



Microchip for ultrafast voltammetry

Philippe Fortgang^a, Christian Amatore^{a,*}, Emmanuel Maisonhaute^{a,*}, Bernd Schöllhorn^{a,b}

^a UMR CNRS 8640 "PASTEUR", Ecole Normale Supérieure, Université Pierre et Marie Curie-Paris 6, 24 rue Lhomond, 75231 Paris Cedex 05, France

^b Université Paris Diderot – CNRS UMR 7591, Laboratoire d'Electrochimie Moléculaire, 15 rue Jean-Antoine de Baïf, 75013 Paris, France

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ABSTRACT

Micrometric band electrodes suitable for the electrochemical investigation of molecular wires were manufactured by lithography. These electrodes are adequate for performing ultrafast voltammetry to ca. 0.5 MV s^{-1} with on-line ohmic drop compensation. At these scan rates, the peak resolution and the reproducibility of the experiment are much higher than when traditional disk or hemispherical electrodes are used due to a better control of the electrode surface state. Hence, this method furnishes a platform for transient studies onto adsorbed molecular electroactive objects.

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1. Introduction

There is an increasing necessity to perform transient measurements onto adsorbed molecular objects under perfectly controlled conditions. Indeed, this allows evaluating the potential efficiency of a device for practical applications in molecular electronics or sensing [1–3]. For that purpose, when electrochemical properties are required, the timescale of the phenomena demands the use of ultrafast voltammetry [4,5]. Yet, in order to perform such measurements, a good and reproducible surface state of the working electrode onto which the nanoobject is anchored is necessary. We relied previously onto near-spherical ultramicroelectrodes obtained by melting a gold microwire in a flame since the surface state of classical disk electrodes embedded in glass often does not allow getting reliable data even after drastic polishing. Nevertheless, this hand-made procedure is not fully reliable and reproducible. The major problem in this method is due to the difficult insulation between glass and metal. The sealing is often leaking, therefore causing a strong increase of stray capacitive current. Moreover, the electrode area is not easily controllable.

Following Chidsey [6], we adapted lithographic procedures to produce band electrodes allowing several hundred kilovolts per second to be reached routinely. Moreover, the electrochemical response of these electrodes is closer to ideality than for ball electrodes, therefore allowing a more precise determination of the kinetic and thermodynamic parameters. The advantages of this procedure have been demonstrated through investigating the fast,

previously well characterized molecular wire 1 depicted in Fig. 1 [4,7,8].

2. Experimental procedure

2.1. Electrochemical measurements

An ultrafast potentiostat equipped with on-line electronic compensation of ohmic drop was used to perform the electrochemical measurements. It was identical to that previously published [9,10]. Briefly, it relies onto large bandwidth amplifiers and allows electronic compensation of ohmic drop. In order that the compensation loop operates in real time, it is necessary that the physical dimensions of the circuit remain in the centimeter range. We have improved the design of the electronic board in order to optimise the stability by decreasing stray capacitances. The active part of the circuit stands on $2 \times 2 \text{ cm}^2$. The current amplifier gain was 2200Ω . All measurements were made in acetonitrile + 1 M tetraethylammonium tetrafluoroborate.

2.2. Electrodes

Band electrodes were produced by conventional lithographic techniques. Glass micro slides of $38 \times 26 \text{ mm}$ were preliminary cleaned with piranha solution (25% H_2O_2 and 75% H_2SO_4), then rinsed with distilled water, acetone and isopropanol and dried under a flow of argon. The following different steps of the lithographic process were performed in a clean room [11].

We relied on using the photosensitive resin AZ5214E (Clariant, USA) for preparing our electrodes. This special resin is an image reversal resin that works in three stages: (i) an initial exposure using a suitable mask defines the final geometry of the device; (ii) a soft bake

* Corresponding author.

E-mail addresses: christian.amatore@ens.fr (C. Amatore), emmanuel.maisonhaute@ens.fr (E. Maisonhaute).

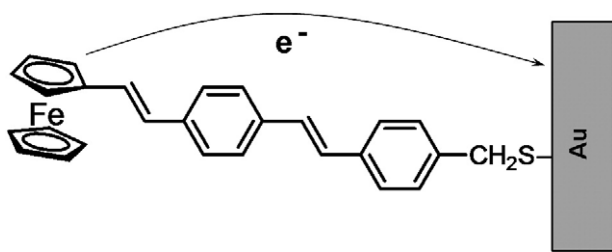


Fig. 1. Principle of the measurement of electron transfer through ferrocenyl oligo(phenylenevinylene) molecular wire 1.

inverts the image; (iii) finally, the previously exposed regions are stabilized by a flood exposure. In the practice, a *c.a.* 2 μm layer of photosensitive resin AZ5214E (Clariant, USA) was spin-coated at 4000 rpm. The resin was then baked at 125 $^{\circ}\text{C}$ for 90 s. After cooling (3 min), it was exposed to UV light ($\lambda = 360$ nm during 6 s) through an optical mask to allow a transfer of the pattern on the resin. A soft baking followed by UV exposure (20 s) without optical mask was used for inverting the polarity of the previously exposed image. The sample was then developed in AZ MIF 726 (Clariant, USA) during 30 s and then rinsed in deionised water and dried with argon. This process removed only the resist area where the future microelectrodes would be deposited. This was performed by electron beam evaporation with an Auto Boc Edwards apparatus and involved the successive deposit of a 15 nm thick Cr layer first (adhesive layer) and a 30 nm thick Au layer. This provided an excellent adhesion to the glass substrate, a good stability and a reproducible electrochemical behaviour. After the metal deposition, the sacrificial resist was removed in acetone (lift-off) to obtain the desired gold pattern on the underlying glass slide (cf. Fig. 2).

The resistance of the sole gold layer is smaller than 150 Ω for a 750 μm long electrode of 5 μm width, therefore much less than the electrolyte one (above 500 Ω is currently measured). The conventional method described above was relatively easy to implement and should have an intrinsic resolution of 2 μm . Smaller patterns would necessitate e-beam lithography. We relied therefore on a minimum width of 5 μm and chose an electrode length of 10 mm. The electrode length was not relevant since the electrode area effectively exposed to the solution is delimited by the electrochemical cell fixed onto it (see below).

2.3. Electrochemical cell

Two different cell configurations were considered. In the first one, a Teflon 3.2 mm diameter conical cell was simply pressed onto the electrodes. This material was adequate for most electrochemical solvents. Another option used in this work consisted in moulding a polydimethylsiloxane (PDMS) microchannel as depicted in Fig. 2. The electrode length was then reduced which allowed faster scan rates to

be used. The exposed length of the band electrode was 750 μm and the channel height was 2.4 mm. The main drawbacks were that PDMS is permeable to oxygen and incompatible with some solvents (HCCl_3 and THF). The PDMS cell was fixed onto the electrodes by activation under air plasma with a Harrick PDC-002 (P/N 191–500) plasma cleaner/sterilizer coupled to a vacuum pump. Two microwells are made with syringe needles so as to introduce incubation and electrolyte solution (cf. Fig. 2). By removing the needle, the injection holes shrunk so that the electrolyte was trapped inside the channel.

2.4. Self Assembled Monolayers (SAMs) preparation

Once the electrochemical cell is ready, the electrodes are incubated first with a 0.3 mM solution of the target molecule for 10 mins. Then 0.3 mM decanethiol is introduced as diluent for 5 mins. All solutions are made in absolute ethanol. The diluent aims at minimizing the interactions between electroactive molecules so that the recorded signal should ideally be the average one of an isolated unit.

3. Results and discussion

Working with electrodes having micrometric dimensions diminishes the time constant and ohmic drop that are the main limiting factors at the short times. Ideally, a spherical geometry is optimum because the field lines then radiate linearly from the electrode surface. However, this geometry is difficult to access experimentally (excepted for mercury) so that the disk shape often prevails. For this geometry the solution resistance R_S is given by:

$$R_S = \frac{\rho}{4r_0} \quad (1)$$

where ρ is the solution resistivity and r_0 the electrode radius.

Nevertheless, although disk electrodes are possible to manufacture by lithographic procedures, this requires more steps since the contact needs to be insulated [12,13], which brings again the problem of edge insulation. We then relied onto band electrodes for which the edge effects may be smaller, although these are micrometric in a single dimension. There is no analytical solution for the resistance for a band geometry yet by definition it is smaller than for a disk of diameter equal to the band width [14–17].

Three electrodes were implemented onto each device, the central one being the working electrode, whose width was chosen to be 5, 10, 15 or 20 μm (cf. Fig. 2). Other electrodes (300 μm width) may be used as pseudo-reference and counter electrodes. Fig. 3 presents voltammograms obtained after incubating our system successively with molecule 1 and then with decanethiol used as a diluent. Acetonitrile instead of water was used as a solvent to perform this voltammetric characterisation in order to demonstrate the reliability of our setup in organic medium. Yet, a drift of the reference electrode with time was

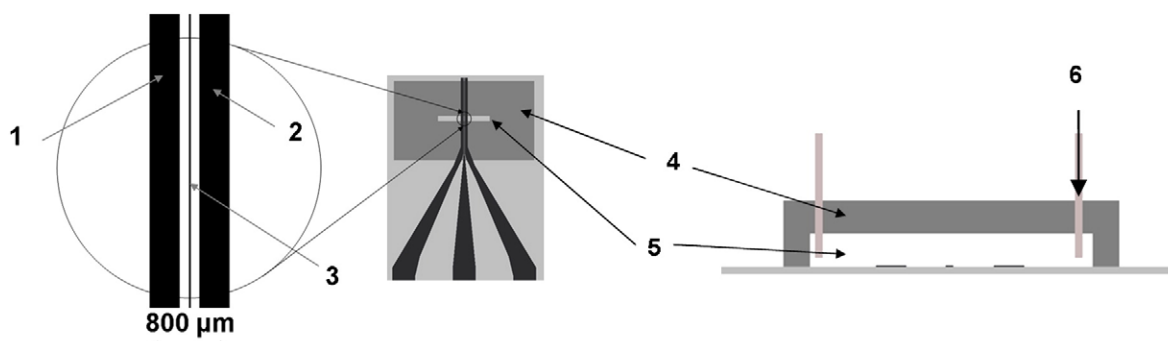


Fig. 2. Scheme of the three electrode device implemented on a glass substrate equipped with a PDMS channel to define the electrochemical cell: 1: reference electrode (300 μm) 2: counter electrode (300 μm) 3: working electrode. 4: PDMS structure. 5: channel. For clarity, the scale is not respected.

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