Anal Bioanal Chem (2009) 395:2371–2376
DOI 10.1007/s00216-009-3127-8

ORIGINAL PAPER

Solid-contact pH-selective electrode using multi-walled carbon nanotubes

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Received: 23 June 2009 / Revised: 31 August 2009 / Accepted: 1 September 2009 / Published online: 17 September 2009

Abstract Multi-walled carbon nanotubes (MWCNT) are shown to be efficient transducers of the ionic-to-electronic current. This enables the development of a new solid-contact pH-selective electrode that is based on the deposition of a 35-μm thick layer of MWCNT between the acrylic ion-selective membrane and the glassy carbon rod used as the electrical conductor. The ion-selective membrane was prepared by incorporating tridodecylamine as the ionophore, potassium tetrakis[3,5-bis(trifluoromethyl)phenyl] borate as the lipophilic additive in a polymerized methylmethacrylate and an *n*-butyl acrylate matrix. The potentiometric response shows Nernstian behaviour and a linear dynamic range between 2.89 and 9.90 pH values. The response time for this electrode was less than 10 s throughout the whole working range. The electrode shows a high selectivity towards interfering ions. Electrochemical impedance spectroscopy and chronopotentiometry techniques were used to characterise the electrochemical behaviour and the stability of the carbon-nanotube-based ion-selective electrodes.

Keywords Potentiometric ion-selective electrodes · Solid-state sensors · pH · Multi-walled carbon nanotubes

Introduction

The expansion of "modern potentiometry" in recent years can be attributed mainly to the development of solid-contact ion-selective electrodes (SC-ISE), the synthesis of new ion-selective membranes and ionophores and the attainment of very low detection limits along with significant selectivity coefficients [1]. Together, these developments have led to the technique being adopted in new analytical applications in many interesting fields [2]. The main advantages of potentiometry are its excellent performance parameters [3] and its simplicity which make this technique comparable, and in some cases better, than other analytical techniques that are more expensive or that require time-consuming preprocessing steps.

In particular, instrumental pH measurements are usually recorded with potentiometric electrodes. The standard pH glass electrode is the most popular sensor because of its high selectivity, reliability and wide dynamic pH range. However, pH glass electrodes have several limitations, most notably their fragility [4]. Moreover, we should also consider the drawbacks resulting from the presence of the internal reference solution. With this configuration, the measurements should always be performed in vertical position and some factors such as high pressure, temperature and small sample volumes can acquire relevance in some environmental, industrial and medical applications [5].

As it is well known, solid-contact electrodes display the inherent advantage, with respect to classical electrodes, of having removed the internal solution. In this sense, the conducting polymer family of solid transducers has been used for several years to develop all-solid-state pH electrodes as well, showing excellent ion-to-electron transducing ability. However, some negative effects like light sensitivity, secondary undesired reactions and the presence of a water layer between the polymeric membrane and the solid-contact transducing polymer affect considerably the potentiometric signal.

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In an attempt to overcome these disadvantages, we report here the development and characterization of the first pH potentiometric solid-contact electrode using a network of non-carboxylated multi-wall carbon nanotubes (MWCNTs) as a transducer layer.

Recently, different carbon-based nanostructured materials such as three-dimensional macroporous carbon [6] and fullerenes [7] have been assayed as ion-to-electron transducers. Our group has shown that single-wall carbon nanotubes (SWCNTs) can perform as solid-contact ion-to-electron transducers, providing additional advantages over electroactive polymers [8]. The high stability of the potential is due to the material's large double-layer capacitance, which in turn is due to its very large surface to volume ratio [9, 10]. Additionally, carbon nanotubes display hydrophobicity, an important feature for preventing water layers forming between the ion-selective membrane and the transducing layer. Moreover, they are insensitive both to light and to species displaying redox behaviour that might induce side reactions.

MWCNTs display structural similarities to SWCNTs, although they are usually much larger in diameter due to the presence of the rolled over concentric graphene layers [11]. In contrast to SWCNT, where the electrical properties depend on their helicity and diameter, MWCNTs are mostly metallic and electronic conduction essentially occurs through the outer shell, although interactions with the inner shells may also influence their electronic properties [12].

In the present paper, we report that MWCNTs can also act as effective transducers in solid-state electrodes, behaving in a similar way to SWCNTs. Metallic nanotubes also transduce the signal in an efficient way in ISEs, in contrast to the alternative potentiometric sensors, field-effect transistors, which need to be semiconducting. To illustrate this, we have developed a solid-state pH electrode using an acrylic ion-selective membrane [13] and MWCNT as the solid transducer.

Experimental section

Chemicals

Methyl methacrylate (MMA), *n*-butyl acrylate (nBA), reagent-grade benzene, dichloromethane, petroleum ether (80–100 °C) and azobisisobutyronitrile initiator (AIBN) were purchased from Fluka. AIBN was recrystallised with warm methanol before use. Lithium acetate dehydrate, potassium, sodium, lithium, ammonium, calcium and magnesium chlorides (all analytical grade) were purchased from Fluka. The hydrogen ion ionophore (tri-*n*-dodecylamine, TDDA) and the lipophilic additive potassium tetrakis[3,5-bis(trifluoromethyl)-phenyl]borate were purchased from Sigma-Aldrich. Multi-wall nanotubes with an outer diameter of 10–20 nm, a length of around 50 μm, a surface area of 400 m^2/g and more than 95% purity were obtained from Heji, Inc. All solutions were prepared using deionized water (18.2 MΩ cm specific resistance) obtained with a Milli-Q PLUS (Millipore Corporation).

Buffer solutions were prepared at constant ionic strength (I=0.01 M) for different pHs, their anion composition being: chloroacetate, pH=2.89; formate, pH=4.16; acetate, pH=4.75; phosphate, pH=6.27 and 7.55; borate, pH=8.86; carbonate, pH=9.9; butylamine, pH=10.87 and 11.54. A universal buffer containing sodium borate, sodium acetate and sodium dihydrogen phosphate was prepared in 1 mM of each component. NaOH or HCl 0.1 M was added to fine-tune the pH of the universal buffer. All of these analytical grade reagents were obtained from Fluka as well.

Preparation of methacrylate/acrylate polymers

The procedure for synthesising the matrix of MMA and nBA was adopted from Heng and Hall [14]. The method uses free radicals to polymerize the solution. This was accomplished by adding 0.40 g of MMA, 5.54 g of nBA and 2.88 mg of AIBN to 3 mL of dry benzene to act as initiators. The MMA–nBA mixture was degassed with nitrogen for 15 min before being heated for 12 h at 80 °C. The MMA–nBA copolymer was then isolated by precipitation with petroleum ether and purified in the same solvent. The transparent and sticky matrix was dried for 2 days in vacuum before use and was characterised by RMN H (data not shown) to determine the ratio between each monomer in the final product (MB 1:10).

Development of the solid-contact pH ISE

The electrodes were developed in our laboratory. A glassy carbon (GC) rod (Sigradur®G, length 50 mm and diameter 3 mm) provided by HTW GmbH was introduced inside a Teflon body in order to provide both the electrode support and the electrical contact between the ion-selective electrode and the potentiometer (the active surface was around 7 mm^2). The electrode was first polished using abrasive paper (Carbimet 600/P1200, Buehler) and subsequently treated using alumina of different grain size (30, 5 and 1 μm Micropolish II, Buehler). A layer of MWCNTs was deposited by spraying an aqueous dispersion containing 10^{-2} wt.% of the non-carboxylated MWCNTs and 1 wt%. of sodium dodecyl sulphate (SDS) onto the GC. Prior to the deposition, the dispersion was homogenised by tip-sonicator for 30 min (amplitude 60 %, cycle 0.5, Ultraschallprozessor UP200S, Dr. Hielscher, Germany). The deposition was achieved in successive steps. After spraying the dispersion of MWCNTs for 2 s, the layer was dried, thoroughly washed with water and dried again. The process was repeated 35 times obtaining a thickness of around 35 μm measured by ESEM.

Ion-selective membrane preparation

The hydrogen ion-selective membrane was composed of 1.95 wt.% ionophore (tri-*n*-dodecylamine, TDDA), 0.58 wt.% KTpClPB and 97.47 wt.% self-placticised MMA–nBA polymeric matrix. Ion-selective membrane (200.06 mg) was dissolved in 2 mL dichloromethane. The mixture was mixed in vortex for 1 h. Then, 150 μL of the membrane cocktail was drop-casted onto the MWCNT layer that had been previously deposited onto the glassy carbon electrode.

The conditioning of the electrodes was fundamental to obtaining reliable and successful results. The electrodes were conditioned in pH=3 for 1 day and then in pH=12 for 2 days [3].

Instruments and EMF measurements

All electromotive forces (EMF) were measured at room temperature (23±2 °C) in stirred solutions and using a 16-channel high-input impedance voltmeter (EMF16, Lawson's Labs, USA). A double-junction Ag/AgCl/3 M KCl reference electrode (type 6.0729.100, Methrom AG) containing a 1 M LiAcO electrolyte bridge was employed. Activity coefficients were calculated using the Debye–Huckel approximation and the potential measurements were corrected by using the Henderson equation to determine the liquid junction potential. The experimental pH values were recorded in parallel with a calibrated glass pH electrode (pH meter GLP21, Crison).

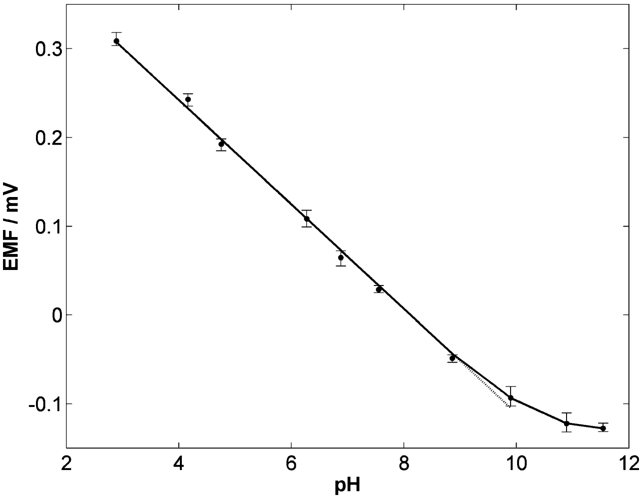

Fig. 1 Calibration curve for MWCNT pH sensors in different buffer solutions at constant ionic strength (I=0.01 M). Slope of 58.8± 0.4 mV/pH unit. The *error bars* represent the standard deviation at each point of the calibration curve for three different electrodes in three different days

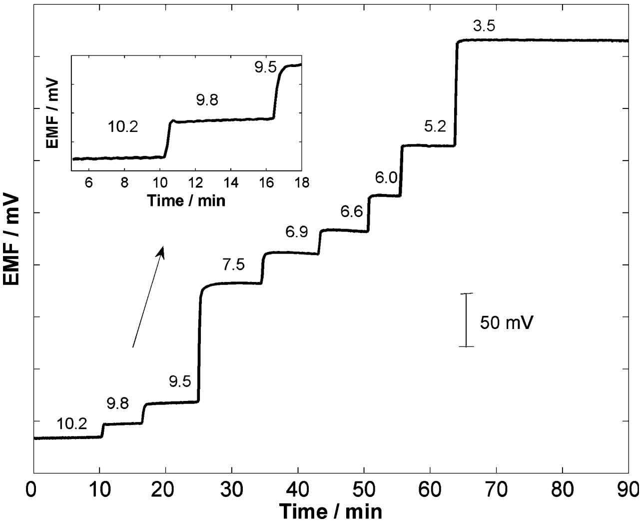

Fig. 2 Response time ($t_{95\%}$) derived from EMF responses of the MWCNT pH sensor over time for increasing pH values in the test solution

Impedance spectra of MWCNT-based hydrogen ion sensor

The measurements were taken under open circuit potential using a one-compartment cell with three electrodes. The working electrode was GC/MWCNT/ISM (area 0.07 cm^2) and the auxiliary electrode was a glassy carbon rod. The reference electrode was an Ag|AgCl|KCl (3 M) single junction (Model 6.0733.100, Metrohm). All measurements were taken at room temperature (23±2 °C). All electrochemical measurements were made using an Autolab general purpose electrochemical system and an Autolab frequency response analyser system (AUT20.FRA2-AUTOLAB, Eco Chemie, B.V., The Netherlands). The

Table 1 Potentiometric selectivity coefficients $\left(\mathrm{Log}K_{ij}^{\mathrm{pot}}\right)$ determined for the MWCNT-based pH electrode incorporating the ionophore tridodecylamine to the methacrylic–acrylic polymeric membrane. The FIM method was employed using 0.1 M concentrations of the secondary ion in all cases

Interference (M)	Slope (mV/decade)	Selectivity $\left(\log K_{\mathrm{H-M}}^{\mathrm{pot}}\right)$
K^+	−60.01	−7.86
NH_4^+	−59.2	−8.90
Li^+	−59.5	−8.90
Na^+	−59.8	−8.90
Ca^{+2}	−29.2	−8.36
Mg^{+2}	−29.8	−9.4

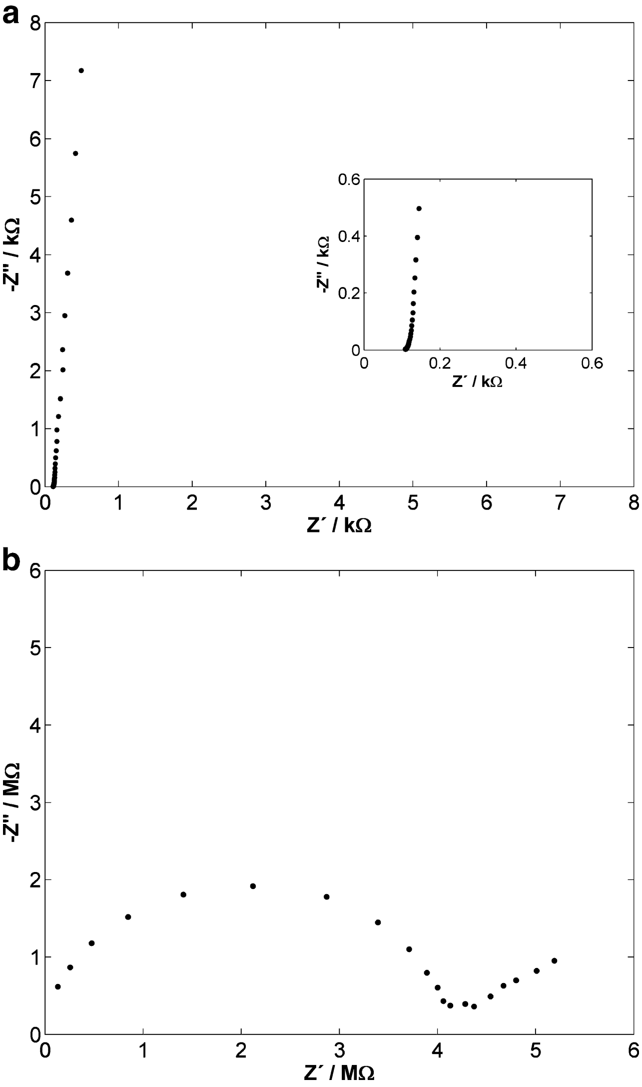

Fig. 3 Experimental data obtained from electrochemical impedance spectrum analysis. **a** Impedance plot of GC/MWCNT recorded at E_{dc}= 0.2 V, range 0.3 Hz–10 kHz. ΔE_{ac}=10 mV in pH=4.16. *Inset* range 3 Hz–10 kHz. Fitting values, Cd=100 µF. **b** Electrochemical Impedance plot of GC/MWCNT/ISM recorded at E_{dc}=0.2 V, range 0.01 Hz–100 kHz. ΔE_{ac}=10 mV in pH=4.16

impedance spectra were recorded within the frequency range of 10 kHz to 0.3 Hz and the amplitude for the sinusoidal excitation signal was 10 mV. Autolab impedance analysis software was used to fit the spectra to an equivalent electrical circuit that had previously been reported by our group [9] for electrodes with SWCNTs as the transducer.

Chronopotentiometric measurements

A constant current of a 1 and 5 nA was applied for 100 s followed by a reversed current of the same magnitude for the same time. The potentials were measured in a solution of pH=4.16 at 23±2 °C. These measurements were recorded with a one-compartment, three-electrode cell in which the electrode under study was the working electrode. The reference electrode was Ag/AgCl/KCl (3 M), and the auxiliary electrode was a glassy carbon rod. All measurements for potentials refer to this reference electrode.

Results and discussion

Figure 1 displays the potentiometric EMF recorded at pH values ranging from 2.89 to 11.54 (while keeping the same ionic strength) using the MWCNTs-ISE. A Nernstian response was obtained for different electrodes, obtaining values of 58.8±0.4 mV/unit of pH. The mean and standard deviation of the slope was evaluated using nine pH points of the calibration curve for three different electrodes in three different days. The linear dynamic range spans seven pH units from 2.89 to 9.90 (Fig. 1).

The response time ($t_{95\%}$) of the electrode has been calculated following the IUPAC criteria [15] and using the calibration curve with successive additions of 0.1 M HCl so as to decrease the pH in the solution from 11 to 3 (Fig. 2). The value obtained for the whole range of pH is shorter than 10 s.

The selectivity coefficients (log K_{ij}) for the MWCNT-based pH ISE were calculated using the fixed interference method [16]. The most common cations in aqueous solutions such as Li^+, Na^+, K^+, NH_4^+, Ca^{2+} and Mg^{2+} were tested. The EMF was measured in the presence of 0.1 M concentration of each secondary ion. For all cases, Nernstian responses were obtained with a high degree of linearity over the reported pH range. Table 1 lists the logarithmic selectivity coefficients, which show that the

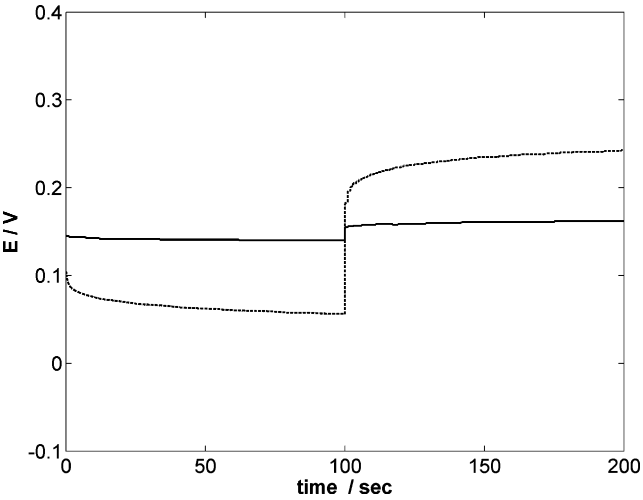

Fig. 4 Chronopotentiometric results for MWCNTs sensor at pH= 4.16. Solid line: applied current −1 nA for 100 s and 1 nA for 100 s. *Dotted line* applied current −5 nA for 100 s and 5 nA for 100 s

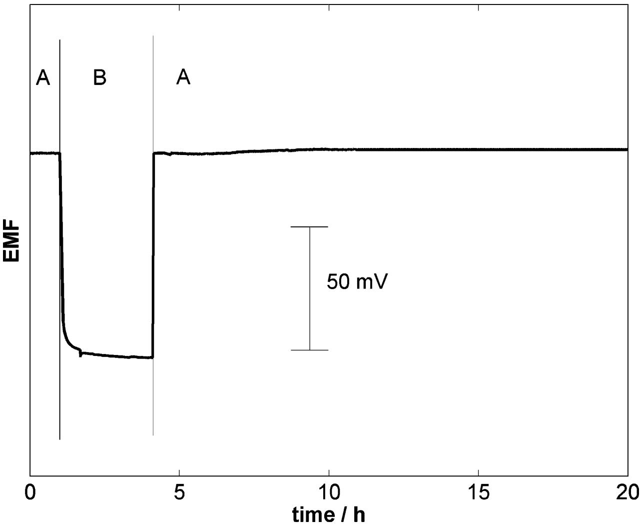

Fig. 5 Water layer test for MWCNT pH sensor. The measurements were recorded in 10^{-3} M HCl (**a**) and in 10^{-3} M KCl at pH=5 (**b**)

ion-selective membrane of the electrode makes it very highly selective towards the secondary ions tested, findings which agree with previously reported results [17].

Figure 3a shows the complex impedance plot for GC/MWCNT where the spectrum is dominated by a 90° capacitive line which extends down to low frequencies (0.3 Hz). At high frequencies, only a slight deviation from the capacitive line can be observed, indicating a fast transduction across the MWCNT film/electrolyte solution. The value for the double-layer capacitance obtained after the fitting was 100 μF. The impedance plot shape agrees with previous spectra reported for carboxylated SWCNTs [9].

Impedance measurement of the GC/MWCNT/membrane was also recorded and is shown in Fig. 3b. This type of spectrum shows the behaviour of the membrane in the electrode. At high frequencies, the signal is mainly dominated by the resistance and the geometric capacitance in parallel with the membrane, as is shown by the small semicircle between 0.1–10 kHz. On the other hand, there is a diffusional component (45° line) at low frequencies which is related to diffusion of the analyte from the solution into the ISM.

Reversal chronopotentiometry has been applied to evaluate the stability of the electrode developed according to Bobacka (Fig. 4) [18]. The potential jump is related to the total resistance (R). The total resistance calculated for the electrodes developed at two levels of current (I=1 and 5 nA) was around R=13 MΩ. From the same experimental plots, the stability of the potentials can be derived from the ratio $\Delta E/\Delta t$. The resulting values were $\Delta E/\Delta t$=40 and 140 μV/s for 1 and 5 nA, respectively. As expected, the value obtained for low frequency capacitances is quite similar for both currents and is close to 30 μF, thus indicating a potentiometric drift of 0.1 mV/h when the flow current in the system is around 10^{-12} A. These results closely agree with the stability parameters obtained in the potentiometric experiments.

Finally, we used the potentiometric water layer test [19] to assess the stability of the MWCNTs-ISE by studying the presence and possible influence of an aqueous solution film at the interface between the ISM and the MWCNTs. The experiment was done in three steps (Fig. 5). Firstly, the EMF was recorded for 1 h in HCl 10^{-3} M, H^+ being the primary analyte. Secondly, the solution was changed to KCl 10^{-3} M (interference) and the potential was recorded for 3 h. Finally, the electrode was submerged again in the initial solution for 24 h. The absence of a positive slope in the second step suggests that no undesirable water film was formed between the solid internal contact and the sensing membrane. The highly hydrophobic character of the MWCNT network could be the main reason for the absent or reduced water layer. In addition, the intermediate term stability was calculated with the data generated in the third step of the test. The value obtained corresponds to 0.5 mV h^{-1} for 16 h.

Conclusions

Results show that an MWCNT network placed between the self-placticised polymeric membrane and the glassy carbon rod is able to efficiently transduce the ionic into electronic current. We have not found a noticeable difference between the transducing behaviour of single-walled and multi-walled carbon nanotubes. Since the main parameter governing the transduction process is attributed to the double-layer capacitance, it is logical that no significant differences appear between semiconducting and metallic carbon nanotubes, unlike in field-effect transistors. The MWCNT-based solid-contact pH electrode displays a Nernstian response with a linear pH range from 2.89 to 9.90. The electrode displays considerable stability, with response times shorter than 10 s. The new pH sensor can successfully discriminate the most common interfering ions present in the usual water samples. Moreover, the absence of an aqueous layer, which is probably due to the hydrophobic character of MWCNTs, increased the stability of the electrodes. The development of solid-contact ion-selective electrodes based on carbon nanotubes enables this type of sensor to be miniaturised, a process that has already started in our laboratory.

Acknowledgements This work was supported by the Spanish MICINN, through the project grants NAN2004-09306-C05-05 and CTQ2006-7-67570/BQU. G.A.C. also acknowledges MICINN for the doctoral fellowship AP2006-04171 and D.G acknowledges the economic support provided by the Universitat Rovira i Virgili.

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