DOI 10.5162/EUROSENSORS2025/MP14

The Effect of Perinone Polymer Potential Polymerization Range on its Effectiveness as a Solid Contact in Ion-Selective Electrodes

Cecylia Wardak[1], Klaudia Morawska[1]
[1] University of Maria Curie-Skłodowska, Faculty of Chemistry, Institute of Chemical Sciences, Department of Analytical Chemistry, Maria Curie-Sklodowska Sq. 3, 20-031 Lublin, Poland
cecylia.wardak@mail.umcs.pl

Summary:

Perinone polymer is the latest type of conductive polymer used in solid contact ion-selective electrodes. This paper presents the application of the above-mentioned perinone polymer in two different potential ranges (-1.3 – 1.45 V and 0 – 1.45V) in potassium-selective electrodes, and the effect of the polymerization range on the basic analytical parameters was determined. The use of the conductive medium applied in both polymerization ranges significantly improved the characteristics of the electrode (higher slope), stability, and reversibility of the electrode.

Keywords: perinone polymer, solid contact, potentiodynamic polymerization, potassium ion-selective electrode

Introduction

Ion-selective electrodes (ISEs) have been developing very rapidly for many decades. Nowadays, the scientific market is dominated by those of the solid contact type (SC-ISEs). Unfortunately, along with the construction of these types of sensors, work began on their improvement – which was and is necessary. This is due to the elimination of the internal solution. For this reason, unmodified SC-ISEs are characterized by poor stability and potential reversibility due to the lack of a medium that acts as a carrier and converter of ions to charge (in the classical liquid-contact version, this role was played by the internal electrolyte). To prevent these disadvantages, an intermediate layer (solid contact) is introduced, which exhibits good ion-to-electron conductivity. Among the materials that are used for this purpose, we can mention carbon derivatives, conducting polymers, or combinations of different materials, so-called composite or hybrid materials[1]. In the present work, perinone polymer (PP) was used as a conducting medium – it belongs to the group of organic conductors. It has all the characteristics that a solid contact should have and performs very well in this role. The effect of the range of potentiodynamic polymerization on the parameters of potassium ion-selective electrodes was compared.

Methods and ISEs preparation

To apply a layer of perinone polymer, pre-prepared glassy carbon electrodes (GCE) were placed in a three-electrode system, where GCE – working electrode, platinum wire – auxiliary electrode, and silver wire – reference electrode were used. Potentiodynamic polymerization was carried out in a saturated solution of perinone polymer (dispersed in 0.1 M solution of tetrabutylammonium hexafluorophosphate in dichloromethane)[2]. Polymerization was carried out in the shorter potential range (0 – 1.45V) for 10 (GCE/10c_PP-SR) and 30 (GCE/30c_PP-SR) cycles and in the wider range (-1.3 – 1.45V) for 10 (GCE/10c_PP-WR) and 30 (GCE/30c_PP-WR) cycles. Electrodes prepared in this way were coated with potassium membrane in three series of 50 µL, every 30 minutes. The control electrode was GCE covered only with the membrane (GCE).

Results and discussion

After the electrodes were conditioned in $1x10^{-3}$ M KNO_3 solution, potentiometric tests were started. To determine whether the electrodes were working properly, calibration was performed using KNO_3 solutions of different concentrations, and calibration curves were plotted for the range of C= $1x10^{-1}$ – $1x10^{-7}$ M. The dependence is shown in Figure 1 for each of the studied electrodes. Based on the responses, the basic parameters were determined (Table 1), which turned out to be the most favorable for GCE/10c_PP-SR – slope 58.51, detection limit – $1.6x10^{-6}$ M. Polymer applied in a narrower potential range in both cases gave us better results (mainly concerning electrode sensitivity). The presence of PP improved the linearity range for the modified ISEs.

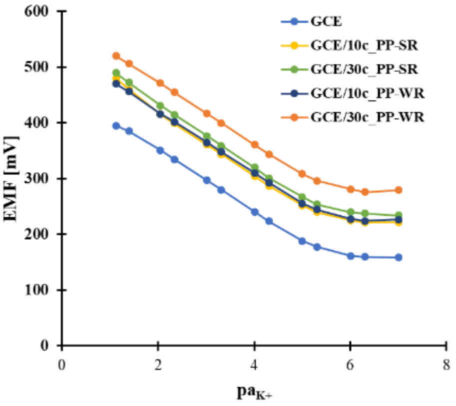

Fig. 1. Calibration curves obtained for each electrode.

Tab. 1: Basic parameters characterizing ion-selective electrodes.

ISE	Slope [mV/dec]	Detection limit [M]	Linearity range [M]
GCE	54.48	$2.9x10^{-6}$	$5x10^{-2}$ – $5x10^{-6}$
GCE/10c_PP-SR	58.51	$1.5x10^{-6}$	$1x10^{-1}$ – $5x10^{-6}$
GCE/30c_PP-SR	57.21	$1.7x10^{-6}$	$1x10^{-1}$ – $5x10^{-6}$
GCE/10c_PP-WR	55.32	$2.4x10^{-6}$	$1x10^{-1}$ – $5x10^{-6}$
GCE/30c_PP-WR	55.29	$2.1x10^{-6}$	$1x10^{-1}$ – $5x10^{-6}$

In addition to calibration, short-term stability was also determined (potential was measured for 2h in $1x10^{-3}$ M KNO_3, and then potential drift values were calculated). The drift values are 2.74, 0.16, 0.59, 0.47, and 0.67 µV/s for GCE, GCE/10c_PP-SR, GCE/30c_PP-SR, GCE/10c_PP-WR, and GCE/30c_PP-WR, respectively. Remarkably, stability improvements were observed for PP-modified electrodes applied in both modes. However, the best values were obtained for PP-modified ISE applied in 10 cycles in the narrow range. Subsequently, the potential reversibility was determined by measuring the EMF alternately at $1x10^{-4}$ and $1x10^{-3}$ M. The curves showing this relation can be found in Figure 2, and the results (standard deviations from the mean value of the potential for 5 measurements, for a certain concentration) are given in Table 2. Similarly, as in the case of potential stability, a significant improvement in this parameter was obtained for electrodes modified with perinone polymer compared to unmodified GCE. Again, the best performing electrode was GCE/10c_PP-SR.

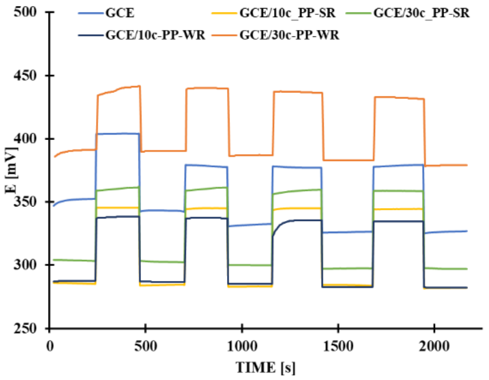

Fig. 1. Reversibility of the potential.

Tab. 2: Standard deviation from mean values for each concentration (n=4) – reversibility of the potential.

ISE	Standard deviation for 10^{-4} M K^+ (n=4)	Standard deviation for 10^{-3} M K^+ (n=4)
GCE	11.06	11.52
GCE/10c_PP-SR	1.01	0.32
GCE/30c_PP-SR	2.72	1.30
GCE/10c_PP-WR	2.90	1.80
GCE/30c_PP-WR	4.97	4.36

As we can assess, the presence of perinone polymer alone (no matter in what number of cycles and in what range of polymerization) contributed to improving the basic parameters of SC-ISEs. However, it should be emphasized that the polymerization range and the number of cycles had a major impact on the quality of the results obtained. The best response, short-term stability and potential reversibility were obtained for GCE/10c_PP-SR. Using a wider range (for 10 and 30 cycles) proved to be a poorer option.

References

[1] Y. Shao, Y. Ying, J. Ping, Recent advances in solid-contact ion-selective electrodes: functional materials, transduction mechanisms, and development trends, *Chemical Society Reviews* 49, 4405-4465 (2020); doi: 10.1039/C9CS00587K

[2] K. Morawska, M. Czichy, P. Janasik, M. Łapkowski, C. Wardak, Novel usage of perinone polymer as solid contact in ion-selective electrodes, *Sensors and Actuators B: Chemical* 422, 136662 (2025); doi: 10.1016/j.snb.2024.136662.