



Short communication

The use of graphene oxide as a fixed charge carrier in ion-selective electrodes



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ABSTRACT

Here we present for the first time the use of graphene oxide nanoparticles as fixed-charge carriers for the development of membrane-based cation selective ion-selective electrodes (ISEs). The GO nanoparticles are dispersed into tetrahydrofuran, and thus easily incorporated into the ISE membrane. The effect of GO concentration on bulk membrane resistance (R_b) is measured using electrochemical impedance spectroscopy, and a significant decrease in R_b is observed with increasing [GO]. The permselectivity of these membranes was investigated using conventional potentiometry, and the results suggest that GO is able to decrease membrane resistance through electrostatic interactions between the negatively charged particles and the positively charged cations. The use of these nanostructures in the pH-sensitive ISE based on ETH-1907 ionophore paves the way to a new method of constructing potentiometric sensors. ISEs with increased lifetimes and stable potentials could be developed based on these materials, allowing ionophore and charge carrier to be combined in a way that promotes miniaturization of ISEs with more optimal analytical characteristics.

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1. Introduction

Ion-selective electrodes (ISEs) are among the most common analytical devices used in clinical and environmental monitoring [1–4]. These sensors are robust, rapid, relatively inexpensive, sensitive over many orders of magnitude in concentration, and selective over competing species. Typical plasticized PVC ISE membranes contain approximately 1% ionophore, 33% polymer and 66% plasticizer, with a small amount of lipophilic additive present in near-equimolar amounts relative to the ionophore [5]. The additive is known to impart many favorable characteristics in to ISE membranes including: decreased resistance, decreased response time, increased selectivity of monovalent over divalent ions, and permselectivity [6–9]. These small lipophilic molecules are able to perform these tasks by increasing the mobile ionic sites within the membrane [5]. Although, their use is ubiquitous in the field, lipophilic additives are not always stable in the membrane phase [10], which is essential for long-term performance of sensors [11].

Recently, carbon nanostructures, including nanotubes, fullerenes, nanofibers and graphene, have been shown to lower the electronic

resistance of composite materials [12,13]. Ion-selective electrodes, however, require that the resistance of the membrane towards ion-transport must be sufficiently low ($\sim k\Omega$). Graphene oxide (GO) is a two-dimensional material, similar to graphene, which is decorated with oxygen functional groups along the edge- and basal-planes and thus has mixed sp^3/sp^2 hybridization [14,15]. Although graphene oxide is not electrically conductive, the significant amount of oxygen functional groups, as well as its negative charge [16], may make it ionically conductive. Thus GO is potentially useful in ion-selective membranes, where conduction is ionic rather than electronic.

We report here the effect that the addition of graphene oxide (GO) has on plasticized-membrane response compared to conventional lipophilic additives. An inverse correlation between the amount of GO in the membrane, and bulk membrane resistance is shown. Membranes prepared in this way show near-Nernstian responses to both mono- and divalent cations. In a direct comparison, H^+ selective electrodes based on the ionophore ETH 1907 with GO membranes are shown to provide excellent analytical response.

2. Experimental

2.1. Materials

All solutions were prepared with $> 18.2 M\Omega$ cm water (Nanopure, Barnstead, MA). Potassium chloride, high molecular weight polyvinylchloride (PVC), 2-nitrophenyl octyl ether (*o*-NPOE),

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potassium[tetrakis(4-chlorophenyl)borate] (KTPClPB) and tetrahydrofuran (THF) were from Sigma. Graphene oxide (GO) was purchased from Nanoinnova Technologies (Spain). Electrochemical and physical characterization of this GO has been previously described in detail [17].

2.2. Electrode construction

GO-containing PVC membranes were prepared by first dispersing GO using ultrasonication in a suitable amount of THF as the membrane solvent (typically 2–6 mL, depending on the amount of GO incorporated) [18]. The PVC and plasticizer, *o*-NPOE, were then mixed with the THF-GO suspension. In order to maintain an equal membrane thickness for resistance studies, the mass of polymer and plasticizer was kept constant, while the amount of GO was varied. With the aid of ultrasonication, the polymer and plasticizer were dissolved and the entire contents poured into a 2.5 cm glass ring affixed to a glass plate. The solvent was then allowed to evaporate, forming a flexible membrane. The compositions of all membranes employed in this study are presented in Table 1. These master membranes were then cut into smaller discs and mechanically sealed into Philips electrode bodies (IS 561, Glasblerei Willis Moller AG, Zürich, Switzerland).

2.3. Electrochemical measurements

Potentiometric measurements were carried out on a 16-channel high-input impedance potentiometer (Lawson Labs, EMF16, Malvern, PA). A double junction Ag|AgCl reference electrode with a 1.0 M LiOAc bridge electrolyte was employed for all potentiometric experiments. Electrochemical impedance spectroscopy was performed on an AutoLab PGSTAT electrochemical workstation with a frequency response analyzer (FRA). All impedance experiments were carried out in a conventional three-electrode cell with a double junction Ag|AgCl reference electrode (ThermoScientific Model 9009) and a platinum coil as the counter. The impedance measurements were performed in quiescent 100 mM KCl solutions. The impedance was measured over the frequency range of 0.01–10⁵ Hz with an amplitude of ±10 mV. At low frequency, the data became very noisy and thus only the portion of the spectra which show the bulk resistance/geometrical capacitance are shown. The impedance spectra were fitted using ZView software (Scribner Associates, Inc), which is a complex least squares regression fitting analysis program [19].

3. Results and discussion

The ability of GO to facilitate charge transport within PVC membranes was studied using electrochemical impedance spectroscopy. Fig. 1 presents Nyquist plots of six different membranes, each prepared with varying amounts of GO dispersed within the polymer matrix (Table 1). As shown in Fig. 1, adding increasing amounts of GO to the polymer–plasticizer matrix caused a decrease in the overall bulk resistance of the membrane. Membranes were fit with an equivalent RC circuit to model the bulk resistance (R_b) and geometric capacitance (C_g) (Table 1) [20]. At very low concentrations of GO, the measured bulk resistance is quite large (3370 ± 285 k Ω), however this value decreases

Table 1
Membrane components and properties containing various amounts of GO.

[GO]	PVC	NPOE	GO	R_b	C_g
wt.%	mass/mg			k Ω	pF
0.7	66.1	122.7	1.3	3370 ± 285	86.6 ± 6.4
1.4	66.3	122.4	2.6	1810 ± 52	56.3 ± 1.4
2.8	66	122.5	5.4	1410 ± 63	56.7 ± 2.1
3.9	65.8	122.8	7.6	814 ± 20	74.2 ± 1.7
5	66.4	123.8	10.1	141 ± 14	125 ± 12
10.4	66.2	122.5	21.8	56.2 ± 5.6	121 ± 10

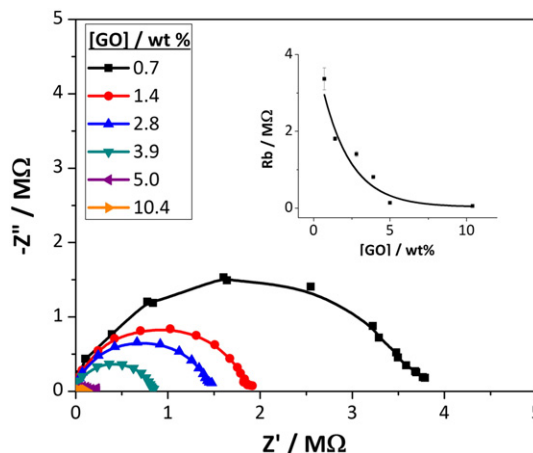


Fig. 1. Nyquist plot of the impedance behavior of *o*-NPOE-PVC membranes doped with various amounts of graphene oxide. Inset: Plot of bulk resistance versus GO concentration.

significantly as more GO is added to the membrane, reaching a value of 56.2 ± 5.6 k Ω for membranes containing 10.4% GO (Fig. 1, inset). As a comparison, a membrane containing 0.4 wt.% of the lipophilic additive potassium[tetrakis(4-chlorophenyl)borate] (KTPClPB) was prepared. The bulk resistance of this membrane was 16.2 ± 0.4 k Ω , which is close to the membrane containing 10.4% GO. This suggests that the addition of GO to PVC membranes is potentially useful as a fixed ionic additive. The geometric capacitance, which is related to the relative permittivity of the membrane, does not change drastically, although a general increasing trend with increasing [GO] was observed. This

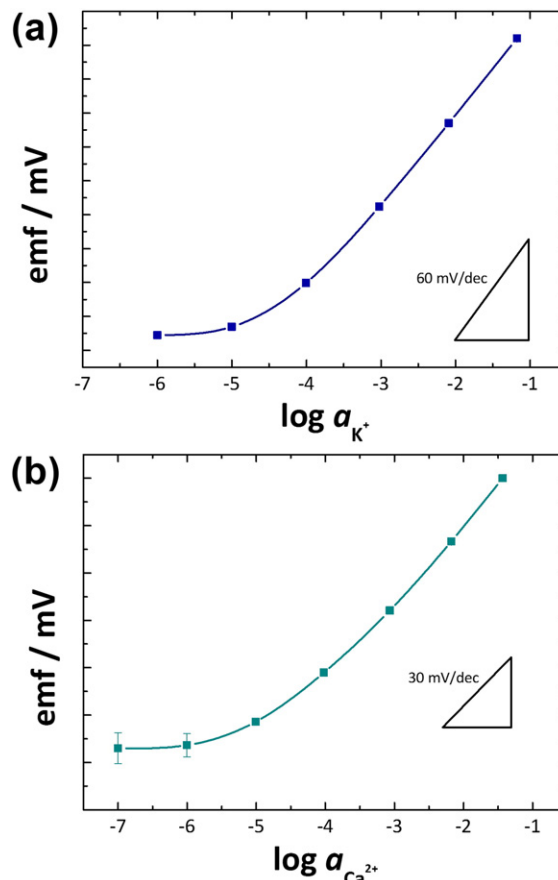


Fig. 2. Calibration curves of *o*-NPOE/PVC membranes containing 10% GO and selective towards (a) K⁺ and (b) Ca²⁺. Error bars represent one standard deviation of three replicate measurements.

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