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Short communication

All-solid-state selective electrodes using carbon black

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ABSTRACT

This study developed new types of all-solid-state ion-selective electrodes based on carbon black (CB). The electrodes were obtained basing on two methods. The first method concerned the addition of the CB as an intermediate layer between an ionophore-doped solvent polymeric membrane and an electrical conductor. The second one used the CB as a polymeric membrane component. The stability of the electrical potential of the new solid-contact electrodes was examined by performing the current-reversal chronopotentiometry and the influence of the interfacial water film was assessed by the potentiometric aqueous-layer test. The performance of the new electrodes was evaluated by the determining K^+ with an ion-selective membrane that contained the well known valinomycin ion carrier. The new electrodes had a Nernstian slope, a high stability, the reproducibility of the standard potential values and a very small potential drift.

1. Introduction

Ion-selective electrodes (ISEs) as important analytical devices have been widely used for the determination of a broad range of ions in clinical and environmental analysis as well as in the process control. The new generation of the ISEs with a solid contact (SC-ISEs) has attracted a lot of attention due to their important advantages over the conventional ISEs with an internal solution [1].

The SC-ISEs based on the coated wire electrodes (CWEs) have been developed as an alternative to the traditional liquid contact ISEs [2]. In CWE, the direct contact of the selective membrane with an electronic conducting phase without the presence of a stable redox pair produces a mixed, non-thermodynamic potential at this interface [3–5]. Under such circumstances, the electrode potential becomes relatively unstable [6].

However, the current development of analytical sciences has led to a need for complete maintenance-free, durable and reliable ion sensors. Therefore over the past years, different research teams have focused on developing new materials that are able to convert effectively an ionic signal into an electronic one [1]. The introduction of conducting polymers (CPs) as ion-to-electron transducers has improved the stability of the CWEs potential [7]. However, several factors have limited the practical usage of CP-based SC-ISEs (i.e. influence of some gases, formation of the water layer between the ion-selective membrane (ISM) and inner contact) [8]. Recently, carbon-based materials such as three-dimensionally ordered macroporous (3DOM) carbon, carbon nanotubes, fullerene or finally carbon cloth and graphene have also been used as ion-to-electron transducers in the SC-ISEs [9–16]. Such carbon materials are insensitive to oxygen or light and did not show any evidence of a water film formation between the ISM and inert solid-contact. These unique properties are unquestionable however the high cost of producing can limit their mass fabrication. In this context, the relatively cheap carbon product – carbon black (CB) was tested as a new material for SC-ISEs.

Carbon black is a great material that has attracted global interest for both its fundamental properties and its applications. It is an extremely fluffy fine powder with a large surface area, composed basically of carbon [17]. There are some active functional groups on the surface of the carbon black. Their nature and number depends of the synthesis or pre-treatment processes [18]. The presence of surface heteroatoms, especially oxygen groups, affects the electrochemical response of the carbon materials. The oxygen groups may determine the wettability by the electrolyte solution or may experience redox reactions [19]. However, there was no oxygen found concerning some kind of carbon blacks, e.g. the conductive carbon black (Printex XE-2). Even after the contact with the atmosphere, there was no reaction with oxygen that took place [20].

One kind of carbon black, namely P-3679, was used as a conductive additive to the ion-to-electron transducer layer based on PVC matrix with plasticizer and ionophore in pH solid-contact electrode. However, the improvement of the potentiometric signal was observed only with the addition of the EI-21 electron-ion-exchanger resin [21].

This communication is the first report that carbon black (CB) can be successfully used as an active ion-to-electron transducer

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layer or as an ion-selective membrane component. The Printex XE-2 CB exhibit many excellent properties such as high conductivity, large surface area, high hydrophobicity and low production cost. Considering the mentioned qualities it becomes obvious that the carbon black is the most advantageous material for the fabrication of the solid-state selective electrodes as it is demonstrated by the developing of the K^+-sensitive SC-ISEs.

2. Experimental

2.1. Materials

A highly conductive black, Printex XE-2 carbon black (BET surface area: 910 m^2/g, Average primary particle size: 30 nm, Iodine absorption: 1075 mg/g, DBP-absorption: 380 mL/100 g, pH-value 8) consisting of fine powder was received from Evonik Degussa Canada Inc. and used without any modifications. Potassium ionophore I (valinomycin), potassium tetrakis(4-chlorophenyl)borate (KTpClPB), o-nitrophenyl octyl ether (o-NPOE), poly(vinyl chloride) (PVC) of high molecular weight and tetrahydrofuran were the selectophore reagents obtained from Fluka. All other chemicals were of analytical-reagent grade. Distilled and deionized water was used to prepare the aqueous solutions.

2.2. Electrodes preparation

Glassy carbon disc (GCD) electrodes consisting of GC rods enveloped by Teflon bodies (GC area = 0.07 cm^2) were first polished with 0.3 μm alumina powder, then rinsed with water and finally cleaned ultrasonically with water and ethanol.

In order to obtain the Printex XE-2 CB modified GCD electrodes (GCD/CB) drop casting method was applied with the use of a sonicated mixture (for ca. 1.5 h). The mixture containing 5 mg of CB dispersed in 1 mL of THF was added on the top of GCD electrodes. After that the GCD/CB electrodes were left to dry for 24 h. To prepare the electrodes denoted as GCD/CB/K^+-ISM, the solid contact layer (GCD/CB) was subsequently coated with 120 μL K^+-ISM cocktail containing 1.1% (w/w) valinomycin, 0.25% (w/w) KTpClPB, 65.65% (w/w) o-NPOE and 33% (w/w) PVC.

For comparison, coated disc electrodes were prepared by covering the bare GCD electrodes with the mentioned membrane.

The GCD/(CB,K^+-ISM) electrodes were prepared by covering the bare GCD substrate with the above membrane containing 5 mg ultrasonically dispersed CB as a component (CB content = 4% (w/w)). All the membrane electrodes were left to dry for 24 h at the room temperature and then conditioned in 0.01 M KCl solution for at least 1 day before further measurements were carried out. The electrodes were kept in the described conditions between the measurements as well. For each kind of the SC-ISEs five identical electrodes were prepared. All of them were studied.

2.3. Apparatus

The potentials were measured using a 16-channel mV-meter (Lawson Labs, Inc., Malvern, PA). The reference electrode was an Ag/AgCl electrode with 3 M KCl solution in a bridge cell (type 6.0733.100 ΩMetrohm, Switzerland) or an Ag/AgCl/3 M KCl (type 6.0729.100 ΩMetrohm, Switzerland) with the salt bridge 1 M lithium acetate.

The chronopotentiometry measurements were performed with the use of an Autolab General Purpose Electrochemical System (AUT32N.FRA2-AUTOLAB, Eco Chemie, The Netherlands) connected to a conventional, three-electrode cell. The reference electrode was an Ag/AgCl/3 M KCl electrode and a glassy carbon rod was used as the auxiliary electrode.

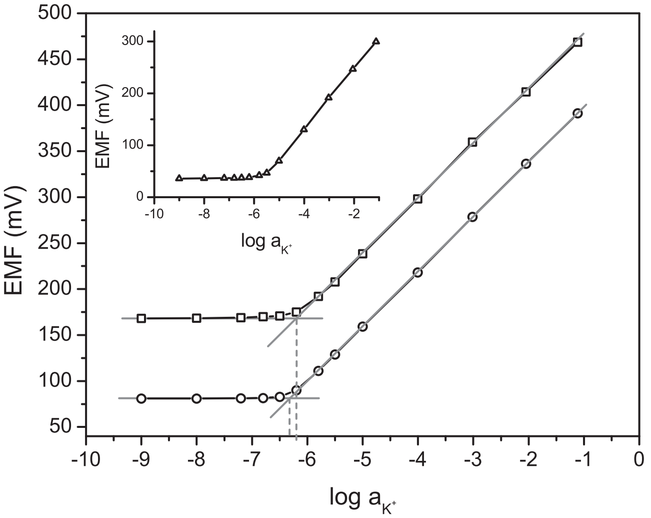

Fig. 1. EMF dependence on K^+ activities for GCD/CB/K^+-ISM (○), GCD/(CB,K^+-ISM) (□), and inset: GCD/K^+-ISM (△) electrodes conditioned in 0.01 M KCl solution.

3. Results and discussion

Fig. 1 shows the $\log a_{K+}$ dependence of the GCD/CB/K^+-ISM, GCD/(CB,K^+-ISM) and GCD/K^+-ISM electrodes by recording the electromotive force (EMF). The slopes calculated from the linear range of the calibration plots were 58.8 (GCD/(CB,K^+-ISM)) and 59.1 (GCD/CB/K^+-ISM) and 57.6 (GCD/K^+-ISM) mV/decade (standard deviation of the slopes is 0.4, 0.2 and 0.7 mV/decade a_{K+} ($n = 5$), $R = 0.9993$, 0.9999 and 0.9989). The limit of detection calculated as the intersection of the two lines in Fig. 1 is $10^{-6.1}$, $10^{-6.4}$ M and $10^{-5.6}$ for, GCD/(CB,K^+-ISM), GCD/CB/K^+-ISM and GCD/K^+-ISM, respectively.

The developed electrodes show a very stable response over time. Even after a long time of the conditioning in 0.01 M KCl (6–7 weeks) the electrodes still showed the linear response in the same range of the potassium activity. The standard potential values of the GCD/CB/K^+-ISM and GCD/(CB,K^+-ISM) electrodes, that were equal to 458.6 mV and 535.4 mV after 2 days conditioning, changed of 5.9 and of 3.1 mV after 7 weeks.

The reproducibility of the standard potential value was 459 ± 1.1 mV and 534 ± 4.3 mV for five different GCD/CB/K^+-ISM and GCD/(CB,K^+-ISM) electrodes.

The potential drift of the GCD/(CB,K^+-ISM) electrode was only 9.3 ± 1.2 μV/h over 72 h, which is a better result than in case of 3DOM carbon-contacted ISEs. Concerning the GCD/CB/K^+-ISM electrodes the potential drift was 15.1 ± 1.3 μV/h over 72 h.

The following potentiometric selectivity coefficients were obtained with a separate solution method according to the traditional procedure [22] using chloride salts of different cations ($n = 3$): $\log K^{pot}_{KNa} = -3.7 \pm 0.1$ and -3.5 ± 0.2, $\log K^{pot}_{KLi} = -4.3 \pm 0.1$ and -4.0 ± 0.2, $\log K^{pot}_{KNH_4} = -2.1 \pm 0.3$ and -1.9 ± 0.3, $\log K^{pot}_{KMg} = -5.7 \pm 0.1$ and -5.5 ± 0.2, $\log K^{pot}_{KCa} = -5.4 \pm 0.2$ and -5.3 ± 0.2 for GCD/(CB,K^+-ISM) and GCD/CB/K^+-ISM, respectively.

The redox sensitivity measurements were carried out for GCD covered with layer of CB (GCD/CB) and for the developed electrodes (GCD/(CB,K^+-ISM) and GCD/CB/K^+-ISM). The solution used was of 0.1 M KCl containing 4.6 mM of total concentration of $Fe(CN)_6{}^{3-/4-}$ redox couple with the ratio of Fe^{3+}/Fe^{2+} equal to 4 and 0.25 (Fig. 2A). Although the GCD/CB electrode shows a clear redox response, the

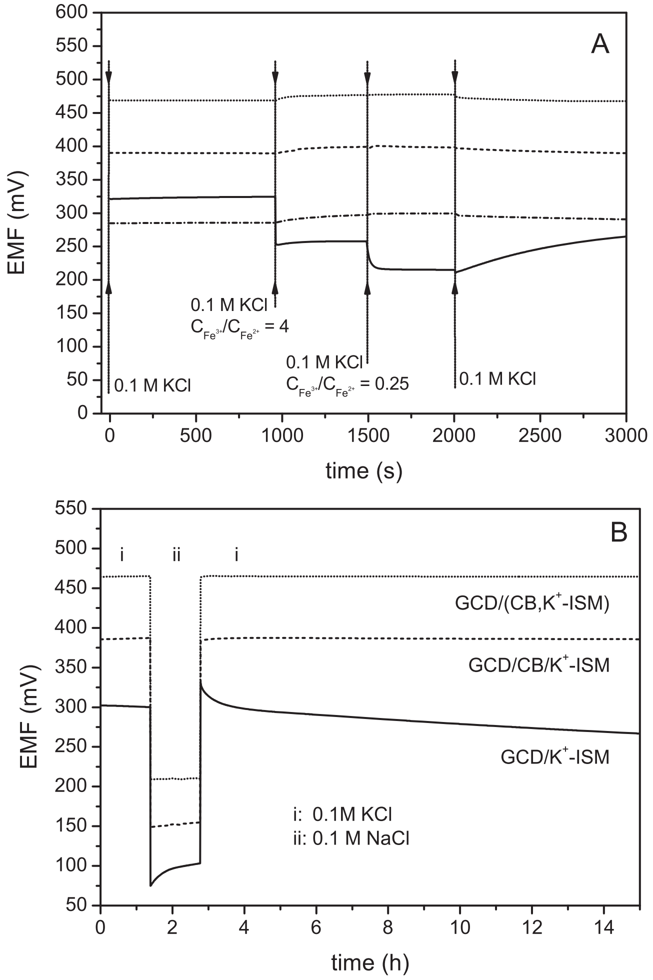

Fig. 2. (A) Redox sensitivity test for the GCD/(CB,K^+-ISM) (dotted line), GCD/CB/K^+-ISM (dashed line) and GCD/K^+-ISM (dotted-dashed line) and GCD/CB (solid line) electrodes (the $Fe(CN)_6{}^{3-/4-}$ redox couple was added as potassium salt). (B) Water layer test for the GCD/(CB,K^+-ISM) (dotted line), GCD/CB/K^+-ISM (dashed line), GCD/K^+-ISM (solid line) electrodes.

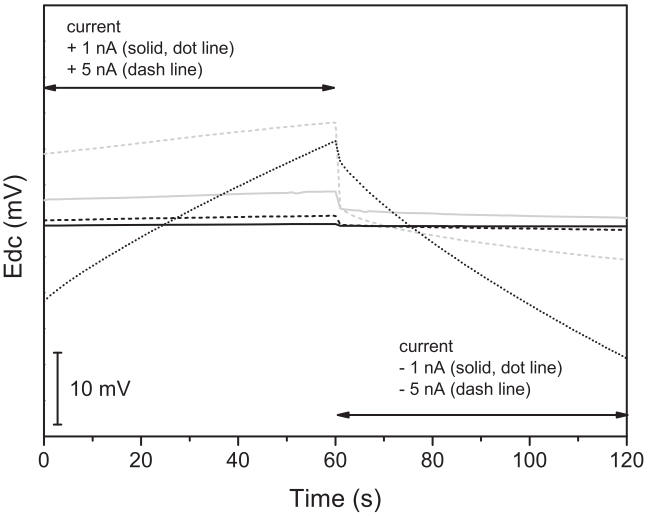

Fig. 3. Chronopotentiograms for GCD/(CB,K^+-ISM) (solid and dashed black lines), GCD/CB/K^+-ISM (solid and dashed gray lines) and GCD/K^+-ISM (dotted black line) recorded in 0.1 M KCl.

GCD/(CB,K^+-ISM) and GCD/CB/K^+-ISM electrodes exhibit only a slight increase in potential, related to the increase of K^+ concentration as the $Fe(CN)_6{}^{3-/4-}$ redox couple was added as potassium salt. There was no redox sensitivity measured, similar to this measured when it's about the electrodes with graphene or 3DOM intermediate layer.

Potentiometric water layer test was carried out according to [8] by first measuring the potential of the electrodes in 0.1 M KCl and then in the solution containing the interfering ion (0.1 M NaCl). Eventually the solution was again changed to 0.1 M KCl. Fig. 2B shows a clear difference in the behavior of the coated disc electrode (GC/K^+-ISM) and the GCD/(CB,K^+-ISM), GCD/CB/K^+-ISM electrodes. It is obvious that the response of the GCD/K^+-ISE showed a substantial positive drift in the interfering ion solution and a negative potential drift when changing back from the sodium ions to potassium ones, that suggested the presence of the water layer. On the contrary, the developed electrodes are stable upon the similar sample changing despite contacting the conditioning solution for a longer period of time. This demonstrates that the water layer was reduced in the developed SC-ISEs due to a highly hydrophobic character of the CB when forming a film or a network.

The sensitivity to O_2 and CO_2 gases of the GCD/CB/K^+-ISM and GCD/(CB,K^+-ISM) electrodes was studied by measuring the potential of the electrodes in 0.1 M KCl solution purged during 1 h with the following gases: N_2, O_2, again N_2, then CO_2 and N_2 once more. The developed ISEs do not show any sensitivity to O_2 and CO_2.

The light sensitivity of the developed SC-ISEs was studied as well. During the experiment the potential of the electrodes in 0.1 M KCl solution was recorded. After being kept in the dark the GCD/(CB,K^+-ISM), GCD/CB/K^+-ISM electrodes were exposed to a room light and to the UV light. Each exposition lasted 1 h. No significant potential change was observed during the measurement.

The current-reversal chronopotentiometry (in which the potential of a working electrode was measured as a function of time during the polarization by constant-current two steps) was used to evaluate the electric capacity of the solid contact and the potential stability of electrodes [4]. Fig. 3 shows a typical change in potential versus time when currents of −1 and −5 nA are applied for 60 s to the working electrodes. Then the currents of +1 and +5 nA are applied respectively for the same time interval. In order to compare, the same plot is presented for the coated-wire electrode. The potential jump observed in the response after the change of the current polarity (ΔEdc) was used to calculate the total resistance of the electrode: $R_{\text{total}} = \Delta Edc/2I$, where the I is the applied current. The estimated values are R_{total} (GCD/CB/K^+-ISM) = 1.21 MΩ (I = 1 nA) and 1.19 MΩ (I = 5 nA), R_{total} (GCD/(CB,K^+-ISM)) = 122 kΩ (I = 1 nA) and 125 kΩ (I = 5 nA), R_{total} (GCD/K^+-ISM) = 1.48 MΩ (I = 1 nA) and 1.45 MΩ (I = 5 nA).

The potential drift [4] of the electrodes was derived from the ratio $\Delta Edc/\Delta t$. The resulting values 19.6 μV/s (I = 1 nA) and 98.4 μV/s (I = 5 nA) calculated for (GCD/CB/K^+-ISM) electrode, and 2.33 μV/s (I = 1 nA) and 11.6 μV/s (I = 5 nA) for (GCD/(CB,K^+-ISM)) are lower than those obtained from the coated-wire electrode developed the under similar conditions ($\Delta Edc/\Delta t$ = 0.8 mV/s, I = 1 nA and 4.1 mV/s, I = 5 nA). According to the equation $\Delta Edc/\Delta t = I/C$, the value of C of the GCD/(CB,K^+-ISM) electrode is estimated to be 429 μF, which is higher than those measured for CPs, graphene and carbon nanotubes based solid-contact transducers. In the case of the solid contact layer CB in the membrane electrode C value is estimated to be 51 μF (in the case of GCD/K^+-ISM electrode C = 1.3 μF).

4. Conclusion

This work demonstrates that Printex XE-2 carbon black can be used as transducer in the solid contact ion-selective electrodes as well as a component of the PVC-based membrane electrodes. The developed electrodes provided a good Nernstian response to potassium, with a detection limit of $10^{-6.1}$ and $10^{-6.4}$ M, which is similar to the value measured for typical SC-ISEs with conducting polymer contacts. It is worth being remarked that the CB-contacted electrode was found to present a greatly improved long-term potential stability and to highlight its good resistance to the interferences from CO_2, O_2 and light. The hydrophobic character of the surface of CB prevents from the formation of an aqueous layer. Moreover, the new type electrodes are very easy to build at very low costs. In conclusion, these excellent properties make the developed electrodes promising for the purpose of appropriate for the miniaturization.

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