A METHANE SENSOR BASED ON POLY[3',4'-DIHEXYL-4,4''-BIS(PENTYLOXY)-2,2':5',2''-TERTHIOPHENE]

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Dedicated to Professor Sergio Roffia on the occasion of his retirement.

I knew Prof. Roffia at the Ciamician Institute of the University of Bologna in 1967. At that time he was involved in a fruitful collaboration with the late Prof. E. Vianello and Prof. J.-M. Savéant. I worked at the Ciamician Institute more than three years and during that period I took a great advantage of the discussions with Prof. Roffia. The time flies and now he is going to retire, but he will remain one of the teachers in the community of the electrochemists. I am very grateful for the opportunity to celebrate, together with other colleagues, the brilliant scientific activity of Prof. Roffia.
                                                                    G. Casalbore-Miceli

I was born in 1967; anyway, in 1991, Prof. Roffia was my electrochemistry teacher at the Bologna University and so I represent the second generation of electrochemists who are grateful for his generous teaching activity.
                                                                    A. Zanelli

3',4'-Dihexyl-4,4''-bis(pentyloxy)-2,2':5',2''-terthiophene was electrochemically polymerized on gold interdigitated electrodes to investigate the impedance variation of the polymer in the exposure to air/methane atmospheres. The higher sensitivity of poly[3',4'-dihexyl-4,4''-bis(pentyloxy)2,2';5',2''-terthiophene] (PHPT) to methane was observed at frequencies of about 100 Hz. The PHPT impedance decreases when the CH_4 concentration increases and shows the highest sensitivity at the lowest methane concentrations. After each concentration step, the impedance decreased as the square root of time indicating that the response time of the PHPT-based sensor was controlled by diffusion of the gas into the material. It is suggested that the absorption of methane into the polymer film affects the rate of interchain charge hopping.

Keywords: Conducting polymers; Methane sensors; Impedance spectroscopy; Poly(alkyl-alkoxythiophene).

The construction of sensors is one of the most promising technological applications of electroactive polymers[1,2]. This application is often based on the variation of the charge mobility through the polymer (and therefore of its electric properties) when the gas to be monitored comes into contact with the material[2]. This variation can be due to intermolecular factors (charge hopping between different macromolecules) or/and intramolecular factors (charge transport along the conjugated π-electrons chain). In fact, a change of charge mobility can be induced by variation of the distance between the molecules[3,4], but the charge mobility can also be affected by the chemiadsorption or by other interactions between pendant groups of the polymer chain (or the polymer chain itself) and the gas[5,6]. These interactions can change the π-electron density in the polyconjugated system and, consequently, the electrical properties of the material. In order to project a highly selective sensor that can discriminate between the gas to be monitored and other gases present in atmospheric environment, a deep investigation of chemical and electric properties of the conjugated polymer is required.

Our objective is a construction of a methane sensor for indoor application based on electroactive polymers. The sensor should satisfy the following demands: high durability, medium sensitivity (>0.5 vol.%), fast response and improved selectivity.

In the present communication we report preliminary results about the response to methane/air mixtures of a solid state sensor based on a film of poly[3′,4′-dihexyl-4,4″-bis(pentyloxy)-2,2′:5′,2″-terthiophene] (PHPT, Fig. 1) deposited by electrochemical methods on a ceramic support equipped with
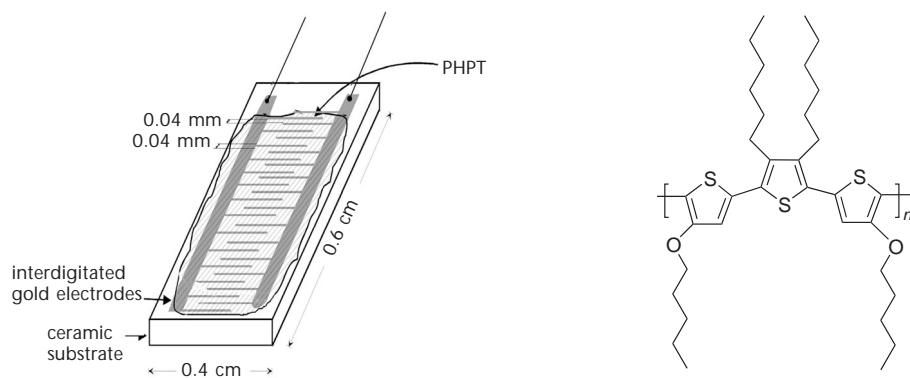

Fig. 1

Schematic design of the solid state sensor (left) and the chemical formula of the sensing material (right)

interdigitated gold electrodes (Fig. 1). The selected monomer fulfils two requirements: an easy electrochemical polymerization assisted by the alkoxy pendants in 4 and 4″ positions[7] and an affinity to the methane, due to the alkyl pendants in 3′ and 4′ position[4]. The electrochemical polymerization is particularly suitable for fast and easy preparation of films of conducting polymers. Moreover, batches of sensors with very similar characteristics can be obtained by the same technique, which is a very important requirement for an industrial application of the devices.

EXPERIMENTAL

Electrochemical Experiments

The monomer, 3′,4′-dihexyl-4,4″-bis(pentyloxy)-2,2′:5′,2″-terthiophene, was prepared by the Suzuki coupling of 2,5-dibromo-3,4-dihexylthiophene with [4-(pentyloxy)-2-thienyl]boronic acid in 1,2-dimethoxyethane–$NaHCO_3$ solution with $[Pd(PPh_3)_4]$ as catalyst.

Polymerization was carried out in an electrochemical cell on interdigitated electrodes by the potentiodynamic method with the monomer (2.5×10^{-3} mol l^{-1}) dissolved in an acetonitrile (AN)–dichloromethane (DM) mixed solvent (1:1 vol./vol.) + 0.1 M tetrabutyl-ammonium perchlorate (TBAP) as supporting electrolyte, cycling the potential at 50 mV s^{-1} between 0.0 and 1.1 V *vs* saturated calomel electrode (SCE). During the potentiodynamic cycles the polymer, starting from the gold tracks (40 μm width, 1 μm thin), gradually covered the interelectrode region (40 μm) and set up an electrical connection between the two pins. Successively, the impedance decreased with the number of cycles. After height cycles and a polymerization charge of about 13 mC, the area involved by gold tracks was uniformly covered with a polymer film whose apparent area was about 4.5 mm^2. At the end of preparation the polymer film was reduced to the neutral form by electrolyzing at –0.1 V. Figure 2 shows the picture of the polymer deposited on an interdigitated electrode (a) and the detail of the filling between the tracks (b).
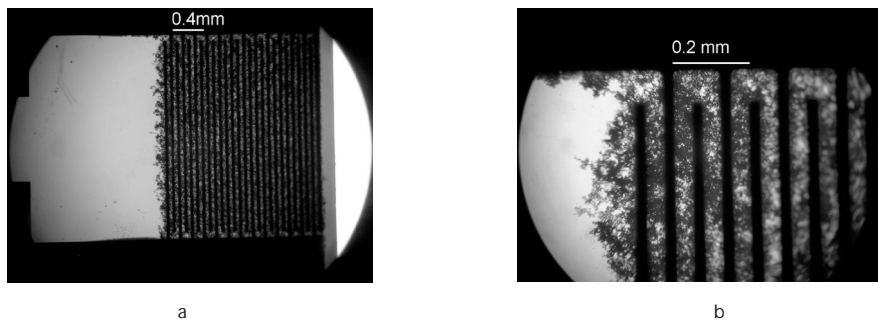

a

b

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Microscope photographs of the solid state device [microscope Leika DMLS magnification 40× (a) and 200× (b); digital camera JVC GL-X3]

Cyclic voltammetries of PHPT films in AN solution of 0.1 M TBAP between –0.1 and 0.9 V *vs* SCE showed a reverzible oxidation process (cyclable charge 1.3 mC, coulomb efficiency 93%, Fig. 3).

Electrochemical polymerization and cyclic voltammetries were carried out under Ar pressure with a Pt wire as counter-electrode and SCE as reference electrode. Both electrodes were separated from the working solution by a glassy septum. An AMEL 5000 multifunction apparatus was used for electrochemical polymerization and characterization.

AN was UVASOL Merck product bubbled and stored under argon flux. DM (Merck ACS product) was dehydrated with $CaCl_2$ for 12 h, then distilled in the presence of P_2O_5 in Ar stream and stored in the dark under Ar pressure. TBAP (Fluka AG *purum*) was crystallized from methanol.

Gas-Sensing Experiments

The solid state sensor was tested in a 6 cm^3 home-made metallic cell where pure air and methane were properly mixed by using a home-made mixing apparatus equipped with Cole–Parmer precision gas flow-meters (0–50 ml min^{-1} for methane, 0–200 ml min^{-1} for air).

The gases used were pure air (from SIAD, Italy, chromatography grade, purity > 99.999, hydrocarbons < 1 ppm vol.) and commercial methane (composition: methane 93.4%, ethane 3.0%, propane 0.7%, butane 0.4%, pentane 0.01%, air 1.1%, CO_2 1.3%).

Impedance measurements were carried out at 0 V bias by a Solartron 1255 frequency response analyser and a Solartron 1294 impedance interface apparatus. The impedance spectra were collected by the software Zplot2 and elaborated by Zwiew2 (Scribner Associated Inc.).

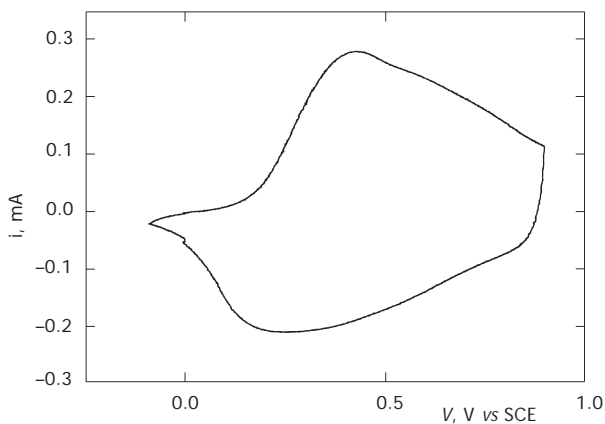All experiments were carried out at room temperature.

FIG. 3
Cyclic voltammetry (second cycle) of PHPT on interdigitated gold electrodes at 50 mV s^{-1}, in AN–0.1 M TBAP

RESULTS AND DISCUSSION

The sensitivity of PHPT to methane was investigated by testing the complex impedance of the solid state device in the methane/air flow. Initially, the device was exposed for several minutes to pure air in order to reach the steady state and to remove humidity; in fact, PHPT is sensitive to the water and researches are in progress to protect it from humidity. The reaching of the steady state was monitored by impedance spectra.

Figures 4 and 5 show the Nyquist plots in the frequency range 1 Hz–1MHz for a device exposed to pure air and pure methane flow under sinusoidal
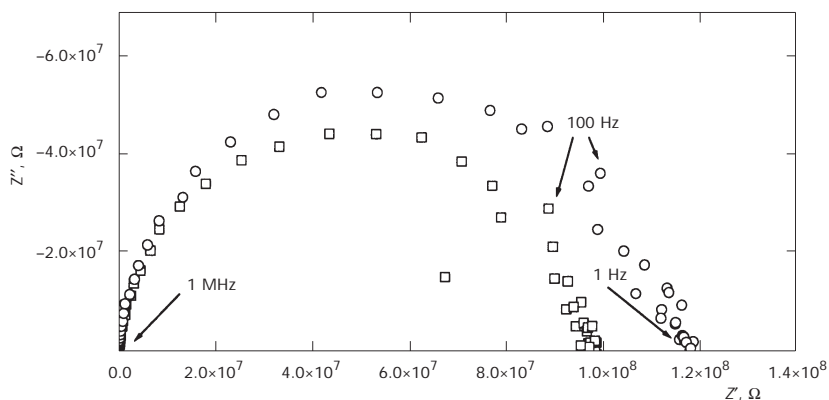

FIG. 4
Nyquist plots (1 Hz–1 MHz) of a PHPT film on interdigitated gold electrodes exposed to air ($\bigcirc$) and to CH_4 ($\square$). SVA = 100 mV
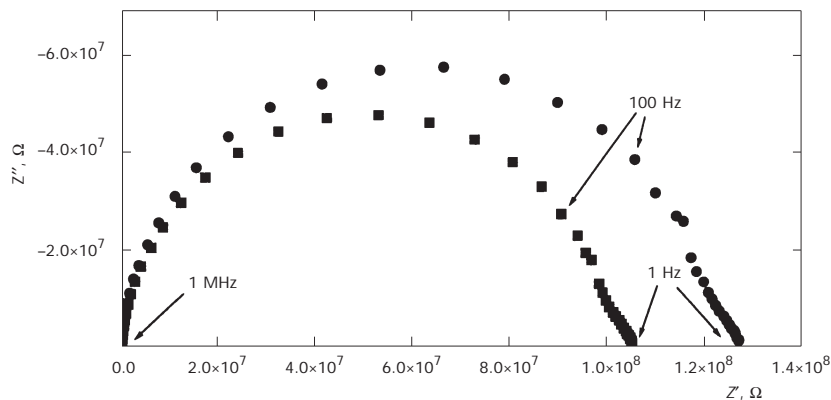

FIG. 5
Nyquist plots (1 Hz–1 MHz) of a PHPT film on interdigitated gold electrodes exposed to air ($\bullet$) and to CH_4 ($\blacksquare$). SVA = 1 V

voltage amplitude (SVA) of 100 mV and 1 V. At frequencies higher than 20–30 Hz, the Nyquist plots show the semicircles reasonably due to the polymer film impedance. The errors in circular fittings were low both for resistance (<2%) and parallel capacitance. The lowering of semicircles were acceptable (≈4%) taking into account the nature of the material and the geometry of the electrodes. At SVA = 100 mV, the semicircles show some scattered points at lower frequencies. At higher SVA, the noise was considerably reduced. The fitting of the impedance spectra recorded in pure air with SVA = 1 V gave a resistance of 118 MΩ and a parallel capacitance of 5.6 pF; in methane the resistance decreased to 99.5 MΩ without any significant capacitance change (5.7 pF).

Figure 6 shows the impedance variation of the sensor exposed to pure methane for 20 min. The 80% of the signal variation was reached in 4 min and the 90% in 9 min. The same Fig. 6 shows the reversible variation of the signal by a subsequent exposure to pure air.

Figure 7 shows the variation of impedance with time by increasing, step by step, the methane/air ratio in the flowing gas (total flux = 50 ml min^{-1}). The measurement was carried out at 100 Hz, the frequency at which Nyquist plots show a negligible noise and a significant impedance variation with gas type. With 10% of CH_4 the impedance decreased by 3–4% in 10 min.

An increase in the CH_4 concentration from 0 to 100% decreased the impedance by about 30% (Fig. 8). PHPT showed the highest sensitivity to
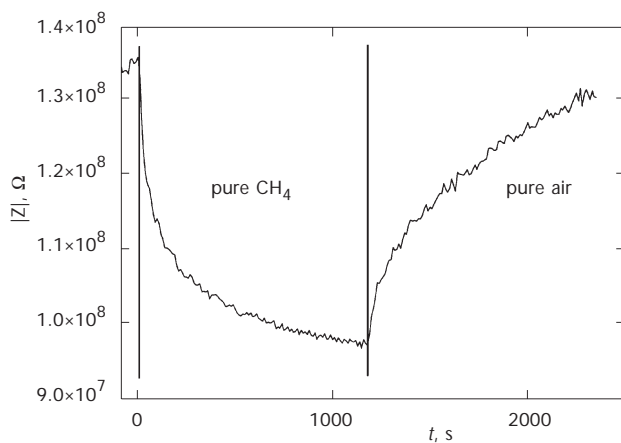

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Impedance variation at 100 Hz of PHPT film on an interdigitated electrode under flux of pure methane and pure air. SVA = 1 V

methane at the lowest hydrocarbon concentration, *i.e.* in the range close to its flash point (5% at room temperature).

The impedance variation with the square root of time, after each concentration change, is shown in Fig. 9. All courses are straight lines indicating that the rate-determining step of the sensing process is the gas diffusion into the polymer.
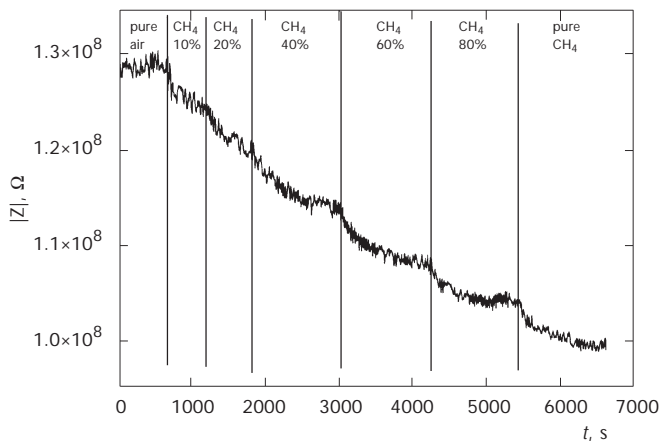

FIG. 7
Impedance variation *vs* time for a PHPT film on interdigitated electrodes under flux of CH_4/air mixture at 7 different relative concentrations. Frequency 100 Hz, SVA = 1 V
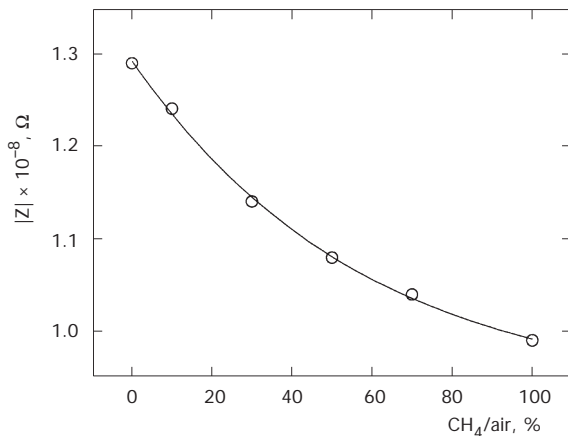

FIG. 8
Steady PHPT impedance *vs* CH_4 concentration at room temperature. Frequency 100 Hz, SVA = 1 V

The response time of this material was of several minutes (80% of the signal variation in 4 min, Fig. 6). This performance could be a drawback for gas sensor applications. However, as the diffusion into the polymer film is the rate-determining step of the process, the response time could be easily improved by varying the cell geometry (*i.e.* the distance between the gold tracks) and the film thickness. In particular, with nearer tracks the contact between the electrodes can be achieved with thinner polymer films during the electrolysis. In this case, if the sensor response follows the gas diffusion through the polymer, the steady state should be sooner attained. Preliminary results in this direction indicate that much higher rates of the sensing process are possible.

The main problem arising from the above results is the elucidation of the mechanism which causes the impedance to decrease when substituting air by methane. The expected low methane–polymer interaction and the diffusion-controlled impedance variation could suggest that the sensing process is due to a change in the rate of intermolecular charge hopping. Unfortunately, the low capacitance variation when replacing methane with air did not help in understanding the sensing mechanism. As a first approach to the problem, it could be hypothesized that the introduction of methane in the fluxing gas induced a different supramolecular organization in the polymer matrix. This probably caused a decrease in the average distance between the hole sites leading to a faster charge transport through the polymer film. An investigation of this problem is in progress.
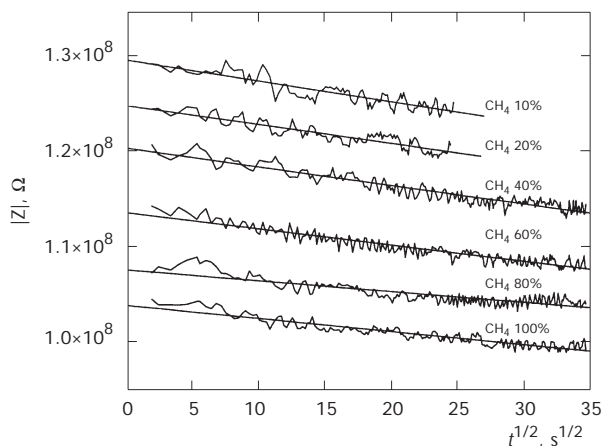

FIG. 9
Variation of impedance *vs* square root of time for a PHPT film in fluxing CH_4/air mixture at 7 different relative concentrations. Frequency 100 Hz, SVA = 1 V

CONCLUSIONS

Electrochemical deposition of an alkylalkoxythiophene-based polymer on interdigitated electrodes allowed to prepare reversible gas-sensitive transducers whose electric output signal was impedance. The impedance of this device decreased with increasing the methane/air ratio and the impedance decrease per methane percentage in air was higher at the lowest methane concentrations. The sensing kinetics was found to be controlled by the diffusion of methane through the polymer film. The response time was rather high for the investigated devices, but it could be reduced by optimizing the cell geometry. The mechanism of impedance variation was not ascertained but an improved intermolecular charge hopping by replacing air with methane can be hypothesized. Anyway, because of the low working temperature and easy construction, this device is promising for a future fabrication of cheap and reliable methane sensors.

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