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Published in:
Talanta

DOI:
[10.1016/j.talanta.2018.04.056](https://doi.org/10.1016/j.talanta.2018.04.056)

Published: 01/01/2018

Document Version
Accepted author manuscript

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[Link to publication](#)

Please cite the original version:

Ocana Tejada, C., Abramova, N., Bratov, A., Lindfors, T., & Bobacka, J. (2018). Calcium-selective electrodes based on photo-cured polyurethane-acrylate membranes covalently attached to methacrylate functionalized poly(3,4-ethylenedioxythiophene) as solid-contact. *Talanta*, 186, 279–285.
<https://doi.org/10.1016/j.talanta.2018.04.056>

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Calcium-selective electrodes based on photo-cured polyurethane-acrylate membranes covalently attached to methacrylate functionalized poly(3,4-ethylenedioxythiophene) as solid-contact

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Abstract

We report here the fabrication of solid-contact calcium-selective electrodes (Ca^{2+} -SCISEs) made of a polyurethane acrylate ion-selective membrane (ISM) that was covalently attached to the underlying ion-to-electron transducer (solid-contact). Methacrylate-functionalized poly(3,4-ethylenedioxythiophene) (Meth-PEDOT) and Meth-PEDOT films containing either multiwalled carbon nanotubes (MWCNT) or carboxylated MWCNT (cMWCNT) were used as solid contacts. The solid contacts were deposited by drop-casting on screen-printed electrodes and characterized by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and potentiometry. Covalent binding between the solid contact and the ISM was obtained via photopolymerization in order to increase the robustness of the Ca^{2+} -SCISEs. The performance of the Ca^{2+} -SCISEs was studied by measuring their potentiometric response and their sensitivity to light, oxygen and carbon dioxide. Meth-PEDOT was found to be a promising solid-contact material to develop low-cost and easy to prepare ISEs.

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2 **Keywords:** tetramethacrylate poly(3,4-ethylenedioxythiophene), MWCNT, all-solid-
3 state ion-selective electrode, calcium, polyurethane membrane.
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6 7 **1. Introduction**

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9 Over the years, the synthesis and characterization of conducting polymers has
10 attracted attention due to their unique electronic and optical properties [1, 2] in many
11 applications such as electrochromic devices [3-5], light emitting diodes [6-8], energy
12 storage devices [9-11], biosensors [12-14] and all-solid-state ion sensors [15-18].
13 Among electronically conducting polymers, there is a considerable interest in using
14 poly(3,4-ethylenedioxythiophene) (PEDOT) because of its low oxidation potential,
15 high stability in ambient environments [19, 20], mechanical flexibility and stable
16 oxidized form [21]. Furthermore, addition of electrically conducting nanomaterials
17 (e.g. graphene or carbon nanotubes) to PEDOT is known to improve the electrical
18 conductivity by better connecting individual conducting PEDOT domains in the
19 composite film [22, 23].
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31 In this work, methacrylate-functionalized PEDOT (Meth-PEDOT), Meth-PEDOT
32 containing MWCNT (Meth-PEDOT-MWCNT) and cMWCNT (Meth-PEDOT-
33 cMWCNT) were used as the ion-to-electron transducer in potentiometric solid-contact
34 calcium-selective electrodes (Ca^{2+} -SCISEs). In recent years, the classical liquid
35 contact ISEs are being replaced by SCISEs due to the possibility of robust
36 miniaturization [24], low-cost production and compatibility with mass production by
37 standard microfabrication techniques [25]. Most of the reported SCISEs with
38 conductive polymers use plasticized poly(vinyl chloride) (PVC) as the ion-selective
39 membrane (ISM) [26-28]. However, the PVC-based ISEs suffer from diffusion of
40 water through the ISM and the possible formation of a water layer or water pools at
41 the ISM/solid-contact (SC) or SC/substrate interfaces resulting in poor potential
42 stability and weakening of the ISM adhesion to the substrate [29, 30].
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54 Photocurable membranes are alternative materials to PVC-ISMs. Several ISEs using
55 photocurable ISMs have been developed since their introduction in the middle of
56 1980s and 1990s [31, 32]. Photo-cured polymeric systems show many advantages
57 over PVC-ISMs such as the possibility to use standard photolithography processes,
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which may be beneficial for mass production of ISEs, and the opportunity to obtain ISMs with low leaching rates of the active components [33]. Urethane-acrylate ISMs are one of the most used photo-cured membrane types because of their fast curing rates and their compatibility with common plasticizers and ionophores [34]. In addition, this type of ISMs present high durability and reduced biofouling when SCISEs are used in biological samples [35] and they may possibly be chemically “anchored” to the solid electrode substrate [32]. However, it must be noted that it is not the first time that Meth-PEDOT and ISM matrix are copolymerized. Rzewuska et al. reported SCISEs based on the copolymerization of polyacrylate-based membrane and Meth-PEDOT on a glassy carbon electrode surface forming a single phase membrane matrix [36]. However, in this approach the polymerization time was 5 minutes and in our previous studies we observed that when the polymerization time increases the selectivity of the SCISEs becomes worse due to the sodium tetrakis[3,5-bis-(trifluoromethyl)phenyl]borate photobleaching [37].

The main aim of this work is electrochemical characterization of Meth-PEDOT, Meth-PEDOT-MWCNT and Meth-PEDOT-cMWCNT and their application as ion-to-electron transducers in polyurethane (PU) based Ca^{2+} -SCISEs. In this paper, we present a simple, low-cost and robust method for preparing Ca^{2+} -SCISEs, which might be beneficial for different fields such as ranching where they require easy to use and semiautomatic analytical systems with very low costs per analysis. The end-capped methacrylate groups of Meth-PEDOT functioned as reactive sites for obtaining better bonding and stronger adhesion to the PU-acrylate ISM during the copolymerization process. This was expected to enhance the durability of the Ca^{2+} -SCISEs.

2. Experimental

2.1. Chemicals

Tetramethacrylate end-capped poly(3,4-ethylenedioxythiophene) solution (Meth-PEDOT, 0.5 wt% dispersion in propylene carbonate carbonate and p-toluenesulfonate as charge compensating ion), KCl, KNO_3 , CaCl_2 , $\text{Ca}(\text{NO}_3)_2$ and carboxylated MWCNTs were obtained from Sigma Aldrich. MWCNTs were obtained from DropSens (Oviedo, Spain). Calcium Ionophore II (ETH 129), bis(2-ethylhexyl) sebacate (DOS), potassium tetrakis(p-chlorophenyl)borate (KTPClPB), ETH500 and

1 hexafluorobutyl acrylate (HFBuA) were obtained from Fluka. Aliphatic urethane
2 diacrylate (oligomer Ebecryl 270), cross-linker and hexanediol diacrylate (HDDA)
3 were from UCB Chemicals and the photoinitiator 2,2- dimethoxy-2-
4 phenylacetophenone (IRG 651) from Ciba-Geigy. All other chemicals used were
5 analytical reagent grade and all solutions were prepared using ultrapure deionized
6 water with the resistivity of 18.2 MΩ cm (Milli-Q system, Millipore, Billerica, MA).
7 Screen-printed electrodes (SPEs) with silver ink and flash gold (d=2 mm) prepared on
8 PET polymer substrates were supplied by FAE (FAE S.A., Spain).
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16 *2.2. Meth-PEDOT, Meth-PEDOT-MWCNT/cMWCNT deposition*

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19 5.0 μL (2×2.5 μL) of Meth-PEDOT solution containing either 0.2-0.5 wt% MWCNT
20 or cMWCNT solution was drop-cast on the screen-printed electrodes to form SC
21 layers of Meth-PEDOT-MWCNT and Meth-PEDOT-cMWCNT. After that, the
22 electrodes were placed on a heating plate at 50 °C to increase the evaporation rate of
23 the propylene carbonate solvent. All further experiments were performed at room
24 temperature.
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31 *2.3. Ca²⁺-selective ISM deposition*

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34 The photocurable ISM composition was prepared as presented previously [38].
35 Briefly, the main polymer composition was prepared by mixing the aliphatic urethane
36 diacrylate oligomer Ebecryl 270 with the reactive diluent HDDA and the
37 photoinitiator Irgacure 651 in the ratio (w/w) of 81:17:2. In the next step, 0.3 g of the
38 main polymer composition was dissolved in 0.2 ml THF and the plasticizers DOS and
39 HFBuA, Ca²⁺-ionophore II and lipophilic salts were then added to this solution. This
40 ISM solution was placed in an ultrasonic bath until it was homogeneous and then left
41 unstirred for several hours to allow evaporation of THF from the solution. This
42 resulted in the following ISM composition: main polymer mixture (56.5 wt%), DOS
43 (20.0 wt%), HFBuA (20.0 wt%), Ca²⁺-ionophore II (1.0%), KTpCIPB (0.5 wt%) and
44 ETH 500 (2.0 wt%).
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55 ISMs were deposited on the screen-printed electrode substrates (Ag and Au) by
56 applying the ISM solution with a microsyringe on the Meth-PEDOT, Meth-PEDOT-
57 MWCNT and Meth-PEDOT-cMWCNT solid-contact layers. After the ISM
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1 deposition, the electrodes were exposed to 365 nm UV light for 20 s using a UV
2 Curing Light Lamp 8141 (Düren, Germany) to form covalent bonds between the
3 ISMs and the acrylate groups of SCs. A scheme of the copolymerization process is
4 shown in Fig.S1. Crosslinking between the PU-ISM and polyaniline functionalized
5 with methacrylate groups was confirmed by FTIR-ATR analysis in previous studies
6 [32]. Therefore, we assume that crosslinking occurs also between the PU-ISM and the
7 Meth-PEDOT used in this work. The thicknesses of the ISM was ca. 200 μm , as
8 measured with a micrometer screw gauge (resolution: 1 μm) after the polymerization
9 process.
10

11 2.4. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS)

12 Cyclic voltammograms and impedance spectra were recorded by using a one-
13 compartment three-electrode cell connected to the Autolab potentiostat equipped with
14 a frequency response analyzer (AUT20.FRA2-AUTOLAB, Eco Chemie, B.V., The
15 Netherlands). The screen-printed electrodes, a glassy carbon rod and a double
16 junction Ag/AgCl/3 M KCl//0.1 M LiOAc served as the working (WE), auxiliary
17 (AE) and reference electrode (RE), respectively. CVs were recorded between -0.5 V
18 and +0.4 V in 0.1 M KNO₃ at a scan rate $\nu = 0.01 \text{ Vs}^{-1}$. The impedance spectra were
19 measured at the open circuit potential (E_{dc}) in 0.1 M KNO₃ within the frequency
20 range ($f = 10 \text{ kHz} - 0.01 \text{ Hz}$) using an excitation signal amplitude $\Delta E_{\text{ac}} = 10 \text{ mV}$. The
21 impedance spectra were fitted to equivalent circuits with the ZView software
22 (Scribner Associates Inc., USA).
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42 2.5. Chronopotentiometric measurements

43 Constant-current chronopotentiograms were recorded in 0.1 M CaCl₂ with the
44 Autolab potentiostat described above by passing a constant current of $\pm 1 \text{ nA}$ through
45 the Ca²⁺-SCISEs for 60 s [39].
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51 2.6. Potentiometric measurements

52 The potentiometric response of the Ca²⁺-SCISEs was measured in a Faraday's cage
53 with a 16-channel potentiometer (Lawson Labs, Inc., input impedance: $10^{15} \Omega$) and by
54 using the double junction Ag/AgCl/3M KCl//0.1 M LiOAc as the RE. The Ca²⁺-
55 SCISEs were preconditioned under stirring in 10^{-3} M CaCl_2 for 3 days prior to the
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1 potentiometric measurements. Calibration plots were obtained in CaCl₂ solutions from
2 10⁻⁷ M to 10⁻² M by stirring the solutions for 2 min at each concentration. The activity
3 coefficients were calculated according to the Debye-Hückel equation.
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6 The selectivity coefficients towards Na⁺, K⁺, Mg²⁺, NH₄⁺ and Li⁺ ions were
7 determined at 0.1 M concentrations of interfering ions with the mixed solution
8 method recommended by IUPAC [40]. The potentiometric aqueous layer tests were
9 performed by recording the Ca²⁺-SCISE potentials in 0.1 M CaCl₂, 0.1 M NaCl and
10 0.1 M CaCl₂ solutions (in this order). The CO₂ and O₂ sensitivities of the Ca²⁺-SCISEs
11 were obtained by measuring the potential of the Ca²⁺-SCISEs in a 0.1 M CaCl₂
12 solution that was purged with pure O₂, N₂ and CO₂ gas in the following sequence: N₂
13 (1h), O₂ (1h), N₂ (1h), CO₂ (1h), N₂ (1h). The light sensitivity was measured in 0.1 M
14 CaCl₂ solution by monitoring the Ca²⁺-SCISE potentials as the illumination of the
15 electrode surfaces changed in the following order: darkness (30 min), ambient room
16 light (30 min), cold light (30 min), ambient room light (30 min) and darkness (30
17 min). The Leica CLS 150 XE cold light source (150 W, 21 V) was directed through
18 the electrolyte solution towards the Ca²⁺-SCISEs surfaces.
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31 **3. Results and discussion**

32 *3.1. CV and EIS characterizations*

33 According to Nikolskii and Materova, the SCISEs must have reversible transition
34 from ionic to electronic conductivity at the ISM/SC interface and sufficiently high
35 exchange currents in comparison with the current generated by the potential
36 measurement circuitry to obtain a stable electrode potential [40]. These requirements
37 imply that the solid-contact should have a high redox capacitance to become less
38 polarizable and provide a more stable potential [41].
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48 As shown in Fig. 1, the CVs of the Meth-PEDOT, Meth-PEDOT-MWCNT and Meth-
49 PEDOT-cMWCNT films measured after 100 potential cycles in 0.1 M KNO₃ showed
50 the typical oxidation and reduction behavior of PEDOT [42]. The rather symmetrical
51 shape of the CVs of all Meth-PEDOT films indicates high reversibility of the doping
52 process. The Meth-PEDOT-MWCNT/cMWCNT films (containing CNTs) give in
53 general higher oxidation and reduction currents than the Meth-PEDOT film prepared
54 without CNTs. The highest currents are obtained with the Meth-PEDOT film
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1 containing 0.5 wt% cMWCNT. The improved redox behavior is due to the MWCNT
2 and cMWCNT facilitating the formation of a more extended electrically conductive
3 network in the Meth-PEDOT matrix by connecting isolated conducting PEDOT
4 domains, which enhances the electron transfer at the PEDOT-SC/screen-printed
5 electrode interface [43]. The improved redox behavior is more significant for
6 cMWCNT than for MWCNT due to the presence of carboxyl groups, which can more
7 efficiently participate in the charge compensation process of the Meth-PEDOT films
8 during its oxidation and reduction in 0.1 M KNO₃.
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16 The impedance spectra of the Meth-PEDOT and Meth-PEDOT-MWCNT/cMWCNT
17 solid-contacts in Fig. 2a support the results obtained by CV. The impedance spectra
18 show an almost vertical capacitive behavior at low frequencies except for Meth-
19 PEDOT, which shows a typical diffusional behavior indicating slower ion and
20 electron transport than in the other SCs. The impedance data for Meth-PEDOT-
21 MWCNT/cMWCNT was fitted to the equivalent circuit presented in Fig. 2b
22 composed by the solution resistance (R), the finite-length Warburg diffusion element
23 (Z_D) and the constant phase element (CPE) in series. The equivalent circuit is similar
24 to the one developed earlier for electropolymerized PEDOT [40]. The Z_D element is
25 related to the diffusional time constant (τ_D), the pseudocapacitance (C_D) and the
26 diffusion resistance ($R_D = \tau_D / C_D$) [44]. Fig. S2 compare the experimental and fitted
27 EIS data in the form of Nyquist plots and Table S1 summarizes the results of the
28 fittings. The impedance spectrum for Meth-PEDOT (0 wt% MWCNT/cMWCNT)
29 differs from the rest of the electrodes (Fig. 2a) and did not give a good fit to the
30 equivalent circuit in Fig. 2b, as shown in Fig. S2. Therefore, Meth-PEDOT (0 wt%
31 MWCNT/cMWCNT) was left out from the comparison shown in Table S1. As
32 expected, the addition of MWCNTs/cMWCNTs increases the capacitance of Meth-
33 PEDOT (Table S1) since the CNTs interconnect isolated PEDOT segments, thus
34 improving the oxidation and reduction of PEDOT and lowering its resistance.
35 Additionally, charging of the MWCNT/cMWCNT surface may also contribute to the
36 higher capacitance. The CPE and n values of 1.10-3.40 mF and 0.94-0.98,
37 respectively, describe almost an ideal capacitor ($n=1$) and the Meth-PEDOT-
38 cMWCNT films show the highest capacitance of all SCs studied here. This
39 assumption is supported by the results of the EIS fittings shown in Table 1 revealing
40 that the Meth-PEDOT-cMWCNTs have the largest redox capacitance (C_D) and the
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smallest diffusion resistance (R_D). These data suggest that the Meth-PEDOT-cMWCNT composite films are best suited as solid-contacts among the Meth-PEDOT films studied here for the PU based Ca^{2+} -SCISEs.

3.2. Potentiometric response of the Meth-PEDOT-based solid-contacts

Initially the potentiometric response of the Meth-PEDOT and Meth-PEDOT-MWCNT/cMWCNT films was studied in the absence of calcium ions in KNO_3 solutions with results presented in Fig. 3. The Meth-PEDOT and the Meth-PEDOT-MWCNTs films showed an anionic response at concentrations $> 10^{-5}$ M implying that the small and mobile NO_3^- (in comparison to the bulky immobilized MWCNTs) function as the main charge compensating anion in the oxidation and reduction reaction of Meth-PEDOT according to equations (1) and (2), which includes also electron transfer between Meth-PEDOT and the electronically conducting substrate (electrical contact). We assume that the less bulky *p*-toluenesulfonate (pTS) used originally as the charge compensating anion in the commercial Meth-PEDOT formulation (according to Sigma-Aldrich) is exchanged to NO_3^- in the PEDOT matrix during the conditioning of the electrodes in 0.1 M KNO_3 . In Equation (2), we assume (for simplicity) that the MWCNTs have a surface charge close to zero:



On the other hand, the potentiometric response of the Meth-PEDOT-cMWCNT films was only slightly anionic indicating that the films exchange both anions and cations, in addition to electron transfer, resulting in a thermodynamically more well-defined ISM/SC interface. The cationic response in presence of mobile Ca^{2+} cations is illustrated by Equation 3:



We may also note here that PEDOT electropolymerized in the presence of the immobile and negatively charged polystyrenesulfonate anion (PSS^-) gives a cationic

1 potentiometric response [19] due to the oxidation-reduction reaction similar to
2 presented in Equation 3.
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5 3.3. Chronopotentiometric measurements with Ca^{2+} -SCISEs 6

7 Constant-current chronopotentiometric measurements were performed in order to
8 critically evaluate the potential stability of the different types of Ca^{2+} -SCISEs [19].
9 The slope ($\Delta E/\Delta t$) of the response curves provides a direct measure of the potential
10 stability of the Ca^{2+} -SCISEs upon passage of a small current. As can be seen in Fig. 4
11 and Table 1, all Ca^{2+} -SCISEs prepared with the Meth-PEDOT and Meth-PEDOT-
12 MWCNT/cMWCNT solid-contacts showed rather similar potential drifts. From these
13 measurements in Fig. 4, we can estimate the total resistance of the PU-ISM and the
14 SC, and the redox capacitance (C_L) of the SC covered by the PU-ISM. We should
15 point out here that the resistance of the SC is usually negligible compared to that of
16 the ISM. For the Ca^{2+} -SCISEs studied, the bulk resistance is obtained from the
17 potential difference (ΔE) in the chronopotentiograms when the current direction is
18 reversed at $t=60$ s. As expected, all PU-ISMs had relatively high bulk resistances of
19 86-117 M Ω (Table 1). However, the buried SCs had rather similar redox capacitances
20 varying between 29-47 μ F. Especially the Meth-PEDOT and Meth-PEDOT-
21 cMWCNTs had almost identical redox capacitances of 29-35 μ F showing that the
22 cMWCNTs do not improve the redox capacitance of the PEDOT-SC in Ca^{2+} -SCISEs.
23 We determined therefore also the redox capacitance of the non-coated Meth-PEDOT
24 and Meth-PEDOT-MWCNT/cMWCNT solid-contacts (without ISM) from the CV
25 and EIS measurements. Table 1 reveals that after deposition of the PU-ISM the
26 capacitances decreased to 3.6-10.7% from their initial values for the uncoated SCs.
27 For the Meth-PEDOT prepared 0.5 wt% cMWCNTs, the redox capacitance dropped
28 to only ca. 1% due to its considerably higher initial capacitance than for the other
29 SCs. It can thus be concluded that the redox process of the SCs beneath the ISM and
30 the ion transport associated with it, which is necessary for the oxidation and reduction
31 reaction of Meth-PEDOT, is hampered by the PU-ISM [39].
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54 3.4. Calibration of the Ca^{2+} -SCISEs 55

56 Fig. 5a shows the potentiometric response of the different Ca^{2+} -SCISEs in 10^{-7} M to
57 10^{-2} M $CaCl_2$ solutions (calibration from low to high concentrations). All electrodes
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1 showed almost Nernstian slopes, which were calculated from the linear part of the
2 calibration curves, and rather similar detection limits (LOD) of $(3.4-8.2) \times 10^{-6}$ M
3 (Table 2). We determined the reproducibility of the standard potential (E^0) by
4 extrapolating the linear section of the calibration curve to $a_{Ca} = 1$ (*i.e.* $\log a_{Ca} = 0$).
5 Table 2 summarizes the reproducibility of the different Ca^{2+} -SCISEs. The best
6 reproducibility was obtained for the Ca^{2+} -SCISEs with Meth-PEDOT and Meth-
7 PEDOT (0.2 wt% cMWCNT) as solid-contact showing the lowest standard deviation
8 of E^0 (± 13 mV; $n = 6$). In contrary to other studies [43, 45], our results indicate that
9 we did not obtain any significantly improvements in the potentiometric response of
10 the Ca^{2+} -SCISEs by adding MWCNTs/cMWCNTs to the methacrylate functionalized
11 PEDOT-SC. This discrepancy can be related to the fact that the transduction
12 mechanism (*i.e.* oxidation and reduction reaction) of the SC is limited by the PU-ISM.
13 This is probably due to the much higher bulk resistance of the PU-ISM (86-117 M Ω)
14 compared to the plasticized PVC-ISM (usually ca. 2-5 M Ω) [19, 40], indicating that
15 the diffusion coefficients of ionic species are lower in the PU-ISM. It cannot therefore
16 provide the SC with a sufficient amount of charge compensating anions or/and cations
17 .Fig. S3 shows the potential traces of the Ca^{2+} -SCISE with Meth-PEDOT in order to
18 illustrate the short-time potential stability and the response time of the sensor.
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35 The selectivity coefficients of the Ca^{2+} -SCISEs towards Na^+ , K^+ , Mg^{2+} and Li^+ were
36 determined by the mixed solution method in the presence of 0.1 M background
37 concentration of the interfering ions (Table S2). We obtained the following selectivity
38 coefficients $\log K_{Ca^{2+}, Na^+} = -3.3$, $\log K_{Ca^{2+}, K^+} = -3.4$, $\log K_{Ca^{2+}, Li^+} = -3.1$ and $\log K_{Ca^{2+},$
39 $Mg^{2+}} = -3.8$. These values are in good agreement with previously reported selectivity
40 coefficients for ISFETs and Ca^{2+} -SCISEs with the same ISM composition as used in
41 this work [32, 38]. This indicates that the selectivity of the Ca^{2+} -SCISEs is not
42 influenced by the type of the SC. It may be mentioned that ISE with PVC
43 membranes prepared with 2-nitrophenyl octyl plasticizer show better selectivity [46].
44 However, it is not possible to use compounds containing nitro-group in formulations
45 of photocurable polymers as this nitro-group inhibits the radical initiation of the
46 polymerization.
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59 3.5. Potentiometric aqueous layer test.

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1 One of the major problems of SCISEs is penetration of water through the polymer
2 membrane and its condensation at the membrane/SC interface. This produces
3 instabilities in sensor response and membrane adhesion failure. The water layer/pool
4 formation at the interface PU-ISM/SC was studied by the potentiometric aqueous
5 layer test, in which the potential drifts of the Ca^{2+} -SCISEs were measured in primary
6 and interfering ion solutions for more than 20 h [47]. As can be seen in Fig. 5b, Ca^{2+} -
7 SCISEs prepared with and without MWCNT showed rather stable potentials and
8 relatively quick recovery of the sensor signal after changing the solutions. This
9 indicates that the cross-linking between the SCs and the ISM prevents the aqueous
10 layer formation at the PU-ISM/SC interface.
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20 *3.6. Oxygen, carbon dioxide and light sensitivity of the Ca^{2+} -SCISEs.*

21 We also investigated the influence of oxygen (O_2) and carbon dioxide (CO_2) on the
22 potential stability of the Ca^{2+} -SCISEs which are of fundamental importance to
23 optimize the performance of the sensors. Fig. S4 reveals that all the Ca^{2+} -SCISEs
24 showed practically no O_2 sensitivity and negligible CO_2 sensitivity. In order to
25 determine the light sensitivity, the potential drift of the Ca^{2+} -SCISEs were measured
26 when the illumination conditions changed from darkness, room light to cold light. Fig.
27 S5 shows stable electrode potentials for the Ca^{2+} -SCISEs prepared with Meth-PEDOT
28 and Meth-PEDOT containing 0.2wt % cMWCNT, whereas the electrodes prepared
29 with Meth-PEDOT-MWCNT showed a minor potential drift during the first hour after
30 the illumination was changed from dark to room light. We conclude that the Ca^{2+} -
31 SCISEs based on Meth-PEDOT and Meth-PEDOT containing cMWCNT are not light
32 sensitive under normal measurement conditions in room light.
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45 *3.7. Durability of the Ca^{2+} -SCISEs*

46 To check the quality of the membrane/conducting polymer interface formed by
47 copolymerization in prevention of water penetration Ca^{2+} -SCISEs were kept in
48 constant contact with 10^{-3} M CaCl_2 solution during three months. After this period of
49 time it was found that all electrodes except those prepared with Meth-PEDOT
50 containing 0.2 wt% MWCNT (no response) and 0.5 wt% cMWCNT show close to
51 Nernstian slopes of 26 ± 1 mV/p Ca^{2+} . The Meth-PEDOT-0.2 % MWCNT lost its
52 response and sensors with 0.5 % cMWCNT showed sensitivity less than 20
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1 mV/decade. The average E^0 drift during this time was ca. 2 mV per day and detection
2 limits remained as low as 5×10^{-6} M. These data confirm that the cross-linking
3 between the conductive Meth-PEDOT-SC and the PU-ISM gives SCISEs with a
4 relatively long lifetime compared with other developed SCISEs which have lifetime
5 between 2 and 6 month [48-50]. These results also show that the adhesion between
6 the ISM and the screen-printed substrate is excellent.
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11 **4. Conclusions**

12 We report here a low-cost and simple fabrication method of disposable Ca-ion sensors
13 based on ISE with solid contact formed by Meth-PEDOT and Meth-PEDOT-
14 MWCNT/cMWCNT conducting polymer films. Electrochemical characterization was
15 performed using cyclic voltammetry, electrochemical impedance measurements and
16 potentiometric measurements. The results of CV and EIS experiments reveal that the
17 Meth-PEDOT-cMWCNT has a higher redox capacitance than Meth-PEDOT-
18 MWCNT and Meth-PEDOT. However, after coating the solid contacts with a photo-
19 cured polyurethane-based Ca^{2+} -selective membrane (ISM) the redox capacitance of
20 the solid contact was essentially limited by the high bulk resistance of the ISM.
21 Consequently, no significant improvements in potentiometric response of the Ca^{2+} -
22 SCISEs were obtained by adding MWCNT into the conducting polymer films in
23 terms of sensitivity, selectivity, LOD, lifetime as well as robustness to the influence
24 of light, O_2 and CO_2 . No aqueous layer formation was detected at the interfaces
25 between the solid-contacts and the membranes of the Ca^{2+} -SCISEs by using the water
26 layer test. Based on the results of this work it can be concluded that Meth-PEDOT is a
27 promising solid-contact material to develop low-cost and easy to prepare ISEs.
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46 **Acknowledgments**

47 This work was supported by the People Programme (Marie Curie Actions) of the 7th
48 Framework Programme of the European Union (FP7/2007-2013) under REA grant
49 agreement no. 600388 (TECNIOspring programme) and from the Agency for
50 Business Competitiveness of the Government of Catalonia (ACCIÓ). N.A. also
51 acknowledges the Government of Russian Federation (Grant 074-U01)
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Table 1. Results of the chronopotentiometry measurements with the Ca^{2+} -SCISEs where R , $\Delta E/\Delta t$ and C_L are the bulk resistance of the ISM, potential drift of the Ca^{2+} -SCISEs and the redox capacitance of the SC. We also show for comparison the redox capacitances of the bare Meth-PEDOT and Meth-PEDOT-MWCNT/cMWCNT solid-contacts (prepared on screen-printed electrodes, without ISM) obtained for from CV (C_{CV}) and EIS (C_{EIS}) measurements.

wt% MWCNT	wt% cMWCNT	R ($\text{M}\Omega$)	$\Delta E/\Delta t$ ($\mu\text{V}/\text{s}$)	C_L (μF)	C_{CV} (μF)	C_{EIS} (μF)
-	-	89.1	34.4	29.1 ± 8.2	400	- ^a
0.2	-	89.3	21.1	47.3 ± 7.9	521	250
0.5	-	91.1	21.9	45.7 ± 11	943	382
-	0.2	116.8	28.2	35.3 ± 9.2	980	610
-	0.5	85.7	33.3	30.0 ± 10	3070	2475

^a Value not available, because EIS data were not fitted to the equivalent circuit.

Table 2. Reproducibility of the standard potential (E^0), potentiometric slopes (S) of the linear part of the calibration curves and the detection limit (LOD) for the Ca^{2+} -SCISEs (n = 6).

wt % MWCNT	wt % cMWCNT	E^0 (mV)	S (mV/pCa)	LOD (M)
-	-	429.2 ± 12.9	28.8 ± 0.8	$(8.2 \pm 2.1) \cdot 10^{-6}$
0.2	-	422.4 ± 50.2	29.3 ± 1.0	$(3.4 \pm 3.1) \cdot 10^{-6}$
0.5	-	461.4 ± 16.3	30.3 ± 1.9	$(7.8 \pm 3.9) \cdot 10^{-6}$
-	0.2	484.9 ± 13.2	30.6 ± 0.7	$(6.3 \pm 2.0) \cdot 10^{-6}$
-	0.5	366.6 ± 37.0	29.3 ± 1.9	$(7.1 \pm 2.4) \cdot 10^{-6}$

Figure Captions

Figure 1. CVs of screen-printed Meth-PEDOT electrodes containing: (1) 0 wt% MWCNT/cMWCNT, (2) 0.2 wt% MWCNT, (3) 0.5 wt% MWCNT, (4) 0.2 wt% cMWCNT and (5) 0.5 wt% cMWCNT; CVs show the 100th cycle in 0.1 M KNO₃ with $v = 10 \text{ mV s}^{-1}$.

Figure 2. a) Electrochemical impedance spectra of the screen-printed Meth-PEDOT electrodes containing: (1) 0 wt% MWCNT/cMWCNT, (2) 0.2 wt% MWCNT, (3) 0.5 wt% MWCNT, (4) 0.2 wt% cMWCNT and (5) 0.5 wt% cMWCNT. The spectra were measured at the open circuit potential (E_{dc}) in 0.1 M KNO₃ with $\Delta E_{ac} = 10 \text{ mV}$ and $f = 100 \text{ kHz} - 10 \text{ mHz}$. **b)** The equivalent circuit used for fitting the impedance spectra where R , Z_D and CPE are the solution resistance, finite-length Warburg diffusion element and constant phase element, respectively.

Figure 3. Potentiometric response of screen-printed Meth-PEDOT solid-contacts containing either MWCNTs or cMWCNTs in 10^{-8} - 10^{-1} M KNO₃: (1) 0 wt% MWCNT/cMWCNT, (2) 0.2 wt% MWCNT, (3) 0.5 wt% MWCNT, (4) 0.2 wt% cMWCNT and (5) 0.5 wt% cMWCNT.

Figure 4. Chronopotentiograms of the Ca²⁺-SCISEs prepared with the Meth-PEDOT solid-contacts containing: (1) 0 wt% MWCNT/cMWCNT, (2) 0.2 wt% MWCNT, (3) 0.5 wt% MWCNT, (4) 0.2 wt% cMWCNT and (5) 0.5 wt% cMWCNT. The measurements were done in 0.1 M CaCl₂ by first applying +1 nA for 60 s and then -1 nA for 60 s.

Figure 5. a) Calibrations plots of the Ca²⁺-SCISEs in 10^{-7} to 10^{-2} M CaCl₂ solution. **b)** The potentiometric aqueous layer test in 0.1 M primary ion (Ca²⁺) and interfering ion (Na⁺) solutions for the Ca²⁺-SCISEs prepared with the Meth-PEDOT solid-contacts containing: (1) 0 wt% MWCNT/cMWCNT, (2) 0.2 wt% MWCNT, (3) 0.5 wt% MWCNT, (4) 0.2 wt% cMWCNT and (5) 0.5 wt% cMWCNT. Dotted line represents the ideal Nernstian plot.

Figure 1

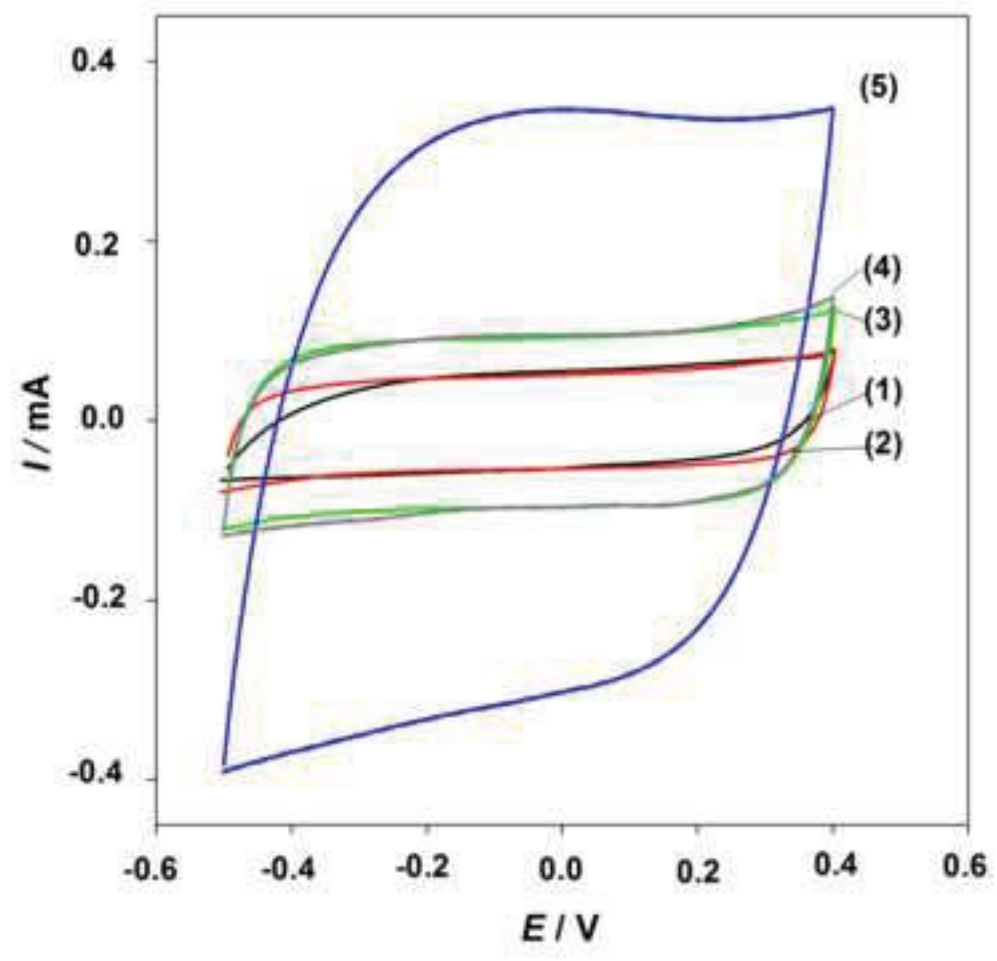
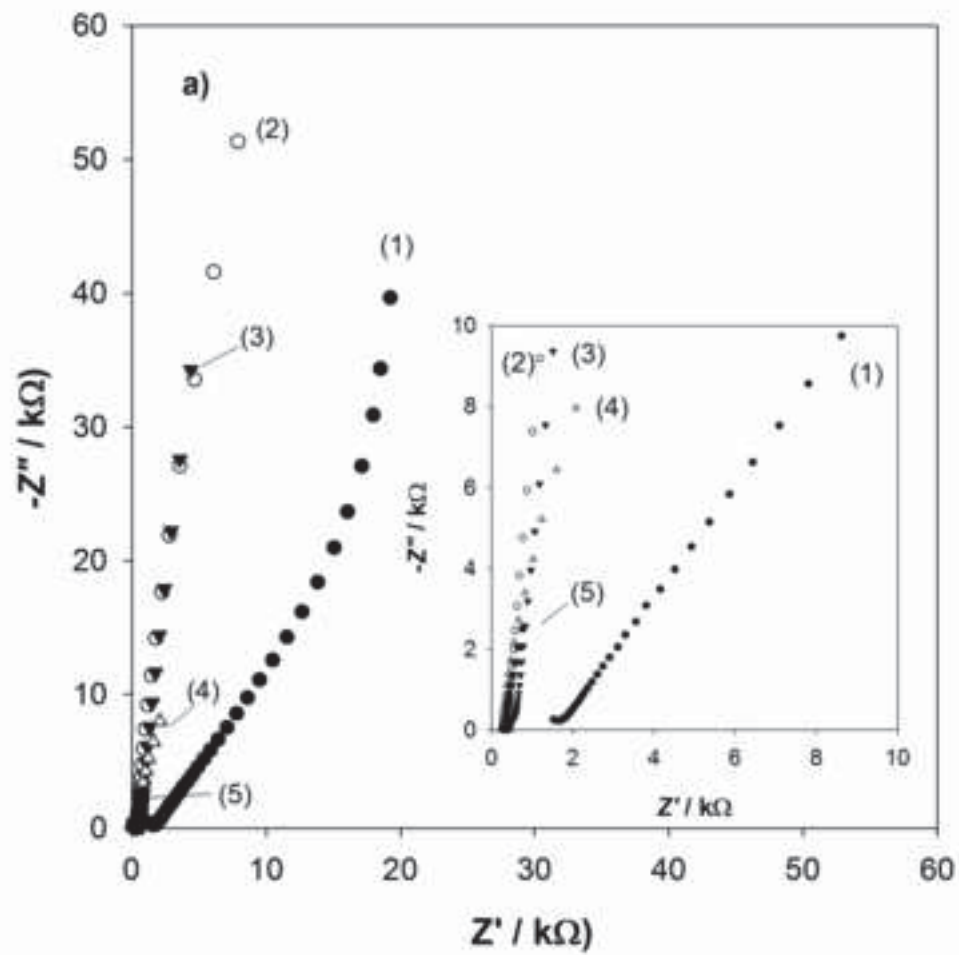


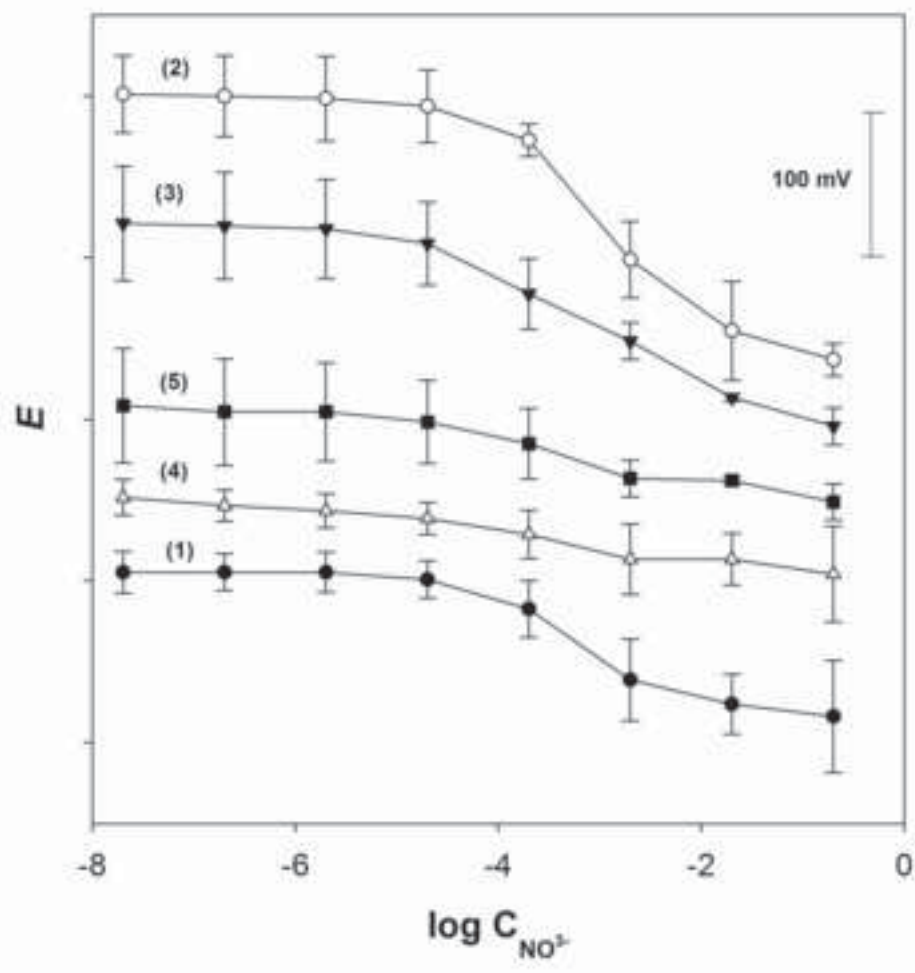
Figure 2



b)

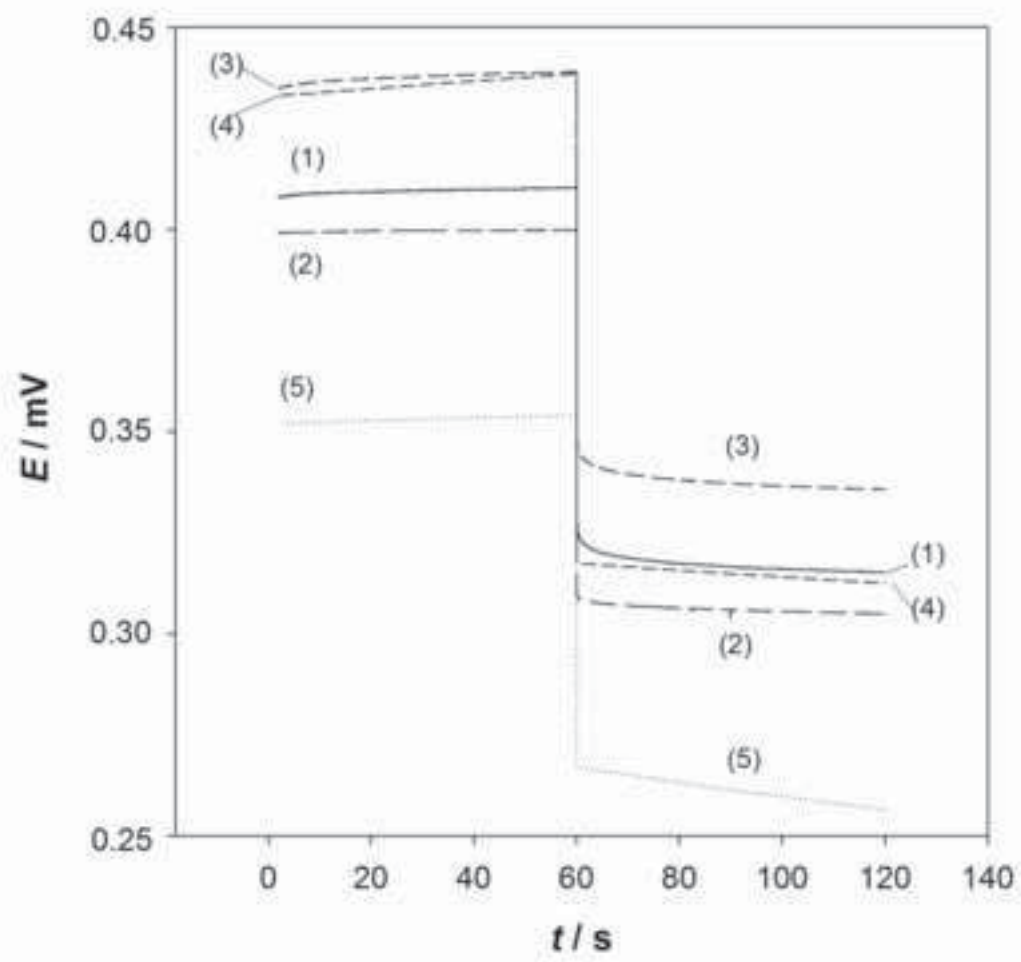


Figure 3

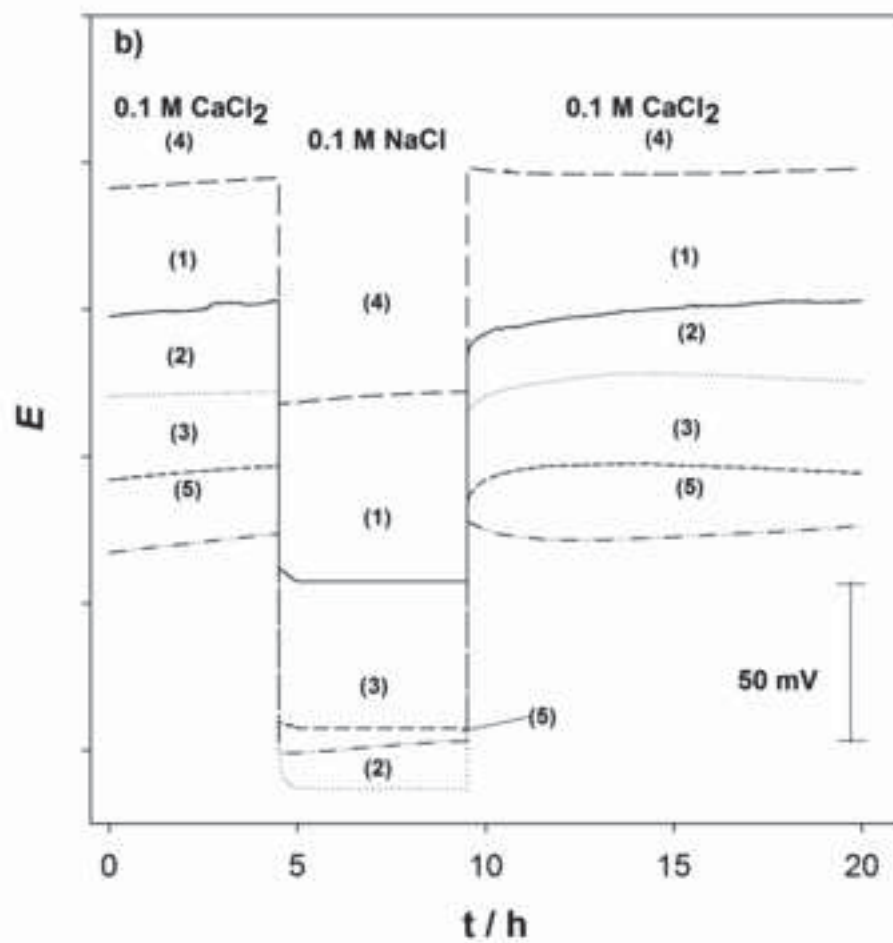
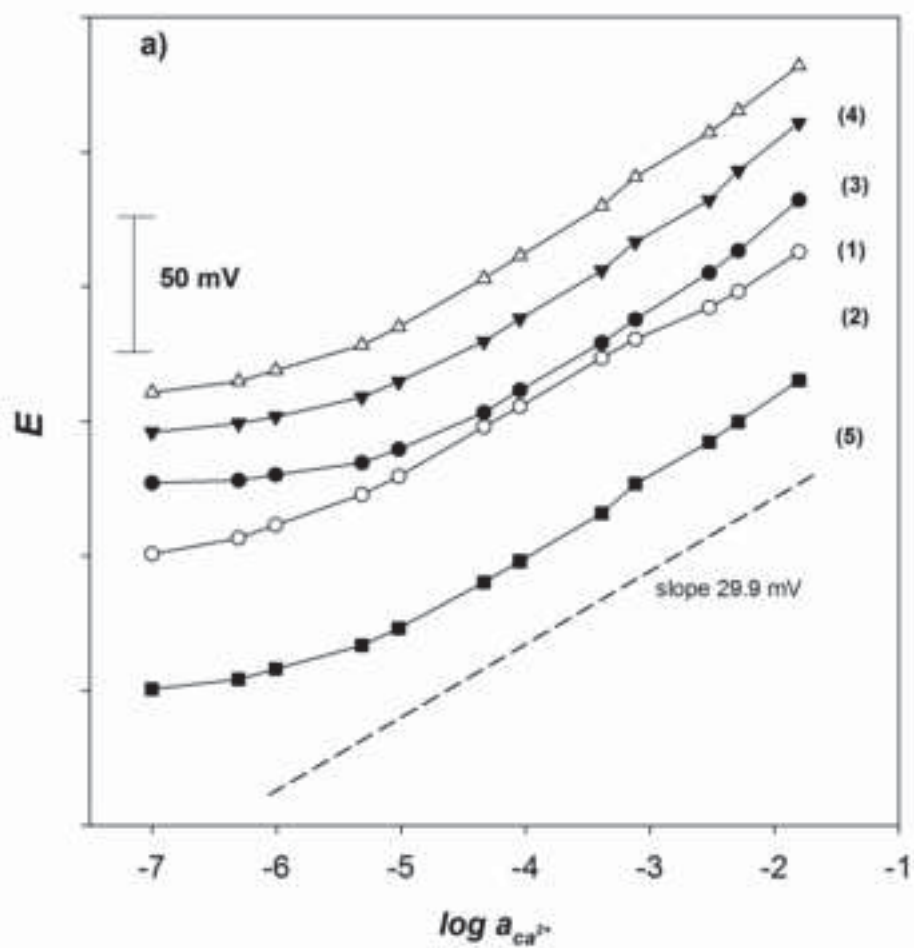


Figure

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