A polyaniline-based microelectrochemical transistor with an electrocatalytic gate

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The transconductance of an electrochemical transistor-like sensor device derived from coating and connecting three closely-spaced microelectrodes with polyaniline film has been shown to be effectively controlled by an electrocatalytic reaction (*e.g.* SO_2 oxidation in acid media) occurring at the surface of the electropolymer.

Certain special features of polyaniline: electric conductivity, ion-exchange properties and electrochemical and electrocatalytic activity, make it promising for microelectronic and sensor applications.[1–5] Of particular interest is the fact that electrochemical oxidation and reduction of polyaniline is accompanied by changes in the doping level and its electric conductivity is therefore drastically dependent upon the applied potential.[4] This effect has successfully been utilized in pH-sensitive devices with the intrinsic amplification of the chemical signal (the chemotronic analogues of ion-sensitive field-effect transistors)[4,5] that operate in a ‘potentiometric’ mode, since the changes in their output characteristics are governed by ion sorption at the polyaniline surface. On the other hand, the fact that the electrochemical reactions at the polyaniline-modified electrodes proceed as mediated ones,[6] and are therefore accompanied by the effective depolarization of the polymer film,[7] enables the development of amperometric devices in which the lateral conductivity of the polyaniline sensitive element depends on the intensity of the analytic reaction occurring at its surface. In this paper we consider the potential of such an approach, using as an example a polyaniline-based microelectrochemical transistor responsive to SO_2 dissolved in the contacting aqueous medium.

An array of three copper microelectrodes (250 μm wide and 1 cm long parallel strips 25 μm apart) were formed at the polyimide film by means of a photoselective copper-deposition technique described elsewhere.[8] Nickel and gold sub-layers were successively plated on the resulting copper strips from standard $NiSO_4/NiCl_2$ and $KAu(CN)_3$ galvanic baths,[9] whereupon the array was platinized using a 5×10^{-3} mol dm^{-3} K_2PtCl_6 solution (pH 1, 50 °C) and sealed with an epoxy resin leaving a segment 3 mm in length to be exposed to the contacting solution. The microelectrode array was derivatized with a coverage of polyaniline by potentiostatic oxidation of 0.1 mol dm^{-3} aniline/0.125 mol dm^{-3} H_2SO_4 aqueous solution at +0.7 V (*vs.* Ag/AgCl, Cl^- sat.) so as to connect all three microelectrodes with the grown polymer film. The charge associated with the oxidation and reduction of the bound polymer estimated from cyclic voltammetry when all microelectrodes in the array were driven simultaneously was *ca.* 10^{-1} C cm^{-2}.

The polyaniline-derivatized microelectrodes were connected in the circuit as shown in Figure 1. The potential of the middle electrode was controlled relative to Ag/AgCl, Cl^- sat. electrode by means of a potentiostat. The resulting microelectrochemical device mimics the fundamental characteristics of a conventional solid-state field-effect transistor, since the resistance between the two outer electrodes depends on the redox state of polyaniline governed by the potential applied to the middle electrode. This potential is equivalent to the gate potential V_g, while the potential difference between outer electrodes is akin to the drain voltage V_d.

Figure 1 shows the steady-state output characteristics of a fabricated microelectrochemical transistor at fixed bias $V_g = +0.35$ V, *i.e.* when the conversion of polyaniline into the emeraldine (partially oxidized conducting form of polyaniline) occurs. Note that the V_g value should not exceed +0.5 V, which corresponds to the onset of emeraldine conversion into the fully oxidized ‘pernigraniline’ form prone to hydrolytic degradation in acid media.[10] The latter restriction does not affect the operating characteristics of the device reported here since the conductivity of pernigraniline is poor and the potential $V_g = +0.35$ V appears to be optimum for both the stability and transconductance of polyaniline film contacting with the acid aqueous solution.

It has been shown previously[7] that polyaniline is an effective catalyst for SO_2 oxidation because of the high basicity of emeraldine, which creates favourable conditions for the proceeding of the deprotonation stage (known to be a limiting step in SO_2 oxidation[11]). In our experiments no degradation in the electrochemical response of polyaniline during long-term oxidation of SO_2 at +0.35 V has been observed. It should be noted that the selective amperometric determination of SO_2 dissolved in solution cannot be successfully performed using metal (*e.g.* platinum) electrodes because of the poisoning of the electrode surface by dithionates formed during electrolysis.[12]

Since the catalytic oxidation of SO_2 at polyaniline is accompanied by the effective depolarization of the polymer electrode,[7] the value of the drain current appears to be very sensitive to the presence of sulfite in the contacting electrolyte. It is seen from Figure 1 that i_d falls off when sulfite oxidation occurs at the middle electrode (*i.e.* at the gate). It should be noted that the drain current, which saturates when sulfite concentration amounts to *ca.* 10^{-2} mol dm^{-3}, can be utilized to

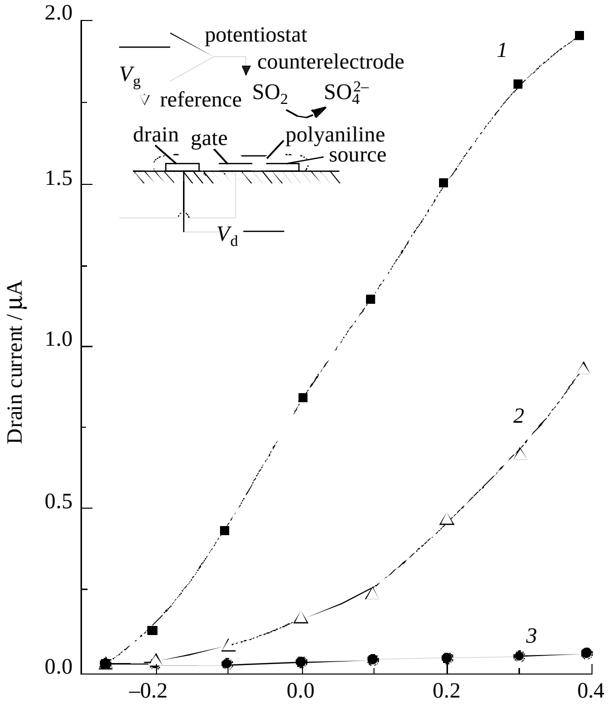

Figure 1 Output characteristics for the microelectrochemical device shown in the insert. Electrolyte: (*1*) 0.25 mol dm^{-3} Na_2SO_4/H_2SO_4, pH 1; (*2*) 10^{-3} mol dm^{-3} SO_2 + 0.25 mol dm^{-3} Na_2SO_4/H_2SO_4, pH 1; (*3*) 10^{-2} mol dm^{-3} SO_2 + 0.25 mol dm^{-3} Na_2SO_4/H_2SO_4, pH 1.

monitor SO_2 content only at a range of low concentrations, while the current through the gate can be used as the sensing signal in more concentrated solutions. On the other hand, these two analytic signals can be mutually amplified by an external measuring circuit that can provide a considerable increase in sensitivity and interference suppression. Moreover, since polyaniline is known to be a good conductive support for catalysts (metal and semiconductor particles, metal complexes, enzymes, *etc.*),[13–15] polyaniline-based sensors can be readily adapted to the desired analytical reactions.

This work was financially supported by the Basic Research Foundation of Belarus and the International Soros Science Education Program.

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Received: Moscow, 2nd September 1996
Cambridge, 21th October 1996; Com. 6/06072B