

**UCLA**

**Technical Reports**

**Title**

Long-lived solid state perchlorate ion selective sensor based on doped poly(3,4-ethylenedioxythiophene) (PEDOT) films

**Permalink**

<https://escholarship.org/uc/item/7fs3g0c5>

**Authors**

Tatyana A. Bendikov  
Thomas C. Harmon

**Publication Date**

2005

## CENS Technical Report

### **Long-lived solid state perchlorate ion selective sensor based on doped poly(3,4-ethylenedioxythiophene) (PEDOT) films**

Tatyana A. Bendikov<sup>1†</sup> and Thomas C. Harmon<sup>2\*</sup>

*<sup>1</sup>Department of Civil and Environmental Engineering and Center for Embedded Networked Sensing, University of California, Los Angeles, CA 90095*

*<sup>2</sup>School of Engineering, University of California, P.O. Box 2039, Merced, CA 95344*

\* Corresponding author. Phone: +1-209-724-4337; FAX: +1-209-724-4356; E-mail address: tharmon@ucmerced.edu.

† Current address: Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel.

## **Abstract**

This work describes the development and fabrication of stable potentiometric solid state sensors for the perchlorate ion ( $\text{ClO}_4^-$ ) based on doped poly(3,4-ethylenedioxythiophene) (PEDOT) films. PEDOT, one of the most promising conducting polymers, is extremely stable in its oxidized state. Using PEDOT( $\text{ClO}_4^-$ ) films as sensing material in ion selective electrodes presents a unique opportunity to create sensors having a longer lifetime compared to analogous sensors, such as those created using doped polypyrrole. Over the eight month period of this study, the PEDOT( $\text{ClO}_4^-$ ) sensors exhibited a stable, linear response spanning at least five orders of magnitude in concentration ( $1 \text{ M} - 1 \times 10^{-5} \text{ M}$  perchlorate) with near-Nernstian slopes approaching  $-50 \text{ mV/decade}$  of  $\text{ClO}_4^-$  concentration and a limit of detection of  $5 \times 10^{-6} \text{ M}$ . Carbon fibers and pencil leads were employed as alternative and inexpensive substrates for EDOT polymerization, addressing problems with the sensor's form (miniature size, flexibility) and cost.

*Keywords:* Perchlorate solid state sensor; PEDOT; Potentiometry; Carbon fibers; Pencil leads

# Long-lived solid state perchlorate ion selective sensor based on doped poly(3,4-ethylenedioxythiophene) (PEDOT) films

Tatyana A. Bendikov<sup>1†</sup> and Thomas C. Harmon<sup>2\*</sup>

<sup>1</sup>*Department of Civil and Environmental Engineering and Center for Embedded Networked Sensing, University of California, Los Angeles, CA 90095*

<sup>2</sup>*School of Engineering, University of California, P.O. Box 2039, Merced, CA 95344*

## 1. Introduction

Perchlorate ( $\text{ClO}_4^-$ ) is a component of solid phase rocket fuel and other industrial products that is being discovered with increasing frequency in the environment. Perchlorate interferes with iodine uptake by the thyroid gland and is associated with disruption of thyroid function, potentially leading to thyroid tumor formation [1-3]. In 1999 the US Environmental Protection Agency (EPA) required drinking water monitoring for perchlorate and stipulated the protective health level dosage of  $\text{ClO}_4^-$  as  $3 \times 10^{-5}$  mg/kg/day [4]. In the last several years interest in the determination of perchlorate ion ( $\text{ClO}_4^-$ ) levels in environmental matrices (soil and water) and food samples has significantly increased. Prior to the 1990s, the analytical methods for the determination of  $\text{ClO}_4^-$  were based on gravimetric or spectrophotometric techniques [5]. In the 1990s, mass spectroscopy and separation methods, such as ion chromatography and capillary electrophoresis, began to dominate [6-8]. The main drawbacks of these techniques include the requirements of expensive instrumentation and/or extensive sample pretreatment. In this context, a miniature, sensitive, nontoxic and inexpensive sensor for the reliable *in situ* estimation of perchlorate levels in environmental samples is highly desirable. Ion selective electrodes (ISEs) are one way to address this need.

Several perchlorate selective electrodes have been recently reported in the literature [9-15]. This body of research is concerned mainly with the development and synthesis of new  $\text{ClO}_4^-$  ion carriers (ionophores, receptors) for PVC-based plasticized membranes [10-15]. Commercial  $\text{ClO}_4^-$  ISEs, such as those based on an organophylic membrane containing a perchlorate-selective ion exchanger [16], are available but not suitable for direct measurements in soils and small volume aqueous samples because they are relatively large (diameter 1-2 cm, length 10-15 cm) and structurally rigid. In addition these off-the-shelf ISEs are relatively expensive to purchase and maintain (on the order of several hundred \$ per several months of laboratory measurements), an issue that is especially important when numerous sensors are required for synoptic sampling.

Conducting polymers are attractive candidates for sensing material in ISEs [17-23]. In their oxidized state these polymers show high selectivity toward the dopant ion, a selectivity which depends more on the size of the ion than its lipophilicity [17,18,24]. A variety of potentiometric ISEs based on doped polypyrrole (PPy) films have been reported [17-19, 25-29]. The main drawback of these electrodes is their relatively rapid deterioration (over the span of a few months) due to the PPy layer's sensitivity to light and oxygen [18]. Over the last decade thiophene-based conducting polymers have been studied extensively, especially poly(3,4-ethylenedioxythiophene) (PEDOT) [30-40]. For sensor applications this polymer is attractive mainly due to its environmental stability in the oxidized state combined with its high conductivity (up to 1000 S/cm). Thus, PEDOT-based ion selective sensors are expected to deteriorate slower than, for example, PPy-based electrodes. Recently Bobacka et al. reported using PEDOT as ion-to-electron transducers in a potassium ( $\text{K}^+$ ) ISE and briefly mentioned using PEDOT for chloride ion ( $\text{Cl}^-$ ) sensing [41].

Here we report for the first time on the development of a stable solid state potentiometric  $\text{ClO}_4^-$  sensor based on doped PEDOT films. Its characteristics (linear response range,

sensitivity and selectivity) make this sensor very competitive with commercial  $\text{ClO}_4^-$  ISE [16] with a stability exceeding that of analogs fabricated using doped PPy films. Alternative, inexpensive substrates for EDOT polymerization, such as carbon fibers or pencil lead (instead of commonly used glassy carbon or platinum) render the sensors scaleable to distributed environmental problems in terms of form factor (miniature size, fibrous structure and flexibility) and cost [28-29].

## 2. Experimental

### 2.1. Reagents

3,4-ethylenedioxythiophene (EDOT), tetrabutylammonium perchlorate (TBAP) and sodium perchlorate ( $\geq 99.9\%$ ) were used as purchased from Sigma-Aldrich. Acetonitrile (99.9%, anhydrous) was obtained from Acros Organics. Other sodium salts (nitrate, nitrite, chloride, bromide, fluoride, iodide, bicarbonate, carbonate, sulfate, phosphate monobasic, phosphate dibasic, thiocyanate, acetate, formate, salicylate) were analytically pure grade and were purchased from Sigma-Aldrich or Fisher Scientific. Hygroscopic grade reagents were dried in oven at 80-100 °C before use. All aqueous solutions were prepared using deionized water with a resistivity  $\geq 18 \text{ M}\Omega \times \text{cm}$  (Ultrapure Water System, Nanopure Infinity, Inc.).

### 2.2. Carbon substrates for PEDOT electrodeposition

Commercial glassy carbon (GC) 3 mm diameter disk electrode (Bioanalytical Systems, Inc., area =  $0.07 \text{ cm}^2$ ), pencil lead (PL) [28] and carbon fiber (CF) [29] electrodes were used as working electrodes for PEDOT( $\text{ClO}_4^-$ ) deposition. Pieces of approximately 2.5 cm pencil lead (0.5 mm diameter, softness HB; Micro, China) were connected to copper wire with another thin and flexible copper wire. To guarantee a good contact between the PL and

copper wire, silver paint (Structure Probe, Inc.) was applied to the connection area. One centimeter length of PL was exposed to polymerization solution (working area = 0.159 cm<sup>2</sup>). Sigrafil C30 T045 EPY (SGL Technic, Inc.) carbon fibers (CF) were used for preparation of CF electrodes. Bundles of 20-30 fibers or single filament ( $7 \pm 1$  μm diameter) were connected directly to copper wire using silver paint. A 1.5 cm length of CF was exposed to the polymerization solution (working area  $\sim 3 \times 10^{-3}$  cm<sup>2</sup> for single filament).

### *2.3. Preparation of PEDOT-ClO<sub>4</sub><sup>-</sup> solid state sensors*

Polymerization of EDOT in the presence of perchlorate onto different carbon substrates was performed electrochemically using chronopotentiometric or cyclic voltammetry (CV) techniques. A potentiostat/galvanostat (CH Instruments, Model 660B) was used as current/voltage source for electropolymerization. The polymerization solution consisted of  $2 \times 10^{-2}$  M EDOT and 0.1 M TBAP in acetonitrile. The solution was deoxygenated by purging it with nitrogen for 5 min and by bathing the system headspace with nitrogen gas during the experiment. A one compartment cell was employed with the different carbon-substrate working electrode, an Ag disk/wire (Bioanalytical Systems, Inc.) pseudo-reference electrode (in the polymerization solution the potential of Ag electrode is -0.3 V vs. Ag/AgCl double junction reference electrode) and Pt disk/wire (Bioanalytical Systems, Inc.) counter electrode. For CV the deposition potential was cycled between 1.5 V to -0.8 V for 25 cycles (scan rate: 100 mV/sec). For chronopotentiometric deposition constant current densities in the range of 0.063-0.630 mA/cm<sup>2</sup> were applied for 20 min. Electrodepositions were performed at room temperature ( $22 \pm 1$  °C). The freshly prepared PEDOT(ClO<sub>4</sub><sup>-</sup>) sensors were rinsed with water and conditioned for at least 24 hours in a  $1 \times 10^{-2}$  M NaClO<sub>4</sub> solution at room temperature.

#### 2.4. Potentiometric measurements

Potentiometric measurements were performed with a pH/ISE meter (Orion Research, Inc., Model 720). Potential differences were measured between the fabricated PEDOT(ClO<sub>4</sub><sup>-</sup>) electrode and an Ag/AgCl double junction reference electrode (Bioanalytical Systems, Inc.). Measurements were performed at room temperature (22 ± 1 °C). Temperature dependence experiments employed a 5 L water bath (Fisher Scientific) to heat solutions (30-70 °C) and a refrigerated circulator (Fisher Scientific, Model 910) for cooling solutions (0-20 °C). Between measurements the electrodes were stored in the conditioning solution at room temperature.

#### 2.5. SEM analysis and film thickness measurements

The surface of the carbon fibers and PEDOT films was observed using a cold field emission scanning electron microscope (SEM, Hitachi S4700). The thickness of the polymer layers was evaluated from the SEM images by comparing uncoated and PEDOT(ClO<sub>4</sub><sup>-</sup>) coated fibers.

### 3. Results and discussion

#### 3.1. Electrochemical synthesis of PEDOT(ClO<sub>4</sub><sup>-</sup>) films and their potentiometric response to ClO<sub>4</sub><sup>-</sup> ion

PEDOT(ClO<sub>4</sub><sup>-</sup>) films were deposited onto various carbon substrates (glassy carbon, pencil lead, carbon fiber) using cyclic voltammetry or chronopotentiometric techniques. Multisweep voltammograms obtained during deposition onto GC substrate are shown in Fig. 1a. Each cycle is characterized by several reduction and oxidation peaks which are typical [32,33] for irreversible EDOT oxidation (~ 1.4 -1.5 V), PEDOT<sup>+</sup> reduction (~ 0.4 V and -0.3 V) and PEDOT oxidation (~ -0.2 V and 0.5 V, except the first cycle). All potentials are



reported relative to the Ag reference electrode. The potentiometric responses of the sensor to  $\text{ClO}_4^-$  prepared at conditions described in Fig. 1a and measured 4.5 and 8 months after deposition are shown in Fig. 1b. The sensors exhibited near-Nernstian slopes of  $-46.3 \pm 0.1$  mV/decade with a linear response spanning five orders of magnitude ( $1 \text{ M} - 1 \times 10^{-5} \text{ M}$  of  $\text{ClO}_4^-$ ) and a detection limit of  $5 \times 10^{-6} \text{ M}$  of perchlorate.

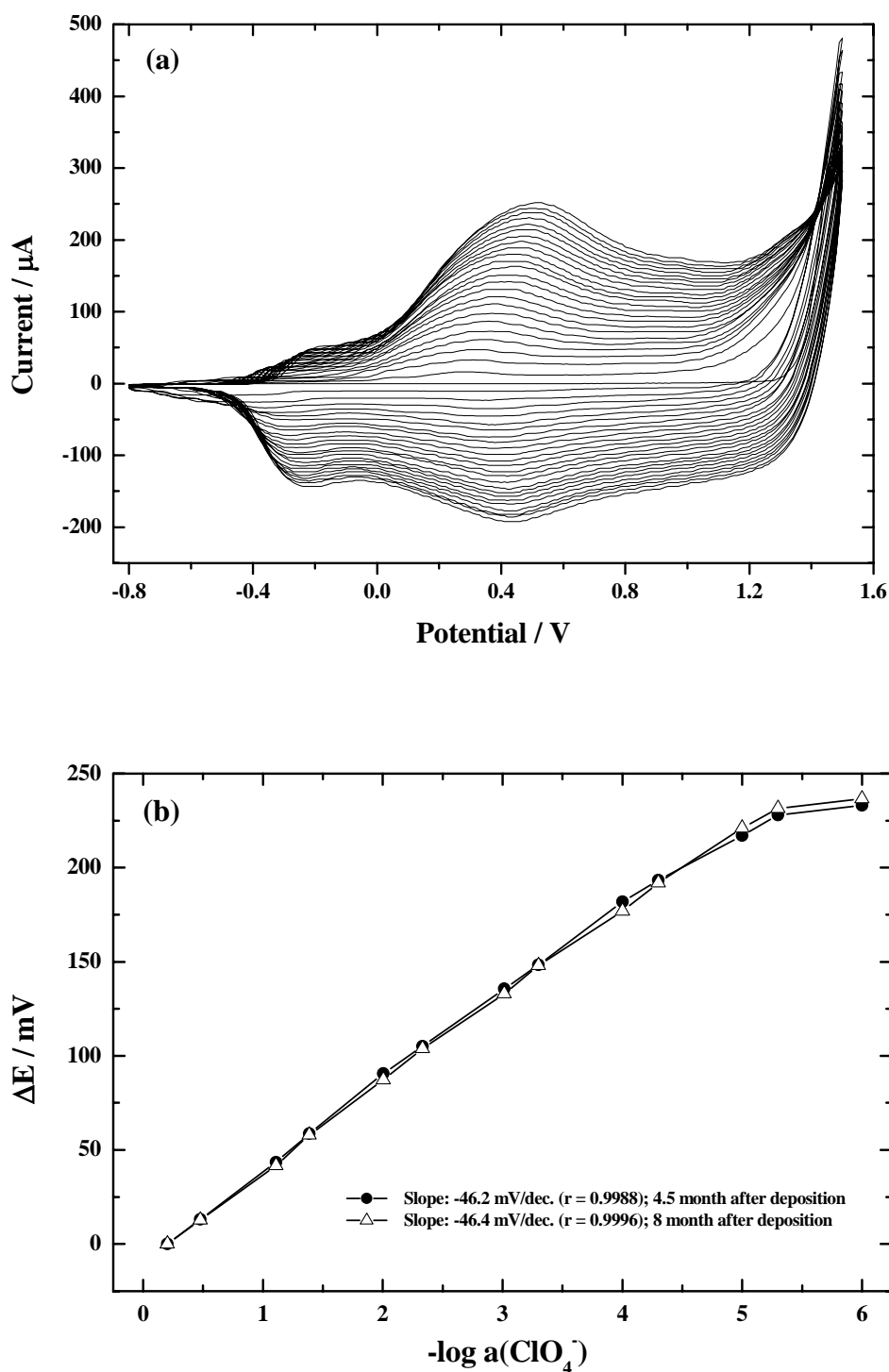


Fig. 1. (a) Multisweep voltammograms of PEDOT deposited onto the glassy carbon (GC) substrate. Solution: EDOT  $2 \times 10^{-2}$  M, BuNClO<sub>4</sub> 0.1 M in acetonitrile. Scan rate: 100 mV/s. 25 cycles. (b) Potentiometric response to ClO<sub>4</sub><sup>-</sup> ion 4.5 and 8 month after deposition for PEDOT(ClO<sub>4</sub><sup>-</sup>) sensor prepared as described in (a).

In the case of constant current deposition of PEDOT(ClO<sub>4</sub><sup>-</sup>) films (Fig. 2) current densities in the range of 0.063 – 0.630 mA/cm<sup>2</sup> were applied. Typical chronopotentiometric curves for depositions at 0.063, 0.125 and 0.630 mA/cm<sup>2</sup> are presented in Fig. 2a. Usually, at low current densities (up to 0.2 mA/cm<sup>2</sup>) the potential was stable during the deposition period (~ 1.3 – 1.4 V vs. Ag reference electrode). At higher current densities (0.2 – 0.6 mA/cm<sup>2</sup>) the deposition potential started at ~ 1.5 V and slowly increased to ~ 1.7 V (vs. Ag reference electrode). The potentiometric responses of three different PL-PEDOT(ClO<sub>4</sub><sup>-</sup>) sensors prepared at conditions described in Fig. 2a are shown in Fig. 2b. These sensors exhibited near-Nernstian slopes of -49 to -50 mV/decade, with five orders of magnitude linear range (1 M – 1 × 10<sup>-5</sup> M of ClO<sub>4</sub><sup>-</sup>) and a limit of detection of 5 × 10<sup>-6</sup> M of perchlorate.

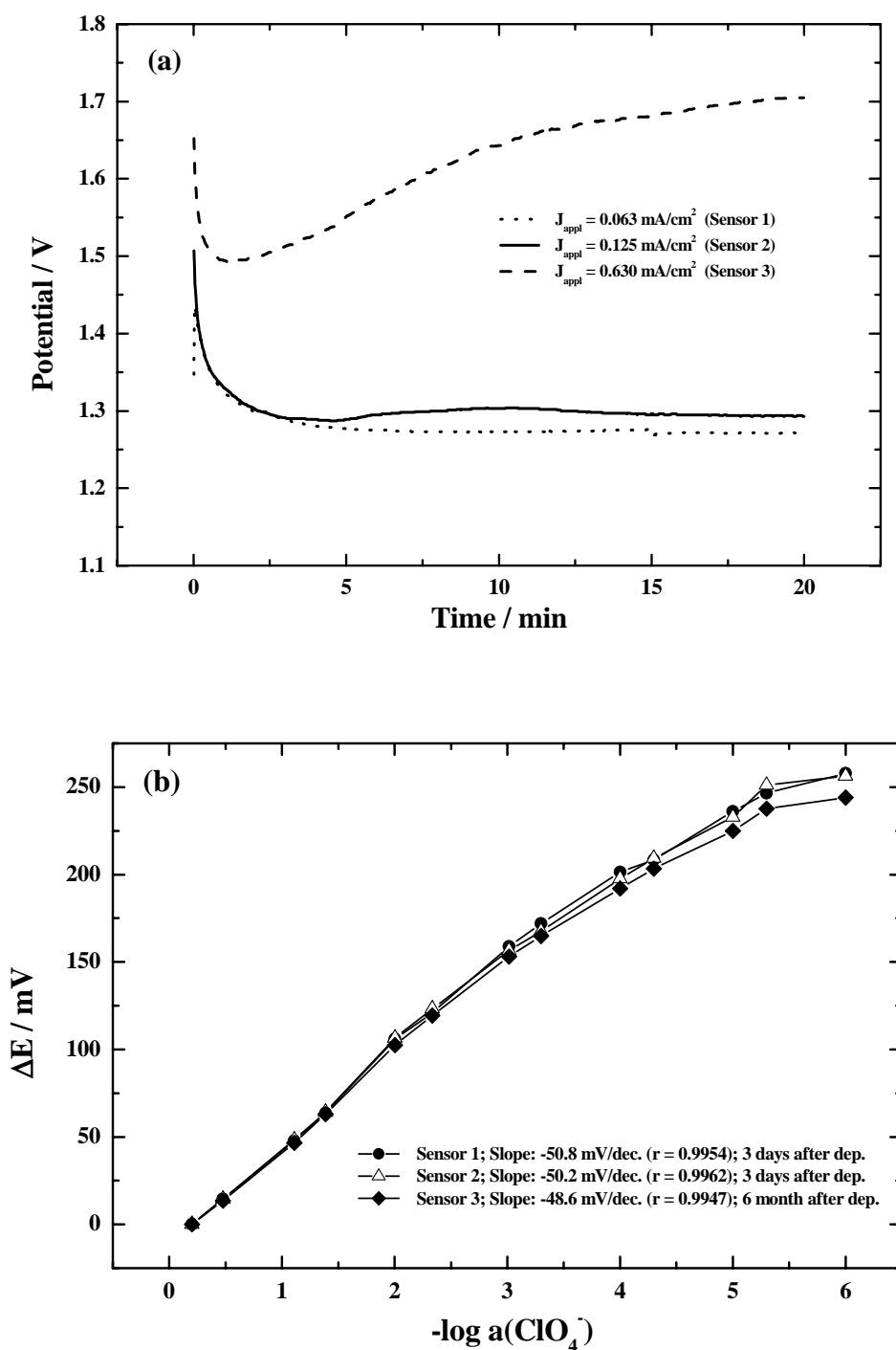


Fig. 2. (a) Chronopotentiometric curves for PEDOT electropolymerization onto pencil lead (PL) substrate at different current densities. Solution: EDOT  $2 \times 10^{-2} \text{ M}$ , BuNClO<sub>4</sub> 0.1 M in acetonitrile. (b) Potentiometric response to ClO<sub>4</sub><sup>-</sup> ion of three different PEDOT(ClO<sub>4</sub><sup>-</sup>) sensors prepared as described in (a).

### 3.2. Lifetime of PEDOT(ClO<sub>4</sub><sup>-</sup>) solid state sensors

One of the advantages of PEDOT vs. polypyrrole and other conducting polymers is its high stability in the oxidized form [30,31]. Accordingly, sensors based on doped PEDOT films are expected to have a long lifetime, which is a very desirable parameter, particularly for *in situ* sensor applications. Figs. 1 and 2 are examples of PEDOT(ClO<sub>4</sub><sup>-</sup>) sensor responses at different times after deposition (from 3 days to 8 month) showing no changes in slopes, linear ranges and limits of detection with time. The lifespan issue was studied in more detail. We followed the history of five different sensors, prepared under different conditions (details in Table 1) over eight months following their fabrication. Potentiometric responses to ClO<sub>4</sub><sup>-</sup> were estimated 3 days, 4.5, 6 and 8 months after polymerization (Table 1).

Table 1  
Potentiometric response (slope) and limit of detection (LOD) for five PEDOT(ClO<sub>4</sub><sup>-</sup>) sensors measured at different periods after deposition

|                  | 3 days          |                    | 4.5 month       |                    | 6 month         |                    | 8 month         |                    | $\Delta$ Slope (mV) <sup>f</sup> |
|------------------|-----------------|--------------------|-----------------|--------------------|-----------------|--------------------|-----------------|--------------------|----------------------------------|
|                  | Slope (mv/dec.) | LOD (mol/L)        | Slope (mv/dec.) | LOD (mol/L)        | Slope (mv/dec.) | LOD (mol/L)        | Slope (mv/dec.) | LOD (mol/L)        |                                  |
| # 1 <sup>a</sup> | -46.2           | $1 \times 10^{-5}$ | -46.2           | $5 \times 10^{-6}$ | -46.1           | $1 \times 10^{-5}$ | -46.4           | $5 \times 10^{-6}$ | -0.2                             |
| # 2 <sup>b</sup> | -42.6           | $1 \times 10^{-5}$ | -42.0           | $1 \times 10^{-5}$ | -44.0           | $5 \times 10^{-6}$ | -39.8           | $5 \times 10^{-6}$ | 2.8                              |
| # 3 <sup>c</sup> | -46.5           | $5 \times 10^{-6}$ | -46.4           | $5 \times 10^{-6}$ | -49.0           | $5 \times 10^{-6}$ | -44.1           | $5 \times 10^{-6}$ | 2.4                              |
| # 4 <sup>d</sup> | -42.1           | $1 \times 10^{-5}$ | -45.0           | $5 \times 10^{-6}$ | -46.9           | $5 \times 10^{-6}$ | -42.5           | $5 \times 10^{-6}$ | -0.4                             |
| # 5 <sup>e</sup> | -48.8           | $5 \times 10^{-6}$ | -47.8           | $1 \times 10^{-6}$ | -48.6           | $5 \times 10^{-6}$ | -47.4           | $5 \times 10^{-6}$ | 1.4                              |

<sup>a</sup> # 1: Deposition method (DM): CV (conditions – Figure 1a). Substrate: GC.

<sup>b</sup> # 2: The same as # 1. Substrate: carbon fibers (CF).

<sup>c</sup> # 3: The same as # 1. Substrate: pencil lead (PL).

<sup>d</sup> # 4: DM: Chronopotentiometry (Fig. 2a). Substrate: PL. Current density:  $J = 0.315 \text{ mA/cm}^2$ .

<sup>e</sup> # 5: The same as # 4.  $J = 0.630 \text{ mA/cm}^2$ .

<sup>f</sup> Difference between the last (after 8 month) and the first (after 3 days) values.

Although the sensors were prepared under different conditions, over the eight month period they responded similarly to  $\text{ClO}_4^-$  ion with linear responses spanning at least five orders of magnitude ( $1 \text{ M} - 1 \times 10^{-5} \text{ M}$  of perchlorate), near-Nernstian slopes approaching  $-50 \text{ mV/decade}$  of  $\text{ClO}_4^-$  concentration, and an LOD of  $5 \times 10^{-6} \text{ M}$ . The data in Table 1 indicate no changes in sensor response over an eight month period (slope changes between 3 days and 8 month after deposition are up to  $2.8 \text{ mV}$  which is within the range of experimental error; there is also no decrease in the linear range and detection limits). To our knowledge, this is the first example of a stable solid state potentiometric perchlorate ion sensor based on PEDOT films.

### *3.3. Topography and thickness of PEDOT( $\text{ClO}_4^-$ ) films*

In order to estimate topography and thickness of polymer layers, single carbon fibers (diameter =  $7 \pm 1 \text{ }\mu\text{m}$ ) were used for PEDOT films deposition. Several SEM images of uncoated carbon fibers (top left) and coated with PEDOT( $\text{ClO}_4^-$ ) layer are shown in Fig. 3.

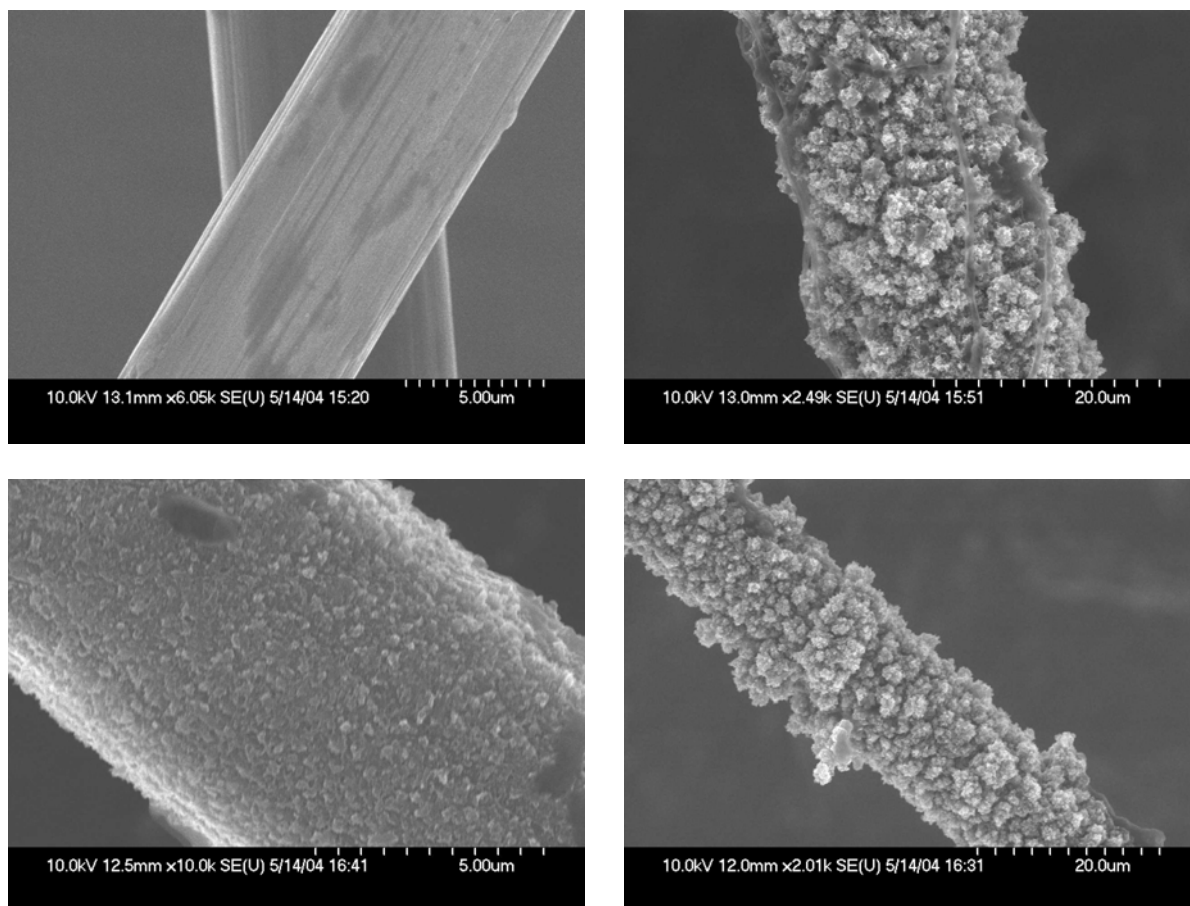


Fig. 3. SEM images of uncoated (top left) and coated carbon fibers. Polymerization conditions reported in Fig. 1 (top right) and in Fig. 2:  $J = 0.063 \text{ mA/cm}^2$  (bottom left) and  $J = 0.630 \text{ mA/cm}^2$  (bottom right).

The surface of the polymer coating is rough, especially when cyclic voltammetry and chronopotentiometry with high current densities were used for polymerization. Thickness of the layer varies spatially along the sensor. According to SEM images, PEDOT layers of  $8.0 \pm 0.8$ ,  $1.55 \pm 0.05$  and  $4.6 \pm 1.1 \text{ } \mu\text{m}$  were obtained for the deposition conditions described in Fig. 3 (top right, bottom left and bottom right, respectively).

### 3.4. Ion selectivity and pH dependence of PEDOT(ClO<sub>4</sub><sup>-</sup>) sensor

The influence of various inorganic and organic anions on the performance of the PEDOT(ClO<sub>4</sub><sup>-</sup>) sensor was studied for 15 anions employing a fixed interference method [42]. The estimated selectivity coefficients of the PEDOT(ClO<sub>4</sub><sup>-</sup>) sensor are summarized in Table 2.

Table 2

Selectivity coefficients ( $K^{\text{pot}}_{\text{ClO}_4^-, \text{X}}$ ) of PEDOT(ClO<sub>4</sub><sup>-</sup>) sensors calculated using fixed interference method

| Interferent anion (X) <sup>a</sup>               | $K^{\text{pot}}_{\text{ClO}_4^-, \text{X}}$ |
|--|---|
| SCN <sup>-</sup>                                 | 0.159                                       |
| CO <sub>3</sub> <sup>2-</sup>                    | 0.15  |
| I <sup>-</sup>                                   | 0.104                                       |
| OHC <sub>6</sub> H <sub>4</sub> COO <sup>-</sup> | $5.37 \times 10^{-2}$                       |
| HCO <sub>3</sub> <sup>-</sup>                    | $4.34 \times 10^{-2}$                       |
| NO <sub>3</sub> <sup>-</sup>                     | $1.98 \times 10^{-2}$                       |
| NO <sub>2</sub> <sup>-</sup>                     | $1.98 \times 10^{-2}$                       |
| Br <sup>-</sup>                                  | $1.84 \times 10^{-2}$                       |
| Cl <sup>-</sup>                                  | $8.34 \times 10^{-3}$                       |
| H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>      | $5.02 \times 10^{-3}$                       |
| F <sup>-</sup>                                   | $2.83 \times 10^{-3}$                       |
| CH <sub>3</sub> COO <sup>-</sup>                 | $2.63 \times 10^{-3}$                       |
| HPO <sub>4</sub> <sup>2-</sup>                   | $2.52 \times 10^{-3}$                       |
| HCOO <sup>-</sup>                                | $2.19 \times 10^{-3}$                       |
| SO <sub>4</sub> <sup>2-</sup>                    | $1.76 \times 10^{-3}$                       |

<sup>a</sup> Concentration of interferent anion  $1 \times 10^{-2}$  M.

The main interfering anions (10-15% interference) were found to be thiocyanate, carbonate and iodide. SCN<sup>-</sup> and I<sup>-</sup> are known to be strong lipophilic anions [24]. This result demonstrates that, for the PEDOT(ClO<sub>4</sub><sup>-</sup>) sensor, there is a dependence of sensor selectivity on ion lipophilicity. This is the opposite of the behavior reported for polypyrrole-based ion selective electrodes, where the selectivity mainly depends on the size and the shape of the interferant [17,18,28,29]. Sensitivity of the PEDOT(ClO<sub>4</sub><sup>-</sup>) sensor to CO<sub>3</sub><sup>2-</sup> ion is interesting



and might be explained by the high OH<sup>-</sup> concentration formed in the presence of carbonate anion (pH of Na<sub>2</sub>CO<sub>3</sub> 1 × 10<sup>-2</sup> M is ~ 11). Sensitivity of PEDOT(ClO<sub>4</sub><sup>-</sup>) sensors to other ions (see Table 2) is less significant and the selectivity is similar to commercial ClO<sub>4</sub><sup>-</sup> ISE [16].

In order to study effect of pH on the performance of PEDOT(ClO<sub>4</sub><sup>-</sup>) sensor, potentiometric responses of the sensor to ClO<sub>4</sub><sup>-</sup> ion at different concentrations of OH<sup>-</sup> ion (pH = 3-11) were measured. It was observed that in the pH range of 4-9 the sensor exhibited stable behavior with no changes in slope, linear range or limit of detection. At low (3-4) and high (10-11) pH values a decrease in the linear range (extending to 1 × 10<sup>-4</sup> M instead of 1 × 10<sup>-5</sup> M) and an elevated detection limit (1 × 10<sup>-4</sup> M instead of 5 × 10<sup>-6</sup> M) were observed.

### 3.5. Effect of temperature on the performance of PEDOT(ClO<sub>4</sub><sup>-</sup>) sensor

The Nernst equation predicts ~ 2 mV increase in slope (absolute value) per 10 °C temperature increase. The effect of temperature on the performance of PEDOT(ClO<sub>4</sub><sup>-</sup>) was studied by measuring the potentiometric responses of two different sensors over a temperature range of 10 to 70 °C (with 10 °C step changes). Table 3 summarizes the data for three temperatures (10, 40 and 70 °C).

Table 3  
Potentiometric response (slope) and linear range (LR) for two PEDOT(ClO<sub>4</sub><sup>-</sup>) sensors measured at different temperatures

|                  | At 10 °C           |                      | At 40 °C           |                      | At 70 °C           |                      |
|------------------|--------------------|----------------------|--------------------|----------------------|--------------------|----------------------|
|                  | Slope<br>(mv/dec.) | LR<br>(mol/L)        | Slope<br>(mv/dec.) | LR<br>(mol/L)        | Slope<br>(mv/dec.) | LR<br>(mol/L)        |
| # 1 <sup>a</sup> | -45.3              | 5 × 10 <sup>-6</sup> | -48.5              | 5 × 10 <sup>-5</sup> | -56.8              | 5 × 10 <sup>-5</sup> |
| # 2 <sup>b</sup> | -51.5              | 5 × 10 <sup>-6</sup> | -53.5              | 5 × 10 <sup>-5</sup> | -61.9              | 5 × 10 <sup>-5</sup> |

<sup>a</sup> # 1: Deposition method (DM): CV (conditions – Fig. 1a). Substrate: PL.

<sup>b</sup> # 2: DM: Chronopot. (Fig. 2a). Substrate: PL. Current density: J = 0.63 mA/cm<sup>2</sup>

Both sensors were stable over the applied temperature range. Although the increase in the slope values with temperature is not constant, slope changes values,  $\Delta\text{slope}/(\Delta T/10)$  (for  $\Delta T = 70 - 10 = 60$  °C), of  $1.92 \text{ mV} / 10$  °C and  $1.73 \text{ mV} / 10$  °C for sensors #1 and #2, respectively, were obtained, which are not far from the theoretical value of  $2 \text{ mV} / 10$  °C.

#### 4. Conclusions

A new solid state potentiometric sensor for perchlorate ion based on doped PEDOT films has been developed. PEDOT, exhibiting very high environmental stability in the oxidized state, was successfully used for sensing perchlorate. Over an eight month period our potentiometric PEDOT( $\text{ClO}_4^-$ ) sensors showed no deterioration or changes in their performance, exhibiting near-Nernstian response with slopes close to  $-50 \text{ mV/decade}$  of  $\text{ClO}_4^-$  concentration, a linear range of  $1 \text{ M} - 1 \times 10^{-5} \text{ M}$  of  $\text{ClO}_4^-$  and LOD of  $5 \times 10^{-6} \text{ M}$ . The influence of 15 anions on the performance of the sensor was investigated and selectivity coefficients were estimated.  $\text{SCN}^-$ ,  $\text{I}^-$  and  $\text{CO}_3^{2-}$  demonstrate significant interfering effects that can be explained by high lipophylicity (for  $\text{SCN}^-$  and  $\text{I}^-$ ) and high pH (for  $\text{CO}_3^{2-}$ ). PEDOT- $\text{ClO}_4^-$  sensors are stable over a pH range of 4-9 and temperature range of 10-70 °C exhibiting similar responses to  $\text{ClO}_4^-$  as those obtained at room temperature and neutral pH. In addition to glassy carbon, alternative carbon substrates, such as carbon fibers or pencil leads, were used for EDOT polymerization. These materials allow miniaturization and flexibility of sensor body which are very desirable for some environmental and possibly biological/medical applications. In addition, utilization of these inexpensive substrates can significantly decrease sensors costs.

## **Acknowledgements**

Funding from the Israeli Science Foundation (Bicura Post-doctoral Scholarship in the field of Environmental Sciences) and UCLA's Center for Embedded Networked Sensing (CENS) under cooperative agreement #CCR-0120778 with the National Science Foundation are gratefully acknowledged.

## References

- [1] K.O. Yu, L. Narayanan, D.R. Mattie, R.J. Godfrey, P.N. Todd, T.R. Sterner, D.A. Mahle, M.N. Lumpkin, J.W. Fisher, *Toxicol. Appl. Pharmac.* 182 (2002) 148.
- [2] J. Van Sande, C. Massart, R. Beauwens, A. Schoutens, S. Costagliola, J.E. Dumont, J. Wolff, *Endocrinol.* 144 (2003) 247.
- [3] R.A. Clewell, E.A. Merrill, K.O. Yu, D.A. Mahle, T.R. Sterner, D.R. Mattie, P.J. Robinson, J.W. Fisher, J.M. Gearhart, *Toxicol. Sci.* 73 (2003) 235.
- [4] U.S. EPA Web Site: <http://www.epa.gov/safewater/ccl/perchlorate/perchlorate.html>
- [5] E.T. Urbansky, *Crit. Rev. Anal. Chem.* 30 (2000) 311.
- [6] P.E. Jackson, M. Laikhtman, J.S. Roher, *J. Chromatogr. A* 850 (1999) 131.
- [7] C.J. Koester, H.R. Beller, R.U. Halden, *Environ. Sci. Technol.* 34 (2000) 1862.
- [8] R. Handy, D. Barnett, R. Guevremont, *J. Anal. At. Spectrom.* 15 (2000) 907.
- [9] R. Perez-Olmos, A. Rios, M.P. Martin, R.A.S. Lapa, J.L.F.C.Lima, *Analyst* 124 (1999) 97.
- [10] J. Casabo, L. Escriche, C. Perez-Jimenez, J.A. Munoz, F. Teixidor, J. Bausell, A. Errachid, *Anal. Chim. Acta* 320 (1996) 63.
- [11] C. Sanchez-Pedreno, J.A. Ortuno, J. Hernandez, *Anal. Chim. Acta* 415 (2000) 159.
- [12] M.-J. Segui, J. Lizondo-Sabater, R. Martinez-Manez, F. Sancenon, J. Soto, *Analyst* 127 (2002) 387.
- [13] J. Lizondo-Sabater, M.-J. Segui, L.M. Lloris, R. Martinez-Manez, T. Padro, F. Sancenon, J. Soto, *Sens. Actuators B* 101 (2004) 20.
- [14] M. Shamsipur, A. Soleymanpour, M. Akhond, H. Sharghi, I.R. Hasaninejad, *Sens. Actuators B* 89 (2003) 9.

- [15] M.R. Ganjali, M. Yousefi, T. Poursaberi, L. Naji, M. Salavati-Niasari, M. Shamsipur, *Electroanalysis* 15 (2003) 1476.
- [16] Perchlorate electrode instrumental manual, model 9381, Thermo Orion,  
<http://www.thermo.com>
- [17] S. Dong, Z. Sun, Z. Lu, *Analyst* 113 (1988) 1525.
- [18] R.S. Hutchins, L.G. Bachas, *Anal. Chem.* 67 (1995) 1654.
- [19] J. Migdalski, T. Blaz, A. Lewenstam, *Anal. Chim. Acta* 322 (1996) 141.
- [20] T. Lindfors, A. Ivaska, *Anal. Chim. Acta* 437 (2001) 171.
- [21] J. Bobacka, A. Ivaska, A. Lewenstam, *Electroanalysis* 15 (2003) 366.
- [22] D.R. Johnson, L.G. Bachas, *Anal. Bioanal. Chem.* 376 (2003) 328.
- [23] A. Michalska, K. Maksymiuk, *Talanta* 63 (2004), 109.
- [24] F. Hofmeister, *Arch. Exp. Pathol. Pharmacol.* 24 (1888) 247.
- [25] Z. Lu, Z. Sun, Z. Dong, *Electroanalysis* 1 (1989) 271.
- [26] J.F. Pearson, J.M. Slater, V. Jovanovich, *Analyst* 117 (1992) 1885.
- [27] A. Ersoz, V.G. Gavalas, L.G. Bachas, *Anal. Bioanal. Chem.* 327 (2002) 786.
- [28] T.A. Bendikov, T.C. Harmon, *J. Chem. Educ.* (2004) in press.
- [29] T.A. Bendikov, Y. Kim, T.C. Harmon, *Sens. Actuators B* (2004) ASAP.
- [30] L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, J.R. Reynolds, *Adv. Mater.* 12 (2000), 481.
- [31] L. Groenendaal, G. Zotti, P.-H. Aubert, J.R. Reynolds, *Adv. Mater.* 15 (2003), 855.
- [32] M. Dietrich, J. Heinze, G. Heywang, F. Jonas, *J. Electroanal. Chem.* 369 (1994), 87.
- [33] H. Randriamahazaka, V. Noel, C. Chevrot, *J. Electroanal. Chem.* 472 (1999) 103.
- [34] V. Noel, H. Randriamahazaka, C. Chevrot, *J. Electroanal. Chem.* 542 (2003), 33.
- [35] R. Kiebooms, A. Aleshin, K. Hutchison, F. Wudl, *J. Phys. Chem.* 101 (1997) 11037.
- [36] C. Xia, R.C. Advincula, A. Baba, W. Knoll, *Langmuir* 18 (2002) 3555.

- [37] J. Bobacka, A. Lewenstam, A. Ivaska, *J. Electroanal. Chem.* 489 (2000) 17.
- [38] H. Yamoto, M. Ohwa, W. Wernet, *J. Electroanal. Chem.* 379 (1995) 163.
- [39] N. Sakmeche, J.J. Aaron, M. Fall, S. Aeiyaeh, M. Jouini, J.C. Lacroix, P.C. Lacaze, *Chem. Comm.* 24 (1996) 2723.
- [40] N. Sakmeche, S. Aeiyaeh, J.J. Aaron, M. Jouini, J.C. Lacroix, P.C. Lacaze, *Langmuir* 15 (1999) 2566.
- [41] J. Bobacka, *Anal. Chem.* 71 (1999) 4932.
- [42] Y. Umezawa, K. Umezawa, H. Sato, *Pure Appl. Chem.* 67 (1995) 507.

Table 1

Potentiometric response (slope) and limit of detection (LOD) for five PEDOT(ClO<sub>4</sub><sup>-</sup>) sensors measured at different periods after deposition

|                  | 3 days          |                    | 4.5 month       |                    | 6 month         |                    | 8 month         |                    | $\Delta$ Slope (mV) <sup>f</sup> |
|------------------|-----------------|--------------------|-----------------|--------------------|-----------------|--------------------|-----------------|--------------------|----------------------------------|
|                  | Slope (mv/dec.) | LOD (mol/L)        | Slope (mv/dec.) | LOD (mol/L)        | Slope (mv/dec.) | LOD (mol/L)        | Slope (mv/dec.) | LOD (mol/L)        |                                  |
| # 1 <sup>a</sup> | -46.2           | $1 \times 10^{-5}$ | -46.2           | $5 \times 10^{-6}$ | -46.1           | $1 \times 10^{-5}$ | -46.4           | $5 \times 10^{-6}$ | -0.2                             |
| # 2 <sup>b</sup> | -42.6           | $1 \times 10^{-5}$ | -42.0           | $1 \times 10^{-5}$ | -44.0           | $5 \times 10^{-6}$ | -39.8           | $5 \times 10^{-6}$ | 2.8                              |
| # 3 <sup>c</sup> | -46.5           | $5 \times 10^{-6}$ | -46.4           | $5 \times 10^{-6}$ | -49.0           | $5 \times 10^{-6}$ | -44.1           | $5 \times 10^{-6}$ | 2.4                              |
| # 4 <sup>d</sup> | -42.1           | $1 \times 10^{-5}$ | -45.0           | $5 \times 10^{-6}$ | -46.9           | $5 \times 10^{-6}$ | -42.5           | $5 \times 10^{-6}$ | -0.4                             |
| # 5 <sup>e</sup> | -48.8           | $5 \times 10^{-6}$ | -47.8           | $1 \times 10^{-6}$ | -48.6           | $5 \times 10^{-6}$ | -47.4           | $5 \times 10^{-6}$ | 1.4                              |

<sup>a</sup> # 1: Deposition method (DM): CV (conditions – Fig. 1a). Substrate: GC.

<sup>b</sup> # 2: The same as # 1. Substrate: carbon fibers (CF).

<sup>c</sup> # 3: The same as # 1. Substrate: pencil lead (PL).

<sup>d</sup> # 4: DM: Chronopotentiometry (Fig. 2a). Substrate: PL. Current density:  $J = 0.315 \text{ mA/cm}^2$ .

<sup>e</sup> # 5: The same as # 4.  $J = 0.630 \text{ mA/cm}^2$ .

<sup>f</sup> Difference between the last (after 8 month) and the first (after 3 days) values.

Table 2

Selectivity coefficients ( $K^{\text{pot}}_{\text{ClO}_4^-, \text{X}}$ ) of PEDOT( $\text{ClO}_4^-$ ) sensors calculated using fixed interference method

| Interferent anion (X) <sup>a</sup>   | $K^{\text{pot}}_{\text{ClO}_4^-, \text{X}}$ |
|--------------------------------------|---|
| $\text{SCN}^-$                       | 0.159                                       |
| $\text{CO}_3^{2-}$                   | 0.15  |
| $\text{I}^-$                         | 0.104                                       |
| $\text{OHC}_6\text{H}_4\text{COO}^-$ | $5.37 \times 10^{-2}$                       |
| $\text{HCO}_3^-$                     | $4.34 \times 10^{-2}$                       |
| $\text{NO}_3^-$                      | $1.98 \times 10^{-2}$                       |
| $\text{NO}_2^-$                      | $1.98 \times 10^{-2}$                       |
| $\text{Br}^-$                        | $1.84 \times 10^{-2}$                       |
| $\text{Cl}^-$                        | $8.34 \times 10^{-3}$                       |
| $\text{H}_2\text{PO}_4^-$            | $5.02 \times 10^{-3}$                       |
| $\text{F}^-$                         | $2.83 \times 10^{-3}$                       |
| $\text{CH}_3\text{COO}^-$            | $2.63 \times 10^{-3}$                       |
| $\text{HPO}_4^{2-}$                  | $2.52 \times 10^{-3}$                       |
| $\text{HCOO}^-$                      | $2.19 \times 10^{-3}$                       |
| $\text{SO}_4^{2-}$                   | $1.76 \times 10^{-3}$                       |

<sup>a</sup> Concentration of interferent anion  $1 \times 10^{-2}$  M.



Table 3  
 Potentiometric response (slope) and linear range (LR) for two PEDOT(ClO<sub>4</sub><sup>-</sup>) sensors measured at different temperatures

|                  | At 10 °C           |                    | At 40 °C           |                    | At 70 °C           |                    |
|------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
|                  | Slope<br>(mv/dec.) | LR<br>(mol/L)      | Slope<br>(mv/dec.) | LR<br>(mol/L)      | Slope<br>(mv/dec.) | LR<br>(mol/L)      |
| # 1 <sup>a</sup> | -45.3              | $5 \times 10^{-6}$ | -48.5              | $5 \times 10^{-5}$ | -56.8              | $5 \times 10^{-5}$ |
| # 2 <sup>b</sup> | -51.5              | $5 \times 10^{-6}$ | -53.5              | $5 \times 10^{-5}$ | -61.9              | $5 \times 10^{-5}$ |

<sup>a</sup> # 1: Deposition method (DM): CV (conditions – Fig. 1a). Substrate: PL.

<sup>b</sup> # 2: DM: Chronopot. (Fig. 2a). Substrate: PL. Current density:  $J = 0.63 \text{ mA/cm}^2$

## Figure legends

Fig. 1. (a) Multisweep voltammograms of PEDOT deposited onto the glassy carbon (GC) substrate. Solution: EDOT  $2 \times 10^{-2}$  M, BuNClO<sub>4</sub> 0.1 M in acetonitrile. Scan rate: 100 mV/s. 25 cycles. (b) Potentiometric response to ClO<sub>4</sub><sup>-</sup> ion 4.5 and 8 month after deposition for PEDOT(ClO<sub>4</sub><sup>-</sup>) sensor prepared as described in (a).

Fig. 2. (a) Chronopotentiometric curves for PEDOT electropolymerization onto pencil lead (PL) substrate at different current densities. Solution: EDOT  $2 \times 10^{-2}$  M, BuNClO<sub>4</sub> 0.1 M in acetonitrile. (b) Potentiometric response to ClO<sub>4</sub><sup>-</sup> ion of three different PEDOT(ClO<sub>4</sub><sup>-</sup>) sensors prepared as described in (a).

Fig. 3. SEM images of uncoated (top left) and coated carbon fibers. Polymerization conditions reported in Fig. 1 (top right) and in Fig. 2:  $J = 0.063 \text{ mA/cm}^2$  (bottom left) and  $J = 0.630 \text{ mA/cm}^2$  (bottom right).

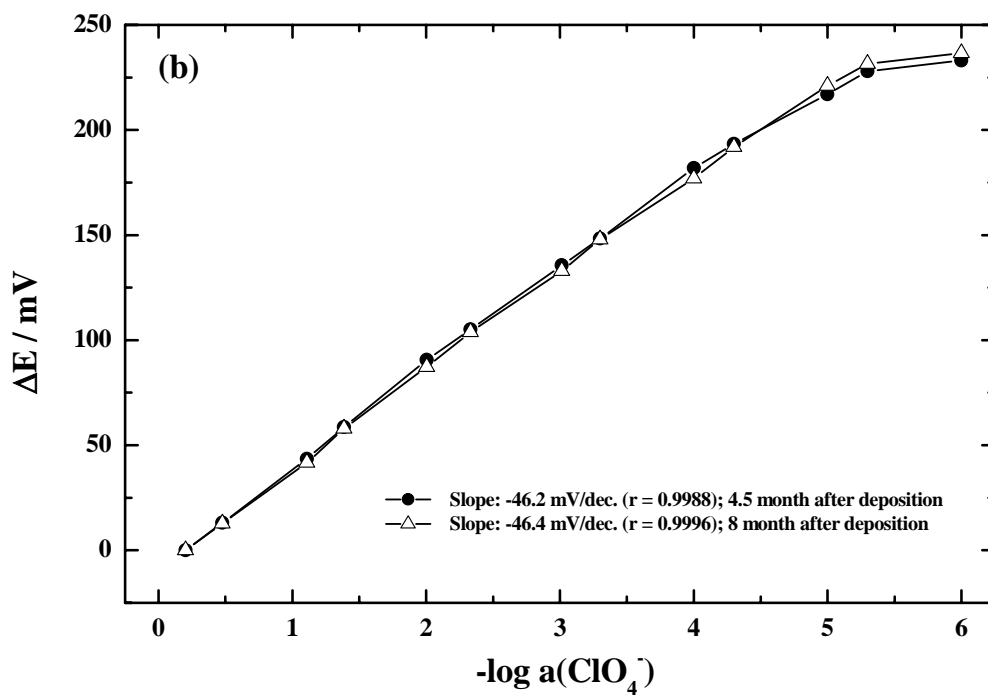
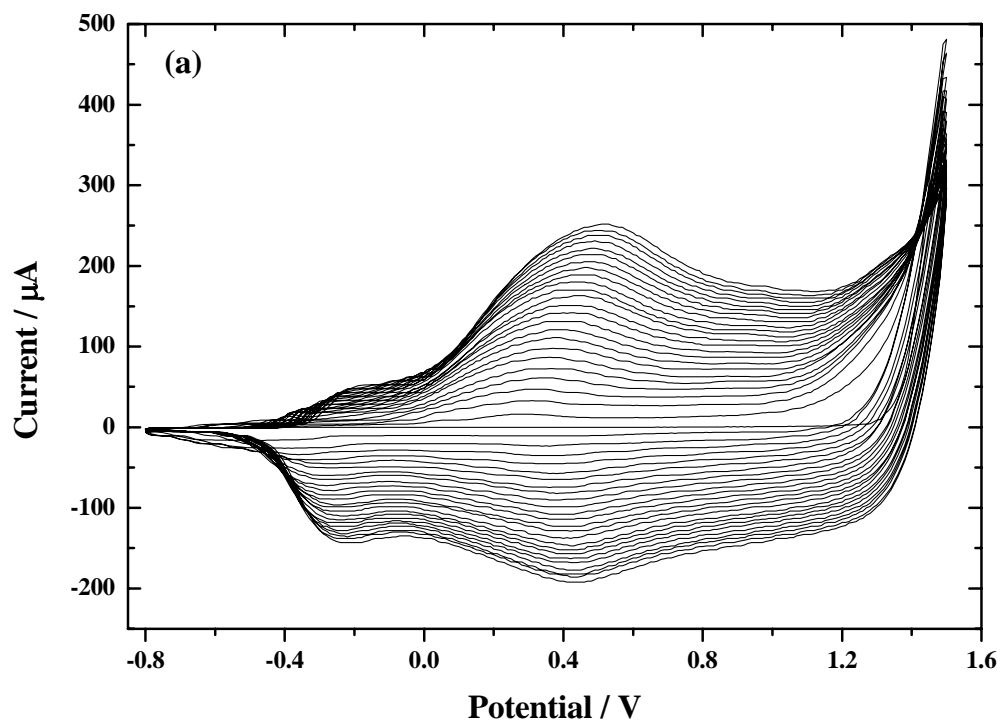


Fig. 1

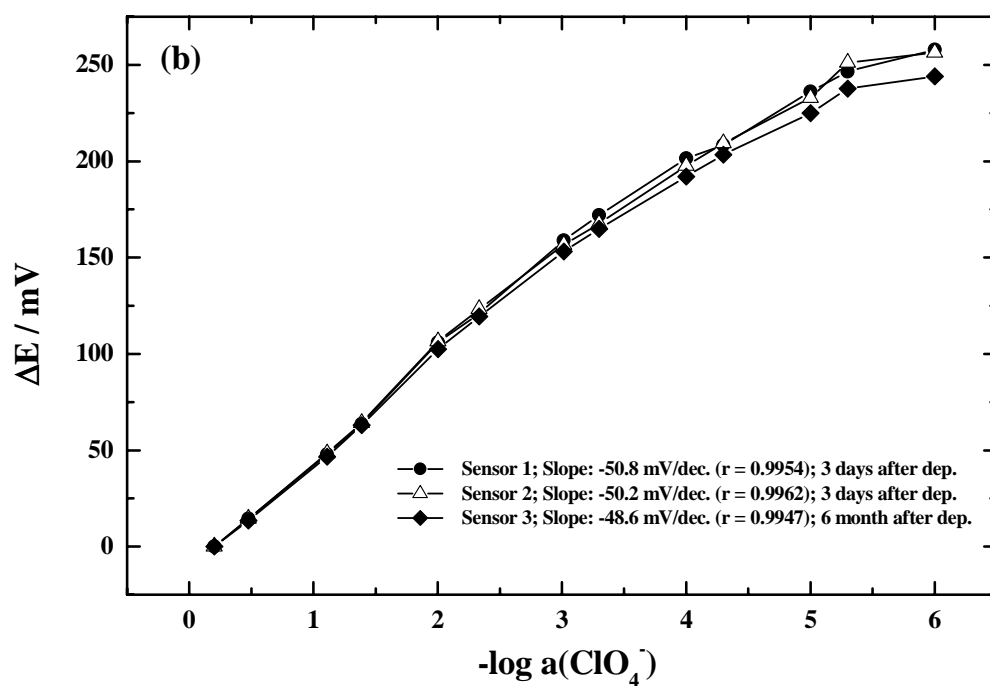
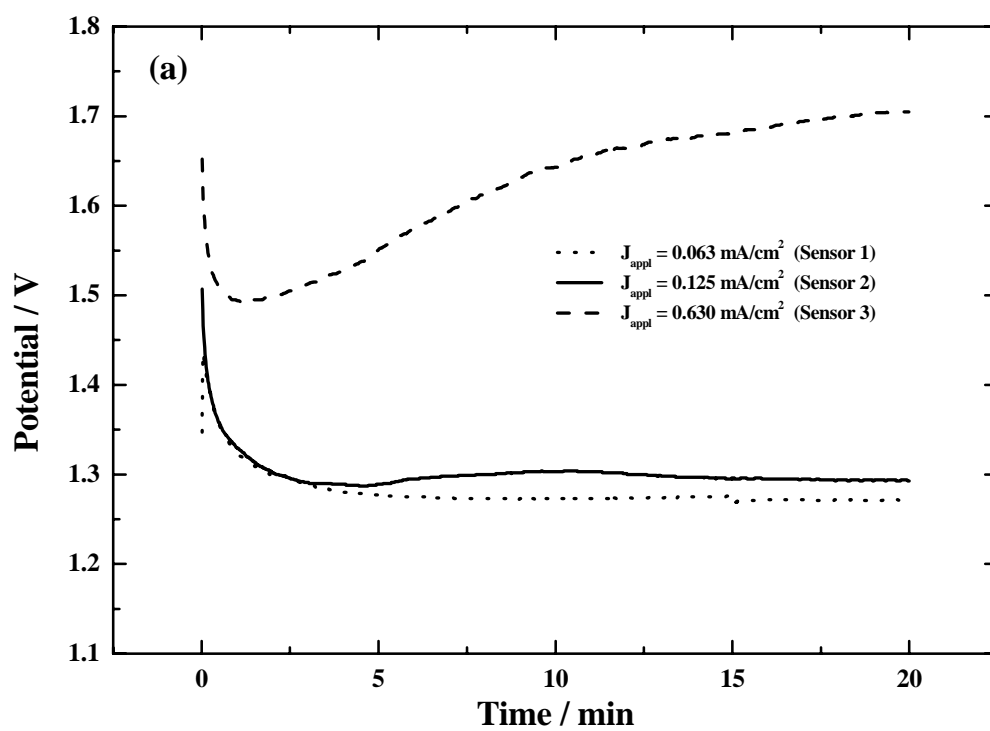


Fig. 2

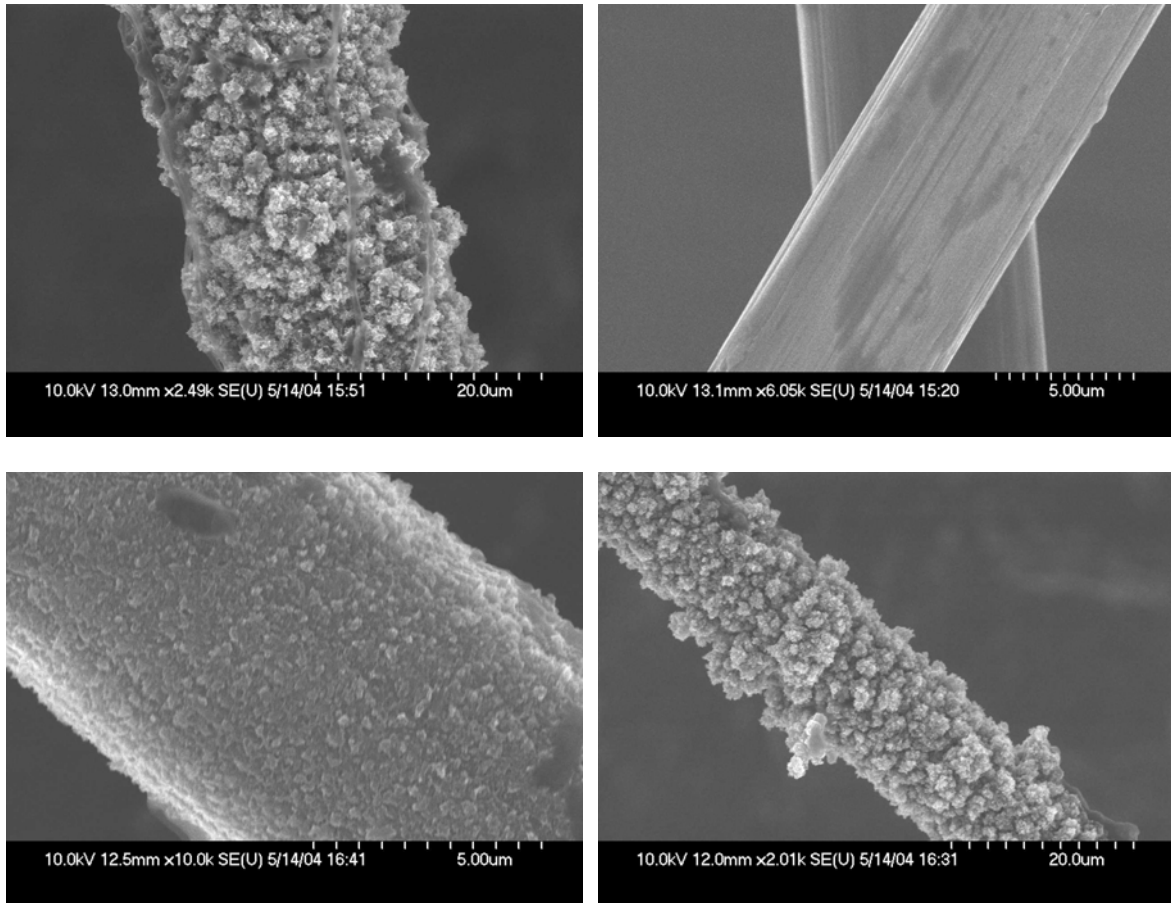


Fig. 3