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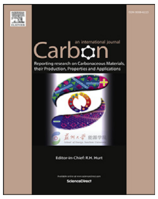

Ion-selective electrodes with superhydrophobic polymer/carbon nanocomposites as solid contact

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ABSTRACT

Possibility of using superhydrophobic polymer/carbon nanocomposites as a new type of solid-contact material for solid-state ion-selective electrodes has been presented for example potassium-sensitive electrodes. The solid contact layers were prepared with the highly porous graphene/carbon black – fluorinated acrylic copolymer. Potassium-selective electrodes were exhibited a good Nernstian response with a slope of 59.10 mV/dec in the range from $10^{-6.5}$ to 10^{-1} M KCl. The stability of the electrical potential of the new solid-contact electrodes was tested by performing current-reversal chronopotentiometry, and the electrodes capacitance is 1471 μF. Due to the large capacitance and super hydrophobic character of the solid contact the developed electrodes exhibit excellent a long-term potential stability.

1. Introduction

Carbon in a variety of forms have attracted considerable research interest over the past decade in both scientific research and industrial applications. Therefore different materials based on carbon encounter the most rapid development over the past decades and represent a very important topic in modern materials science [1]. One of the very promising applications for these materials are multifunctional superhydrophobic films and coatings based on hydrophobic polymers and functional nanostructured materials (e.g. carbon black, nanotubes, nanowires or graphene) [2]. Such superhydrophobic surfaces are characterized by water contact angle larger than 150° and sliding angle smaller than 5° [3].

Graphene (GR), a two – dimensional carbon material with only one atomic layer shows unique properties such as a fast electron transportation, a high surface area, a high thermal conductivity and an excellent mechanical properties [3–5]. However, it is well known that graphene suffers from self-aggregation or re-stacking by the strong cohesive van der Waals interactions between neighboring sheets what leads to loss in effective surface area and electrical conductivity [6].

Carbon black (CB) is another kind of carbon material, forming small particles (fused together) organized in chain-like structures. CB has a semi-graphitic micro-structure, made of nanosized graphitic stacks embedded in amorphous carbon. It possessed many fascinating properties such as a low cost, a high specific surface area, accompanied with a high electrochemical stability and a relatively high electronic conductivity [7].

The incorporation of carbon black into graphene layers not only inhibits the agglomeration of graphene, but also can lead to increase the electrical conductivity [8,9].

Carbon materials (CMs) such as graphene [10], carbon nanotubes [11], carbon cloth [12], carbon black [13,14], colloid-imprinted mesoporous carbon [15] or porous carbon submicrometer spheres [16] were also used in the sensor field as solid contacts for the fabrication of solid-state ion-selective electrodes (SS-ISEs). Due to large double layer capacitances and hydrophobic properties of carbon materials, these SS-ISEs possess high potential stability, and show the absence of an interfacial aqueous layer between a polymeric ion-selective membrane (ISM) and the underlying solid contact. In addition, these carbon materials based SS-ISEs have excellent resistance to some gases (such as oxygen or carbon dioxide), light and redox interferences [10–16].

In this work, the electrochemical properties of the graphene/carbon black nanocomposite -based solid contact were characterized by cyclic voltammetry, chronopotentiometry and impedance spectroscopy, and the possibility of using this nanocomposite of carbon materials with superhydrophobic polymer as the solid contact of ISEs are presented.

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2. Experimental

2.1. Chemicals and materials

Fluorinated acrylic copolymer (FP) dispersion Capstone ST-100 (20 wt% water dispersion of fluorinated acrylic latex) was obtained from DuPont, USA. Acetic acid, dimethylformamide, methanol, acetonitrile, and tetrahydrofuran were purchased from Sigma–Aldrich and used as received. Printex XE2-B carbon black CB-XE2B (BET surface area: 1000 m^2/g, the average primary particle size: 30 nm, pH-value 7.8 [17]) consisting of the granules received from Evonik Degussa GmbH, Inorganic Materials, Frankfurt, Germany and used without any modifications. Single Layer Graphene was purchased from ACS Material, LLC, USA. Potassium ionophore I (valinomycin), potassium tetrakis(4-chlorophenyl)borate (KTpClPB), o-nitrophenyl octyl ether (o-NPOE), poly(vinyl chloride) (PVC) of high molecular weight were the selectophore reagents obtained from Sigma–Aldrich. All other chemicals were of analytical-reagent grade. Distilled and deionized water was used to prepare the aqueous solutions.

2.2. Preparation of electrodes with superhydrophobic conductive composite layer

A drop-casting method was used to obtain modified glassy carbon disc (GCD) electrodes used for ion sensing. Before the surface modification, the GCD electrodes (Mineral, Poland) was carefully polished with 0.3 μm and 0.05 μm alumina slurries to obtain a mirror-like surface. After sonication in methanol and water, the electrode was rinsed with water. The GCD electrodes modified with carbon materials (CMs) were prepared by casting 10 μL of prepared CMs suspension onto the surface of the cleaned GCD electrode. The solvent was then evaporated. In the case of electrodes with carbon materials-fluoropolymer nanocomposite layers (CM-FP) additional thermal treatment were used in order to obtain superhydrophobic coatings by simply place the coatings in an oven at 160 °C for about 0.5 h to completely melt the polymer. As controls, all type of electrodes with CM (GCD/CB, GCD/CB-GR, GCD/GR) and CM-FP (GCD/CB-FP, GCD/CB-GR, GCD/GR-FP) were fabricated with the similar procedures. CM-FP suspension was prepared according [8], however solutions were loaded with 17 weight % of carbon materials.

The carbon nanoparticle dispersions were mixed by sonication for 3 h, then left to rest for 24 h. CB, GR and CB-GR with three different weight ratios were tested: 1:3, 1:1 and 3:1.

The fluoropolymer dispersion and the carbon nanoparticle dispersions were mixed to generate the final coating dispersions by sonication for 30 min.

To prepare the potassium-selective electrodes, solid-contact layers were subsequently coated with a 30 μL THF solution containing 1.1% (w/w) valinomycin, 0.25% (w/w) KTpClPB, 65.65% (w/w) o- NPOE, and 33% (w/w) PVC. The coated disc electrodes (GCD/K^+-ISM) were prepared by covering the bare GCD electrodes with the above-mentioned potassium membrane. After the electrodes were covered with the ion-selective membrane (ISM), they were left in the air for 48 h to ensure complete evaporation of THF. Afterward the potassium-selective electrodes were conditioned in aqueous 0.001 M KCl solutions, for 24 h. The conditioning step was also repeated before every measurement. Five identical electrodes were prepared and examined. All the electrodes were separately conditioned and stored.

2.3. Characterization

Potentiometric measurements were made using an EMF 16-channel meter (Lawson Lab., 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 a 1 M lithium acetate salt bridge.

The chronopotentiometry, the cyclic voltammetry and impedance spectroscopy 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 Ag/AgCl/3 M KCl electrode (type 6.0733.100 ΩMetrohm, Switzerland) was used as a reference, and a glassy carbon rod was used as an auxiliary electrode.

Wettability measurements were determined by sessile drop method (DSA 10 MK2, KRÜSS, Germany). For the experiments, the 5 μL water droplets were dropped onto the sample, and the average value of static water contact were taken from three points on each sample. Measurements were performed at room temperature.

The morphologies of the carbon materials (CMs) layers were examined using a scanning electron microscope (SEM), model LEO 1530, from LEO Electron Microscopy Ltd., model Vantage.

3. Results and discussion

3.1. Superhydrophobic conductive layer

The morphology of the GR and CB-FP layers prepared in varying weight ratio of GR and CB is shown with SEM images in Fig. 1(a–e). Additional the CB layer without FP is also presented (Fig. 1f). It is clearly seen that the CB-FP layer is more porous and rugged.

In addition, Fig. 2, shows two definite layers in the modified electrodes, i.e., a PVC membrane layer and a layer of CB-FP.

Fig. 3 shows the static water contact angle and contact angle hysteresis values obtained for the CM-FP layers prepared in varying weight ratio of GR and CB. As can be seen contact angle hysteresis is very low for 3CB:1GR-FP and CB-FP layers. These nanocomposites showed also the highest static water contact angle (close to 166°).

3.2. Electrochemical characteristics of carbon materials layers

The GCD/CM electrode – electrolyte systems were studied during electrochemical measurements (cyclic voltammetry, chronopotentiometry and impedance spectroscopy).

In cyclic voltammetry the potential of an electrode was changed linearly with the selected rate between two potential extremes (0 and 0.6 V), and then returned to the initial potential. The current recorded as a function of the potential is called cyclic voltammograms. Fig. 4 shows the current versus potential plots recorded for the GCD/GR electrode at scan rates varying from 0.001 to 0.1 V s^{-1} in 0.01 KCl electrolytes. The CV curve area was gradually enlarged with the increase of the potential scan rate, while the shape was kept as quasi-rectangular which indicates the predominant capacitive behavior [18]. The slight deviation from the standard rectangular shape, especially at a relatively high scan rate, could be attributed to the distributed charge storage which is a classical porous electrode behavior [18]. In the case of the less porous electrodes with carbon black more rectangular shape was observed than for the graphene-modified electrodes.

The values of the double layer capacitance (C_{dl}) of the GCD/CM electrodes was estimated from the voltammetric current dependence of the scan rate at constant potential upon the equation: $I = C_{dl}\frac{dE}{dt} = C_{dl}\nu$. The values of C_{dl} were calculated for all electrodes from the slope of the linear part of double layer charging current vs. scan rate curve. An example of voltammograms leading to such plot are shown in Fig. 4a for the GCD/GR electrode whereas the resulting I(ν) plot for all studied electrodes is given in Fig. 4b. A potential of 0.3 V, which is approximately mid-way through the double layer