

# The punctured droplet electrode – A new three-phase electrode with well defined geometry

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Received 8 September 2006; received in revised form 28 September 2006; accepted 29 September 2006

Available online 1 November 2006

## Abstract

A new three-phase electrode allows detailed studies on well-defined three-phase junctions. It consists of a nitrobenzene drop of well controlled size. The drop is dispensed from a capillary and is punctured with a microcylinder electrode. The organic liquid contains an electroactive compound (decamethylferrocene) and, importantly, no supporting electrolyte. The aqueous phase may contain various salts. Well-defined and reproducible linear-scan and square-wave voltammograms and chronoamperograms of oxidation of decamethylferrocene were obtained. The dependence of the formal potential determined from the square-wave voltammograms of decamethylferrocene versus the standard potential of transfer of anions present in the aqueous phase was almost perfectly linear. The developed approach allows the formation of two or more three-phase boundaries within one small drop. Since the drop is well exposed, this electrode geometry also gives a potential possibility of optical/spectrophotometric inspection of the reaction products in the organic phase and of examination of the reaction-layer growth.

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**Keywords:** Three-phase boundary; Cylindrical microelectrode; Nitrobenzene; Voltammetry; Decamethylferrocene

## 1. Introduction

Three-phase electrodes are of great importance in almost all fields of electrochemistry, especially in batteries [1], fuel cells [2], surface modified electrodes for electroanalysis [3], biosensors [4], etc. In most of these cases, however, it is very difficult, if not impossible, to prepare electrodes with a well-defined three-phase junction to study the basic phenomena at that location. This is a very regrettable situation since only the detailed understanding of the electrode reactions at the three-phase junctions will allow understanding of the functioning of three- and also multi-phase electrodes. Many three- and multi-phase electrodes are in use since long, and their overall properties

are well known, whereas their principles of working are still poorly understood. For three-phase electrodes with two solid phases and one electrolyte solution phase, some attempts have been made to elucidate their properties [5], and numerous studies of the NEMCA effect (Non-Faradaic Electrochemical Modification of Catalytic Activity) have been published [6], where usually two solid phases and one gas phase form the three-phase system. In case of the systems with one solid phase (electron conductor) and two liquid phases, the immobilisation of droplets of a water-immiscible organic liquid on the surface of a graphite electrode proved to be very useful. It appeared that it is possible to prepare three-phase electrodes with stable and rather well defined three-phase junctions, although, it has to be admitted that little is known about the molecular structure of these junctions. Such immobilised droplets with a dissolved electroactive probe successfully served for the studies of the thermodynamics of ion transfer that can be driven by electrochemically initiated

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redox reactions of the probe compound [7–15]. The immobilized droplets allowed the studies with inserted microelectrodes to get insight into the geometric procession and the rate of the electrode reaction [16]. Similar results could be obtained using a droplet sandwiched between a transparent electrode and a glass plate, and employing microscopic spectroelectrochemistry [17]. Compton has shown how electrodes with a heterogeneous electrode surface (three-phase and multi-phase systems) can be treated in the simulation of their voltammetric behavior [18].

Recently, the Warsaw group has proposed a new electrochemical setup [19] which represents further development of the above three-phase-electrode system. A very thin gold or platinum wire crosses a two-phase system and plays the role of a microcylindrical, working electrode. The metal microcylinder is placed in a mixture of two immiscible liquids in such a way that the upper part of the wire remains in the aqueous phase and its lower part is totally immersed in the organic liquid. The proposed configuration provides a very reproducible and well-defined length of the three-phase boundary (located along the circumference of the wire) and results in the data of good precision. Moreover, the length of the three-phase junction can be easily controlled by varying the wire diameter. Also, there is a possibility of employing various electrode materials.

In this paper, we demonstrate another approach to the three-phase electrochemistry. We dispense an oil drop of required size from a capillary into the aqueous phase and insert a platinum or gold microwire into the drop. This approach should enable easy change of the drop and renewal of the initial electrochemical conditions. It also leads to the exposition of the organic phase.

## 2. Experimental

Voltammetric measurements were performed in the three-electrode system using an AUTOLAB PGSTAT 30 (Eco-Chemie, Utrecht, Netherlands) potentiostat. A special voltammetric cell has been constructed. A photo of the cell and the measurement scheme are shown in Fig. 1a and b. Platinum cylindrical electrodes of 50, 100 and 300  $\mu\text{m}$  in diameter served as the working electrodes. A silver/silver chloride/saturated KCl ( $E = 0.199\text{ V}$  versus SHE) was used as the reference electrode and a platinum wire served as the auxiliary electrode. The organic phase in the form of a drop was dispensed from a capillary with a help of a precision dispenser (Fig. 1b). This way of dispensing a drop of oil resembles clearly the construction of the hanging mercury drop electrode by Kemula and Kublik. Another micrometer screw was used to control the approach of the wire to the drop. In this way a possible (but sporadic) formation of the meniscus at the three-phase boundary could be compensated. The cell was enclosed in a Faraday cage in order to minimise electrical interferences.

Typical instrumental parameters for square-wave voltammetry (if not specified otherwise) were the following:

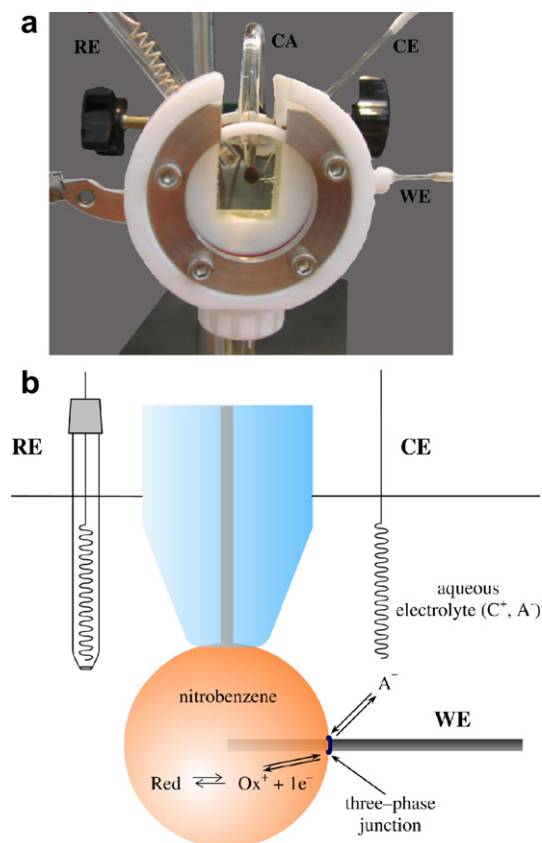


Fig. 1. Photo of the electrochemical cell used (a) and the measurement scheme (b). WE – microcylindrical working electrode, RE – reference electrode, CE – counter electrode, CA – capillary. A dispensed nitrobenzene drop is seen in the centre of the cell.

SW frequency of the potential modulation,  $f$ : 10 Hz; SW height of the potential pulses,  $E_{\text{SW}}$ : 50 mV; and potential step of the staircase ramp,  $dE$ : 1 mV.

The following chemical reagents (purum p.a.): lithium perchlorate ( $\text{LiClO}_4$ ), lithium chloride ( $\text{LiCl}$ ), lithium nitrate ( $\text{LiNO}_3$ ), sodium bromide ( $\text{NaBr}$ ), sodium iodide ( $\text{NaI}$ ), sodium thiocyanate ( $\text{NaSCN}$ ), sodium tetrafluoroborate ( $\text{NaBF}_4$ ) and sodium hexafluorophosphate ( $\text{NaPF}_6$ ) were purchased from Fluka and were used as supporting electrolytes in the aqueous phase. Decamethylferrocene and nitrobenzene were purchased from Aldrich. The aqueous electrolyte solutions were saturated with nitrobenzene and were prepared using high purity water obtained from a Milli-Q Plus/Millipore purification system (conductivity of water:  $0.056\ \mu\text{S cm}^{-1}$ ). All experiments were performed at  $22\text{ }^\circ\text{C}$ .

## 3. Results and discussion

In our approach a platinum wire of known thickness was immersed partially in a nitrobenzene drop and partially in the aqueous phase. These two solvents are of a rather low mutual miscibility, and thus form a well-defined interface. The organic liquid contained only an electroactive compound and the aqueous phase contained various

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