



Few-layer graphene and polyaniline composite as ion-to-electron transducer in silicone rubber solid-contact ion-selective electrodes



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ABSTRACT

We have used for the first time a composite consisting of few-layer exfoliated graphene and electrically conducting polyaniline (PANI) as the ion-to-electron transducer (solid-contact) in Ca^{2+} -selective solid-contact electrodes (CaSCISEs). The drop cast transducer deposited from the graphene–PANI dispersion in *N*-methylpyrrolidone makes use of the synergistic effect of these two materials. It maintains the ion-to-electron transduction which is characteristic for the electrically conducting polymers (ECP), but in addition, graphene improves the reproducibility of the standard potential of the SCISEs compared to the neat PANI based electrodes and increases the hydrophobicity of the transducer (ca. 30° higher water contact angle) which counteracts the water layer formation. Our results reveal that the incorporation of few-layer graphene in the transducer layer improved also the initial potential stability and the response characteristics of the CaSCISEs due to the electrocatalytic effect of the graphene–ECP composite, which facilitates the electron transfer at the transducer/substrate interface. We obtained a potential reproducibility of only ± 4 mV ($n = 3$) for the CaSCISEs having graphene–PANI as the solid-contact. The CaSCISEs in this study had a detection limit of 5×10^{-8} M Ca^{2+} , which was obtained without any sophisticated pre-treatment protocols.

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1. Introduction

Since the first successful isolation of a graphene monolayer in 2004 [1], graphene has attracted tremendous research interest due to its outstanding mechanical properties [2], high specific surface area ($2630 \text{ m}^2 \text{ g}^{-1}$) [3] which is much higher than for graphite ($\sim 10 \text{ m}^2 \text{ g}^{-1}$) and carbon nanotubes (CNTs) [4], excellent electrical [5] and heat conductivity [6], and transparency, which can be utilized in e.g. energy storage devices [7], transparent and flexible displays [8], light emitting diodes [9], paints and coatings [10], and printing [11]. In addition, graphene, graphene oxide (GO) and reduced graphene oxide (RGO) have been used in chemical sensing to detect e.g. biomarkers and DNA [12]. However, the use of graphene and RGO is limited due to their poor dispersibility in water and organic solvents complicating the sensor

fabrication. Therefore, the good water solubility of GO [13] can be advantageously utilized especially in the synthesis of composite materials with electrically conducting polymers (ECPs) [14]. For the chemically [15,16] or electrochemically [14] synthesized ECP–GO composites, the GO incorporated in the ECP matrix can easily be further reduced either chemically [17] or electrochemically [18] to RGO.

Similar to composites of ECPs and CNTs [19], the synergistic effect of the ECPs and the graphene materials originating from non-electrostatic interactions, results in enhanced electron transfer and thus in improved electrocatalytic activity, which is beneficial in electrochemical sensors for obtaining higher signal amplification and better oxidation peak separation in multianalyte solutions [20]. This has been demonstrated for the detection of e.g. dopamine [20], ascorbic acid [21], uric acid [22], and several other species. Due to the ion-to-electron transduction property of the ECPs [23], they have been successfully applied as intermediate transduction layers (solid-contact, SC) in polymer based potentiometric solid-contact ion-selective electrodes (SCISEs) to convert the ionic conductivity of the ion-selective membrane (ISM) to an electronically measurable signal [24]. In the SCISEs, the water layer formation at the buried interfaces (substrate/SC and/or SC/ISM) is one of the

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factors resulting in potential instability because of the transmembrane flux of primary and interfering ions in the ISM [25]. Despite of considerable research efforts [26], the potential stability of the SCISEs – especially for those with ECP based transducers – still remains unsolved which is an obstacle for their commercialization.

It has been shown that hydrophobic ion-to-electron transducer materials like redox-active self-assembled monolayers [27], poly(3-octylthiophene) [28] three-dimensionally ordered mesoporous carbon (MC) [29,30], colloid-imprinted MC [31], lipophilic redox buffers [32,33], CNTs [34,35], RGO [36–39], composites of graphene and silver tetrakis[3,5-bis(trifluoromethyl)phenyl]borate [40], as well as tetradodecylammonium tetrakis(4-chlorophenyl)borate and graphene (or single walled CNTs) composites [41] prevented the water layer formation. This is expected to improve the potential stability and the reproducibility of the standard potential of the SCISEs [28–33,36,40,42]. Among these materials, the pure carbon transducers are hydrophobic and therefore prevent the water layer formation at the substrate/carbon interface, though they still act as electrical double layer capacitors without possessing true ion-to-electron transduction. The improved potential stability of the carbon based SCISEs is based on the relatively high surface area of the carbon materials making them less sensitive to minor fluctuations in the double-layer capacitance (polarization) at the substrate/carbon interface.

In contrast to the pure carbon based SCs, which have been successfully applied in SCISEs, the composites of ECPs and graphene, RGO and CNTs [43] maintain the ion-to-electron transduction at the substrate/SC interface. The incorporation of carbon materials into the ECP based SCs not only increase their hydrophobicity, but also facilitates the electron transfer between the substrate and the ECP (electrocatalytic effect) compared to neat ECPs, which was recently shown for the few-layer graphene and polyaniline (PANI) composite that has been used in this work [15]. This is expected to improve the reproducibility of the standard potential of the SCISEs which is an important parameter for calibration-free ISEs. Compared to the carbon based SCs, the ECP based transducers have much higher (redox) capacitance that can be easily tuned by varying the SC thickness [44]. To further increase the capacitance of the SC, the synergistic effect of the ECPs and graphene/RGO can be utilized which results in a more extensive electrically conducting network formation between the carbon material and the ECP. The carbon–ECP composites have therefore higher redox capacitance than neat ECPs [45]. Moreover, the ECP–GO/RGO composites have very good potential cycling stability up to 10,000 cycles in aqueous electrolyte solutions [46–48] demonstrating their good electrochemical stability which is required in chemical sensing applications. In addition, the graphene/RGO–ECP composites can be prepared with a compact surface structure making the graphene/RGO sheets act as physical barriers for water and gases (CO_2 and O_2) and therefore lowering the amount of water reaching the underlying electrode substrate [18].

It is therefore expected that the composites of ECPs and the graphene materials have several advantages as ion-to-electron transducers in SCISEs. We report here for the first time the application of the few-layer graphene and PANI composite as the ion-to-electron transducer in silicone rubber based Ca^{2+} -selective SCISEs (CaSCISEs). We show that the composite transducer improves the reproducibility of the standard potential of the CaSCISEs compared to the neat PANI transducer and the coated-disc ISEs (CaCDE). The CaSCISE with the graphene–PANI transducer had a fast response and a detection limit (LOD) of $5 \times 10^{-8} \text{ M Ca}^{2+}$, which could be obtained without any sophisticated pre-treatment protocols.

2. Materials and methods

2.1. Chemicals

Aniline was received from Sigma–Aldrich and purified with distillation under reduced pressure. Exfoliated graphite of the AO-1 grade (<3 monolayers of graphene) with the specific surface areas of $510 \text{ m}^2 \text{ g}^{-1}$, average flake thicknesses of 1.6 nm, and average lateral sizes of ca. $10 \mu\text{m}$ was purchased from Graphene Supermarket. Room temperature moisture cured silicone rubber (RTV 3140) was obtained from Dow Corning. Potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (KTFPB), calcium ionophore I (ETH 1001), and tetrahydrofuran (THF) of Selectophore grade were received from Fluka. Suprapur CaCl_2 (99.995%) was obtained from Merck.

2.2. Electrode fabrication

The neat PANI and the PANI–graphene composite was prepared by chemical oxidative polymerization and dispersed in *N*-methylpyrrolidone (NMP) according to the previously published procedure [15]. PANI and PANI–graphene SCs were fabricated by drop casting $0.5 \mu\text{L}$ of the neat PANI and PANI–graphene dispersions on glassy carbon (GC) electrodes incorporated in polyether ether ketone bodies. Before the SC deposition on the GC substrates, they were polished with 9, 3 and $1 \mu\text{m}$ diamond paste, and $0.3 \mu\text{m}$ aluminum oxide to obtain a mirror-like surface and finally thoroughly rinsed with deionized water. The SCs were allowed to dry overnight and were then exposed to HCl vapors (saturated vapor pressure 0.17 bar, 22 C, 36 wt.% HCl) for at least 6 h in a closed vial to protonate the electrically non-conducting emeraldine base form of PANI and convert it to its electrically conducting emeraldine salt form. The Ca^{2+} -selective silicone rubber ISM consisting of 98.1 wt% RTV 3140, 1.0 wt% ETH 1001 and 0.9 wt% KTFPB [49] dissolved in THF (dry weight: 20.0 wt%) was then deposited by drop casting $14 \mu\text{L}$ of the membrane solution on top of the SC. Finally, the ISMs having a thickness of 100–110 μm were cured in the ambient atmosphere for 72 h before the CaSCISEs were exposed to CaCl_2 solutions. For comparison, Ca^{2+} -selective CaCDE without the transducer layer was prepared with the same procedure as the CaSCISEs. Exfoliated graphene is insoluble in NMP and other organic solvents without the use of additional surfactants. We have therefore not prepared CaSCISEs with exfoliated graphene as the SC. The introduction of a surfactant to the SC layer (not present in the other electrode types) would make it more difficult to compare the response characteristics of the exfoliated graphene-surfactant based CaSCISEs with the other CaSCISEs.

2.3. Potentiometric measurements

The potentiometric measurements followed always the same protocol. First, the initial potential stability of the as prepared CaSCISEs and CaCDEs were measured for 48 h in 0.1 M CaCl_2 solutions. The electrodes were then exposed to 0.1 M NaCl for 24 h which was followed by another 24 h in 0.1 M CaCl_2 (aqueous layer test). After this the electrodes were stored overnight in suprapur 10^{-4} M CaCl_2 prior to the calibration in CaCl_2 solution (10^{-4} to 10^{-10} M) with the Metrohm automatic diluting system (Metrohm 700 Dosino pumps and 711 Liquino controller). All potentiometric measurements were carried out in a two-electrode cell placed in a Faraday's cage with the CaSCISE/CaCDE and a low leakage Ag/AgCl/4 M KCl functioning as the indicator and reference electrode, respectively. The potentials were recorded with a 16-channel high impedance ($10^{15} \Omega$) voltmeter (Lawson Lab Inc., Malvern, PA) upon stirring. For the electrode calibrations, the solutions were stirred the first minute of the total measurement time of 5 min at each

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