New electrode substrate for the construction of all solid state ion-selective electrode

Cecylia Wardak, Karolina Pietrzak, Klaudia Morawska

Maria Curie-Sklodowska University, Faculty of Chemistry, , Institute of Chemical Sciences,Department of Analytical Chemistry,
Marie Curie-Sklodowska Square 3, 20-031 Lublin
cecylia.wardak@mail.umcs.pl

Nanostructured surfaces

INTRODUCTION

Ion selective electrodes are among the oldest group of chemical sensors and are now a routine tool for chemical analysis. In addition to applications in laboratory diagnostics or process control, ISEs are often used in monitoring the state of the natural environment for pH measurements and determination of ionic and non-ionic surfactants, heavy metals ions and nitrates in natural waters, wastewater or else plant and animal tissues. Due to many advantages, such as simple construction, low cost of production and small size as well as work in any position solid contact ion-selective electrodes (SCISEs) have attracted more and more attention. Performances of SCISEs depend not only on the properties of ion sensitive membrane but also on the type of internal electrode and intermediate layer between this electrode and the membrane.

PURPOSE AND REALIZATION OF WORK

In this paper properties of potassium and nitrate ion-selective electrodes depending on kind of internal electrode were studied. Three kinds of inner electrode: glassy carbon disc, gold disc and gold microelectrode arrays, were used for sensor construction. The simple coated disc electrodes as well as electrodes with intermediate layer composed with multiwalled carbon nanotubes were prepared and studied.

MEMBRANE COMPOSITION AND ELECTRDE PREPARATION ?

All studied electrodes of the same type have the same membrane based on PVC (poly(vinylchloride. Membrane components and their percentages are shown in the Table 1. Membrane components were dissolwed in THF and added by drop-casting on top of an upside down of inner unmodified or modified electrode (K-ISEs). The electrode surface was modified by drop-casting a mixture containing 10 mg multiwalled carbon nanotubes (MWCNT) dispersed in 1 mL THF.

Table 1. Quantitative and qualitative composition of electrode membrane

Component	Content, % wt./wt.	
	K-ISE	NO_3-ISE
PVC	32	32
Plasticizer	64 (dioctyl sebacate)	62 (o-nitrophenyl octyl ether)
Ionophore	3 (valinomycin)	6 $TDMANO_3$ (tridodecylmethyl ammonium nitrate)
Ionic additive	1 KTPClPB	

REPRODUCIBILITY OF THE POTENTIAL

Reversibility of the electrode potential was tested at concentrations of $^{-4}$ $1x10^{-4}$ mol L^{-1} and $1x10^{-3}$ mol L^{-1} KNO_3. Table 2 presents the mean potential values and standatd deviations of 5 measurements determined forunmodified eltrods.

Table 2. Reproducibility of the electrode potential for tested electrodes a) K-ISESs b) NO_3 -ISEs

a)

Type of internal electrode ▶		GCE	GE	GME
Potential in $1x10^{-4}$	Mean	144.41	204.94	64.66
	SD	2.89	7.40	1.78
Potential in $1x10^{-3}$	Mean	199,28	263,25	119,69
	SD	2.08	6.92	0.86

b)

Type of internal electrode ▶		GCE	GE	GME
Potential in $1x10^{-4}$	Mean	340.97	342.69	298.02
	SD	1.50	4.02	1.32
Potential in $1x10^{-3}$	Mean	285.50	287.70	241.47
	SD	1.26	2.69	0.88

where the internal electrodes are: GCE – glassy carbon electrode, GE – gold electrode, GME – gold microelectrode; Unmod E – unmodified electrode, Mod E – modified electrode and SD - standard deviation.

CALIBRATION CURVES

The calibration curves of the tested electrode were determined in KNO_3 solutions in the concentration range $1x10^{-1}$-$1x10^{-6}$ mol L^{-1} (from low to high and high to low concentrations) by measuring the SEM of the cell made of the tested ion-selective electrode and the reference electrode. The effect of mixing the sample solution on the obtained calibration curves was examined. The results obtained for unmodified and modified electrodes are shown in Fig. 1.

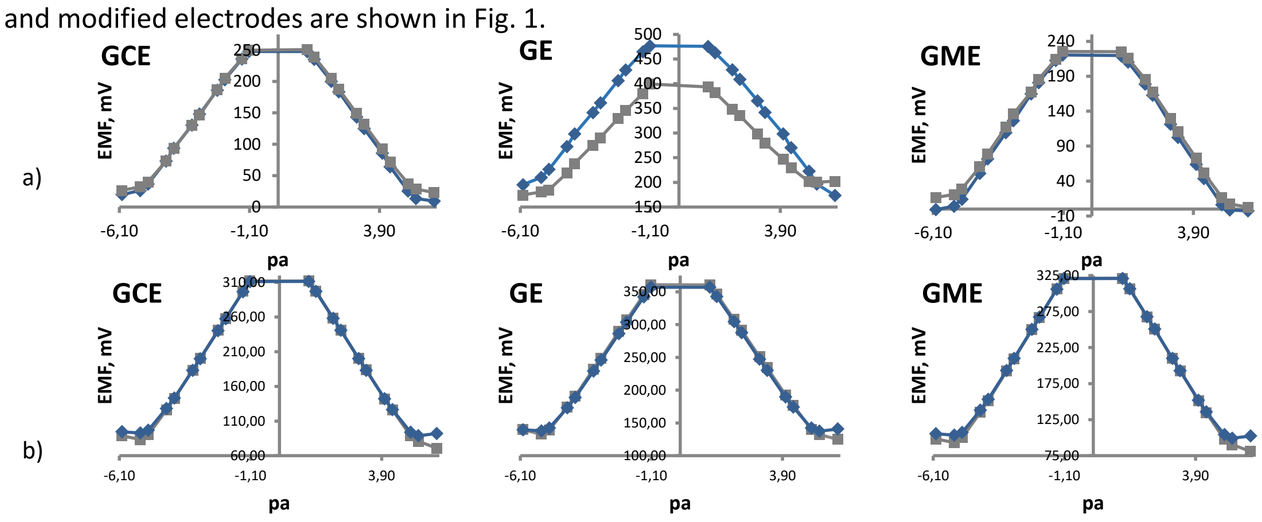

Fig 1. Calibration curves of K-ISEs : a) unmodified and b) modified electrodes determined in mixed (◆) and unmixed (■) solutions

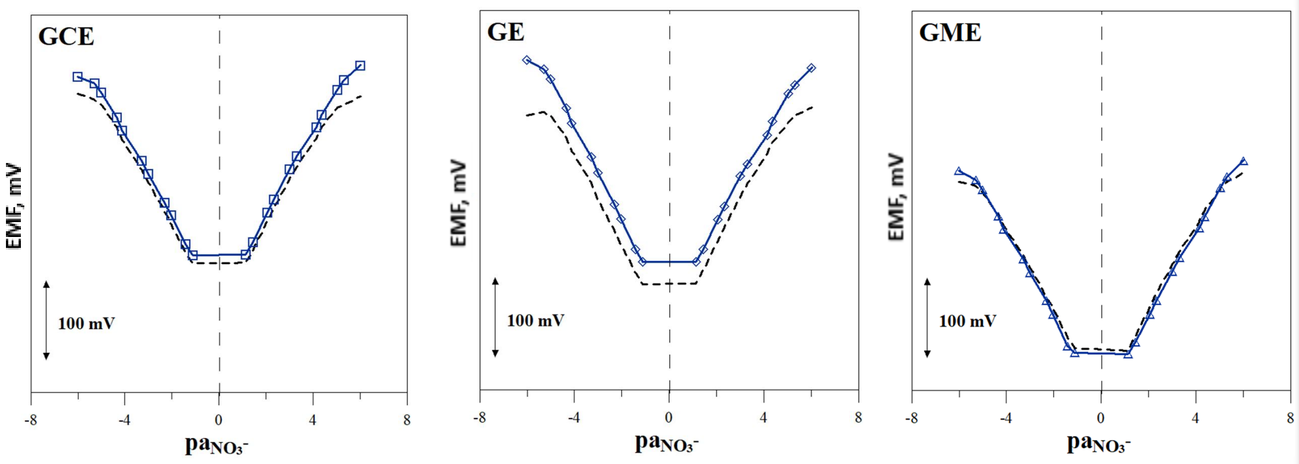

Fig 2. Calibration curves of unmodified NO_3-ISEs determined in mixed (■) and unmixed solutions.

GOLD MICROELECTRODE ARRAY - what is this?

One of the internal electrodes used for construction of ion-selective electrodes with solid contact in this work was gold microelectrode array shown in Fig. 3. It consist of about 400 single microelectrodes and has ca 3 mm diametr.

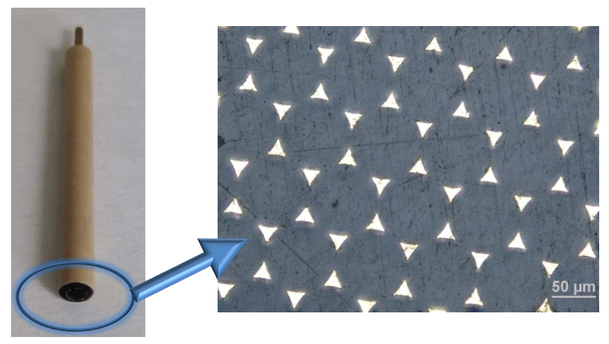

Fig 3. Picture of ion-selective electrode based on gold microelektrode array and SEM image of GME.

POTENTIAL DRIFT

The potential drift for modified and unmodified electrodes was measured in 10^{-1} mol L^{-1} solutions for 3 hours. The obtained dependences for K-ISEs are presented below in Fig. 4.

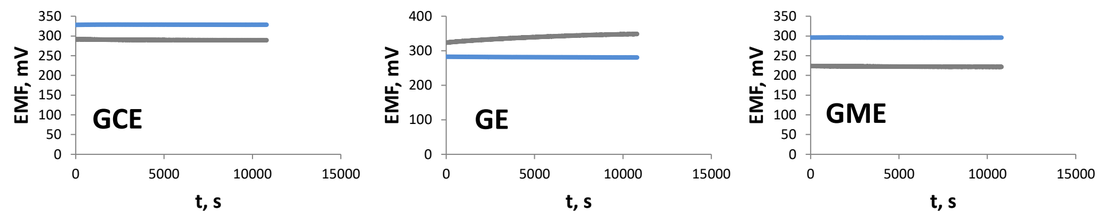

Fig 4. Potential drift for unmodified (■) and modified (■) electrodes

Table 2. Potential drift determined for tested electrodes K-ISESs (unmodified and modified) and NO_3-ISEs (unmodified) in $1x10^{-1}$ mol L^{-1} KNO_3 solutions

Type of internal electrode ▶		GCE	GE	GME
Potential in $1x10^{-1}$, mV/h	Unmodified K-ISE	8.44	9.72	0.72
	Modified K-ISE	0.72	1.40	0.03
	Unmodified NO_3-ISE	4.69	7.45	0.51

SELECTIVITY

The selectivity of the tested electrodes was estimated by determining the selectivity coefficients in relation to the interfering ions (K^+, Ca^{2+}, Mg^{2+}, Li^+ and Na^+ for K-ISEs and SO_4^{2-}, CO_3^{2-}, CH_3COO^-, F^- for KNO_3-ISEs) by means of separate solutions (extrapolating the response curves to ai=aj=1 mol L^{-1}). The results show that the selectivity of the electrodes is not significantly influenced by the kind of internal electrode and its modification.

CONCLUSIONS

Various types of ion-sensitive electrodes sensitive to K^+ and NO ions were tested, differing in the material from which the internal electrode was made. All electrodes exchibited theoretical slope of the characteristic curve and linearity in the concentration range from $1x10^{-1}$ - $5x10^{-5}$ mol L^{-1} KNO_3. Depending on the type of internal electrode, ISEs differed in stability and potential reversibility. The best results were obtained for electrodes obtained on the basis of GME. For these electrodes (even without modification with carbon nanotubes) good measurement results and reproducible course of calibration curves were obtained, regardless of the direction of concentration changes or solution mixing.
The obtained results confirm that the applied new electrode substrate in the form of a gold microelectrode array a promising substrate in the construction of SCISEs.

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