive electrodes show a good selectivity towards the investigated interferents. A more extended study of selectivity may open a good perspective for their use in the determination of these ions in real samples.

CONCLUSIONS

The aim of the paper was to study the functional performances of some self-made cation and anion sensitive, coated wire type ISEs, based on ATO nanostructured thin film. The electrical properties of the films obtained by using the sol-gel technique, investigated by EIS and sheet resistance measurements, revealed high number of free charge carriers, relatively large exchange current, low charge transfer resistance, low sheet resistance. The AFM measurements revealed the nanostructured morphology of the obtained films. These characteristics make the prepared ATO films adequate to replace a conventional metallic conductor in the construction of ISEs of this type. Considering the functional characteristics of the ISEs prepared by coating the

ATO film with a PVC based membrane containing potassium tetraphenylborate and cetylpiridinium chloride, respectively, as electroactive compounds, the prepared ISEs can be used especially for the determination K^+ and NO_3^-. The ISEs show wide linear response ranges, almost Nernstian sensitivities, good repeatability and lack of memory effect. Even if the life time of the ISEs is not longer than 8 days, considering the convenient cost of the materials involved, the ISEs based on ATO nanstructured thin films can be considered as useful and reliable tools that can replace successfully the conventional coated-wire type electrodes for quantitative determinations on real samples, too.

EXPERIMENTAL SECTION

1. Materials

$SnCl_4 \times 5H_2O$, $SbCl_3$, n-propanol, ammonia, PVC, tetrahydrofurane, dioctylphtalate, potassium tetraphenylborate, cetylpyridinium chloride, KCl, NH_4Cl, $TlNO_3$, $KClO_4$, KSCN, $Mg(NO_3)_2$, $K_4[Fe(CN)_6]$, $K_3[Fe(CN)_6]$, Na_2SO_4, $CaCl_2$ analytical grade, were purchased from Fluka and Merck.

2. ATO films preparation and characterization

2.1. Sol-gel technique: $SnCl_4 \cdot 5H_2O$ and $SbCl_3$, 45/2 (weight ratio), were dissolved in n-propanol under continuous stirring at 25^0C. After adjusting the pH to 5-6 with dilute ammonia solution, the mixture was heated under stirring at 70^0C for 1 hour. The ATO films were obtained by one step dip-coating using a Nima Tensiometer. Glass rods, with a diameter of 3 mm, were immersed in the sol with a 5mm/min constant speed and withdrawn in the same conditions. The glass rods were previously cleaned with neutral washing powder and rinsed with distilled water. The layer was heated up to 600^0C with a constant rate of 20^0C/minute and annealed for 1 hour.

2.2. Characterization of the ATO films:

2.2.1. Electrical conductivity measurements: the sheet resistance was measured with a self made device using the four-point method.

2.2.2. EIS measurements: were performed with a Solartron 1250 type frequency analyzer and a Solartron 1286 type potentiostat. The electrochemical cell was a three-electrode type. The electrolyte was 0.5M Na_2SO_4 for free charge carriers determination and 10^{-3}M $K_4[Fe(CN)_6]/K_3[Fe(CN)_6]$ for the exchange current density determination, respectively. The working electrode was the ATO film, the reference electrode was SCE type and the counter electrode was Pt. Frequency was varied between 10 mHz-65KHz.

2.2.3. AFM investigation: the surface morphology of the ATO films was investigated using a Nanoscope Dimension 3100 type AFM.

3. Obtaining of ISE's

The glass rods covered with the ATO films, were immersed in a mixture containing: 5% (w/w) PVC, 74.5% (w/w) tetrahydrofuran, 20% (w/w) dioctylphtalate and 0.5% (w/w) electroactive compound: potassium tetraphenylborate and cetylpyridinium chloride, respectively. The covered rods were dried in air for 24 hours. Two ISEs of each type were prepared following this route.

4. Potentiometric measurements

Solutions in the concentration range 10^{-6}-1M of all tested ions were prepared from the appropriate salts. The ionic force was kept constant j=0.1M with $CaCl_2$ 0.033M and Na_2SO_4 0.033M, respectively. The reference electrode was a SCE type. Measurements were performed with an Autolab PGSTAT type ion-meter, accuracy $\pm$0.1 mV, from low to high and high to low concentrations. The pH measurements were done by using a pH combined glass electrode, Senzorom, SRL HC type.

REFERENCES

1. L. Cunningham, H. Freiser, *Analytica Chemica Acta*, **1986**, *180*, 271.
2. Y.M. Issa, N.T. Abdel-Ghani, A.F. Shoukry, M.H. Ahmed, *Analytical Sciences: the international journal of the Japan Society for Analytical Chemistry,* **2005**, *21,* 1037.
3. M.A. Plesha, B.J. Van Wie, J.M. Mullin, D.A. Kidwell, *Analytica Chimica Acta*, **2006**, *570*, 186.
4. N. Alizadeh, H. Teymousian, M. Aghamohammadi, S. Meghdadi, M. Amirnasr, *Sensors Journal, IEEE*, **2007**, *7*, 1727.
5. M. Ardakani, M. Savalati-Niasari, M. Khayat Kashani, *Analytical and Bioanalytical Chemistry*, **2009**, *378*, 1659.
6. J. Ni, X. Zhao, J. Zhao, B. Liu, *Acta Materialia*, **2009**, *57*, 278.
7. C.M. Ragel, M. da Cunha Belo, *Portugaliae Electrochemica Acta*, **2004**, *22*, 295.
8. Xiaoge Gregory Zhang, "Electrochemistry of Silicon and its Oxides" Kluwer Academic/Plenum Publishers, New York, **2001**, chap.1.
9. I.R. Lauks, *Accounts of Chemical Research*, **1998**, *31*, 317.