

Improving Analytical Parameters of Ammonium Potentiometric Sensors Using Carbon Nanocomposite

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Summary:

The main goal of this work was to optimize and, at the same time, improve the analytical performance of ammonium ion-selective electrodes with a solid contact. A carbon nanocomposite consisting of multi-walled carbon nanotubes and carbon nanofibers was used as the mediation layer. The results obtained for the modified working electrode were compared with the unmodified (control) electrode. The incorporation of transducer media (carbon nanocomposite) not only improved the response of the electrodes but also favorably affected the stability and reversibility of the potential.

Keywords: ion-selective electrodes, nanocomposite, solid contact, ammonium, carbon

Introduction

With the development of industry and global progress, not only is our civilization evolving, but in many ways this is leading to massive destruction and pollution of the ecosystem. As Paracelsus said “All things are poison, and nothing is without poison; the dosage alone makes it so a thing is not a poison”. This is why monitoring the levels of particular elements and compounds in the soil is so important, and to guard ourselves and our surroundings from exposure to excess levels of different compounds. Ammonium ions are one of the ions to which we should pay particular attention (especially in agricultural areas). Among other things, their excess causes eutrophication of waters, which leads to the destruction of aquatic environments, but is also unhealthy for humans [1]. One of the methods used to monitor NH_4^+ ion levels is potentiometry, in which we use sensors – ion-selective electrodes (ISEs). Our team is engaged in the development of new potentiometric sensors with the type of solid contact, which, due to their imperfection resulting from poor transduction and charge transfer (the result of the inefficiency of this process is poor reversibility and stability of the potential), must be modified by introducing a material that exhibits ion-to-electron conductivity[2]. In this case, our team used a carbon nanocomposite as a solid contact, which significantly improved the performance of the electrode.

Methods and Electrode Preparation

To develop a new type of sensor, ISEs with an inner electrode made of glassy carbon (GCE) were used. Before modification, the GCEs were

cleaned on wetted alumina, on felt, and then cleaned in an ultrasonic bath and rinsed with distilled water. Two sets of electrodes were prepared: (1) a control electrode coated with an ion-sensitive membrane (GCE/ISM) and (2) an electrode coated with a solid contact consisting of carbon nanocomposite and an ion-sensitive membrane (GCE/CNC/ISM). The nanocomposite was created by mixing in a 1:1 ratio multi-walled carbon nanotubes (1.5 mg) and carbon nanofibers (1.5 mg), which were dispersed in 3 ml of tetrahydrofuran. The mixture of nanocomposite was then homogenized by placing it in an ultrasonic bath for 2h. The mixture prepared in this way was spotted onto the GCE surface in a volume of 15 μL . After two hours, a membrane with a total volume of 150 μL was spotted in three series (every 30 minutes). The membrane consisted of 3% nonactin, 0.86% potassium tetrakis(4-chlorophenyl) borate, 30% polyvinyl chloride, and 66.14% bis(1-butylpentyl) adipate. After 24 hours, the electrodes were placed in 1×10^{-3} M NH_4NO_3 to perform conditioning.

Results and Discussion

As a preliminary step, the responses of the tested electrodes were determined by measuring the potential in the concentration range of 10^{-1} – 10^{-7} M (the specified concentrations were obtained using the standard addition method). Based on the obtained values, the dependence of the electromotive force (EMF) on the negative logarithm of the activity of the main ion was determined. Based on the results, the electrodes were characterized by determining the sensitivity (slope) (S), limit of detection (LOD), and range of

linearity (LR) - the results are placed in Table 1. The use of carbon nanocomposite increased the sensitivity (almost Nernst response – 58.41 mV/decade), gently decreased the limit of detection but did not affect the range of linearity.

Tab. 1: Basic parameters determined from the characteristics of the electrodes.

Parameter	GCE/ISM	GCE/CNC/ISM
S [mv/decade]	55.84	58.41
LOD [M]	6.3×10^{-6}	3.9×10^{-6}
LR [M]	10^{-5} - 10^{-1}	10^{-5} - 10^{-1}

Subsequently, the stability of the potential (measurement of EMF in 1×10^{-3} M NH_4NO_3 for 1h) and the reversibility of the potential (alternate measurement of EMF in solutions of 1×10^{-2} , 1×10^{-3} , 1×10^{-4} M NH_4NO_3 successively) were determined. Graphs showing these two parameters for both ISEs are presented in Figure 1. Based on the obtained results, the potential drift (determining stability) and the average potential values with standard deviations for each concentration (describing reversibility) were calculated – Table 2. By introducing a mediation layer in the form of a MWCNTs:CNFs composite, almost 50 times better stability was obtained relative to the non-modified electrode, and an improvement in reversibility was attained. This proves that the use of the above-mentioned composite as a solid contact was a good solution. This proves that the material has excellent ion-to-electron conductivity, as evidenced by the test results obtained.

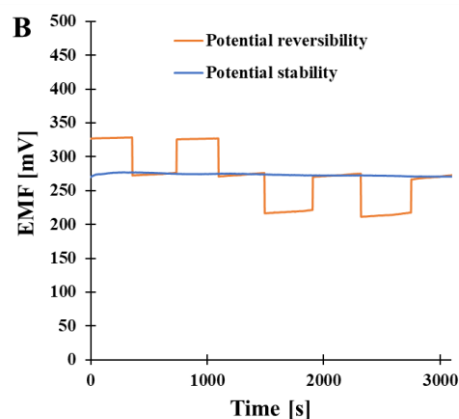
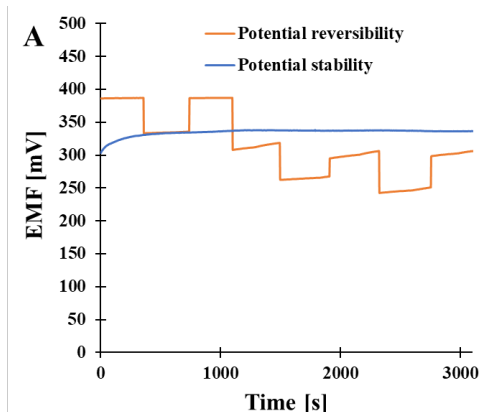


Fig. 1. Potential stability and reversibility for GCE/ISM (A) and GCE/CNC/ISM (B).

Tab. 2: Calculated results for stability and reversibility of the potential.

Parameter	GCE/ISM	GCE/CNC/ISM
Potential drift [$\mu\text{V/s}$]	2.20	0.05
Mean potential value for 10^{-2} M NH_4^+	387.29 ± 0.70	327.67 ± 0.11
Mean potential value for 10^{-3} M NH_4^+	327.14 ± 8.59	276.24 ± 0.18
Mean potential value for 10^{-4} M NH_4^+	258.99 ± 8.34	219.89 ± 1.61

The effect of external conditions, i.e., different illumination of the sample, the presence of oxygen and carbon dioxide in the sample, as well as sensitivity to changes in the redox potential, were also investigated. The electrode modified with the nanocomposite showed an unchanged potential under all the mentioned conditions, while for GCE/ISM, not only a drift of the potential was noted but also a variation. Modification with the carbon nanocomposite had the intended effect – it was possible to improve the parameters of ISEs.

References

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