Copper-sensitive ion-selective electrode with solid contact based on copper oxide nanoparticles-multiwalled carbon nanotubes-nanopomposite

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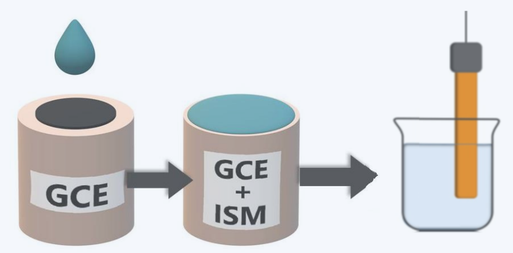
Among the various types of ion-selective electrodes (ISEs), those with solid contact are becoming increasingly popular. In comparison to conventional ISEs they are characterized by unquestionable advantages including small size, simple construction, lower cost of production, and ability to operate in high pressure environments. Moreover they can have various shapes, sizes and can work in any position. Unfortunately solid contact ion-selective electrodes (SCISEs) often exhibited big potential drift and poor reproducibility because of blocked interface between ion-selective membrane with ionic conductivity and electronic conductor.In this paper electrodes sensitive to copper (II) ions, in which copper (II) oxide nanoparticles-multi-walled carbon nanotubes (MWCNTs) composite was used as an additional membrane component to solve this problem and improve electrode performance.

Electrode preparation

Table1. Composition of electrode membrane

	Copper ionophore(IV) [%]	KpTBCl [%]	NPOE [%]	PVC [%]	MWCNTs [%]	MWCNTs/CuONPs nanocomposite [%]
ISE(0)	1,0	0,5	65,5	33,0	-	-
ISE(I)	1,0	0,5	64,5	33,0	1,0	-
ISE(II)	1,0	0,5	63,5	33,0	-	2,0

Preparation of membrane mixture and its homogenization → Drop casting of the membrane mixture onto the surface of the inner electrode (GCE) and evaporation of the solvent (24 hours) → Conditioning of the electrode in the main ion solution $1x10^{-3}$ M



Potentiometric measurements

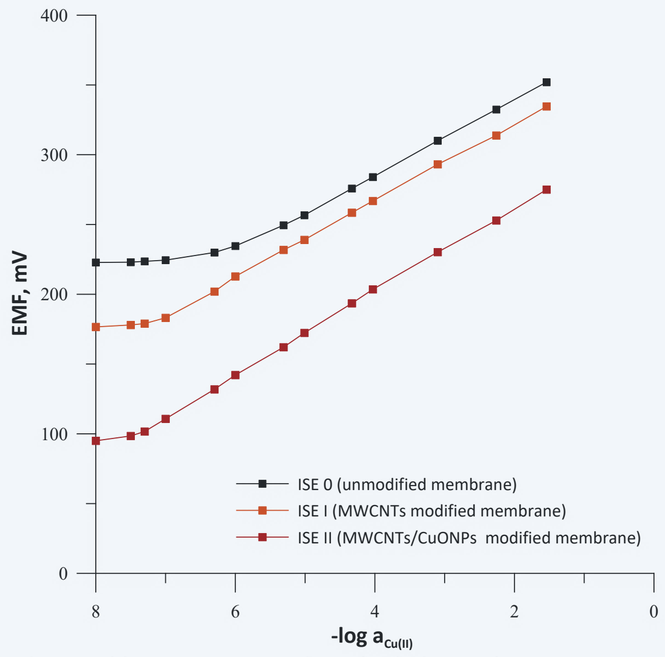


Fig. 1 Calibration curves of studied electrodes

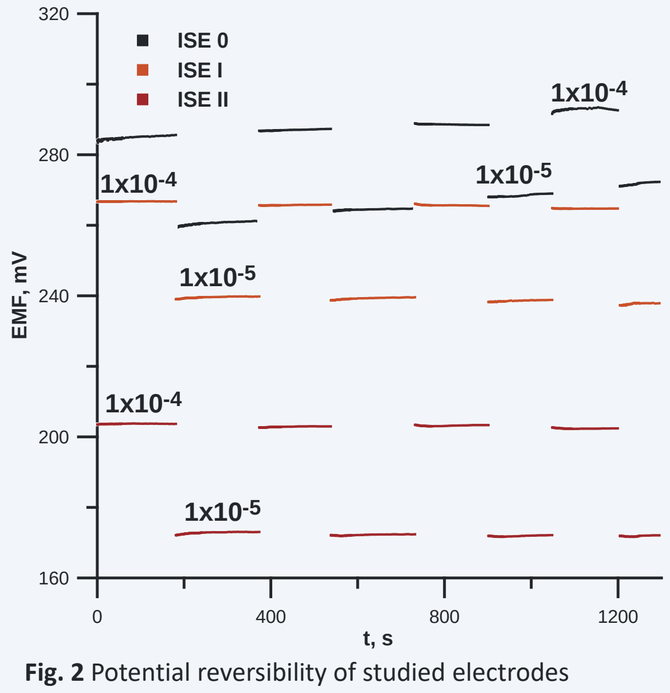


Fig. 2 Potential reversibility of studied electrodes

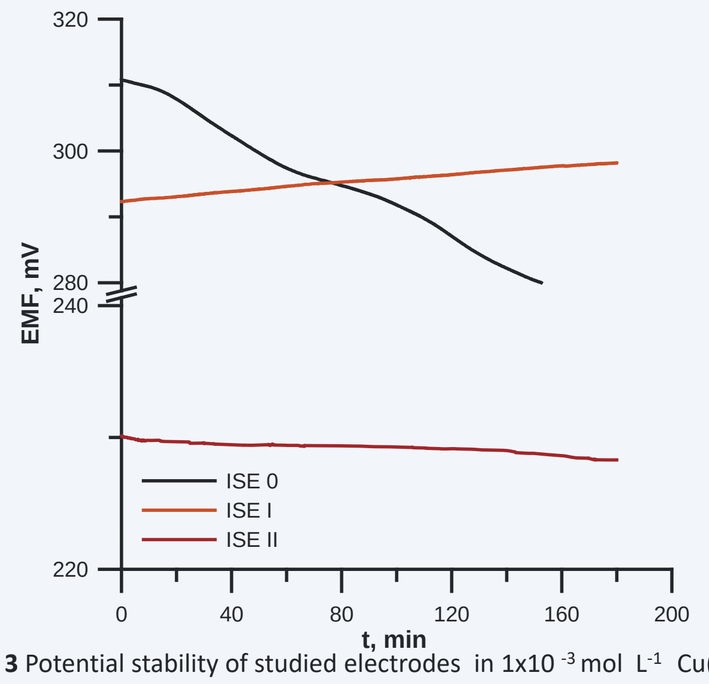
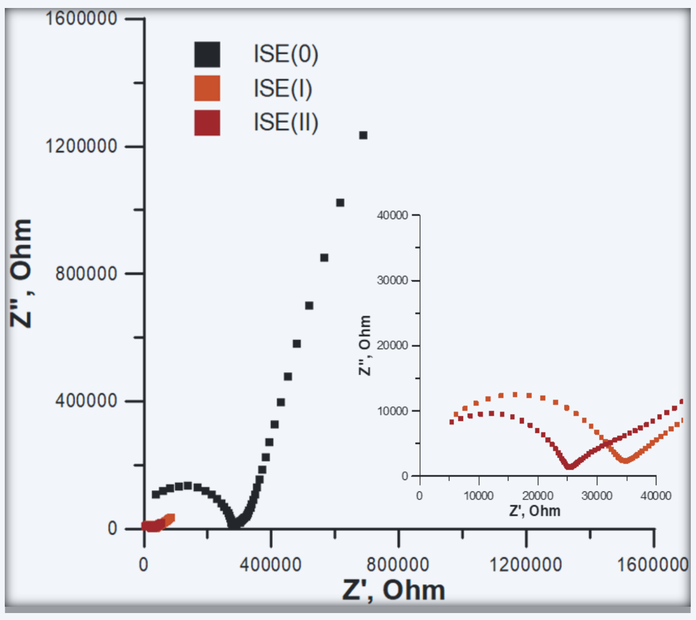


Fig. 3 Potential stability of studied electrodes in $1x10^{-3}$ mol L^{-1} Cu(II) ions. .

EIS measurements



Measurements conditions:

- Frequency range: 0.1-100 kHz
- Amplitude: 10 mV
- Open circuit potential
- Three electrode system:

-working electrode:ISE
-reference electrode: Ag/AgCl
-auxiliary electrode: GCE

- Apparaturs: AUTOLAB (Eco Chemie, Netherlands)
- Software: Nova 2.1.

← **Fig.4** EIS spectra of studied electrodes .

Table2. Comparison of analytical parametres of studied Cu-ISEs

Parameter	ISE(0)	ISE(I)	ISE(II)
Slope [mV/Dec]	28.67	29.71	29.20
Linear range [mol L^{-1}]	1×10^{-6} - 1×10^{-1}	1×10^{-7} - 1×10^{-1}	5×10^{-8} - 1×10^{-1}
Limit of detection [mol L^{-1}]	6.81×10^{-7}	1.24×10^{-8}	4.51×10^{-8}
Short term potential drift [mV/min]	0.183	0.032	0.011
Long term potential drift [mV/day]	5.564	0.296	0.206
Membrane resistance [kΩ]	309	36	27
Double layer capacitance [µF]	45.7	2360	8793