ELECTROCHEMISTRY WITH AN INVERTED ELECTROCHEMICAL CELL

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Abstract: Microcapillary electrochemical cell has been proven to be a suitable experimental arrangement for a variety of electrochemical applications, such as solid-state electrochemical measurements, meniscus-confined three-dimensional electrodeposition, and corrosion studies. With such experimental system the electrochemical experiment is made by using supporting electrolyte in a microcapillary (commonly with a diameter less than 1000 μm) that is in contact with the surface of an external working electrode. Yet, there are still technical limitations of the microcapillary system to be overcome in terms of high electrical resistance, low reproducibility, complexity and costly instruments (e.g., piezo-positioning system, optical microscope, camera etc.).

Herein we report on a simple, novel experimental arrangement of an electrochemical experiment with the use of an inverted electrochemical cell. Although principally similar to microcapillary system, the proposed arrangement consists of a simple, inverted macroscopic electrochemical cell, being in a contact with a large, externally positioned working electrode. The contact with the working electrode is made by meniscus of a droplet hanging out of the macroscopic capillary ending of the cell. Macro-reference and counter electrodes were inserted inside the inverted electrochemical cell, demonstrating that there is no need for using microelectrodes and complex electrochemical setup. Without using any sophisticated instrumentation it has been shown that there is no significant electrochemical resistance compared to a common electrochemical experiment, while the reproducibility of voltammetric measurements was quite satisfactory. With a preliminary set of experiments under conditions of cyclic voltammetry it is demonstrated that the inverted electrochemical cell is a versatile experimental tool to be used as a scanning probe to study the morphology of the underlying substrate acting as a working electrode, as well as for detection of immobilized solid microparticles. Moreover, the proposed cell is a highly suited system for detection of gaseous species, as exemplified with sensing of gaseous H_2O_2, which is of exceptional importance for medical applications and for detection of hydrogen peroxide based explosives.

Keywords: electrochemical cell, external working electrode, electrochemical sensor

1. INTRODUCTION

Modern electrochemical science is concerned with the study of charge transfer phenomena across an interface formed between two phases; most frequently it is an interface between solid working electrode and an electrolyte solution. When the charge is carried out by electron flow, a solid and chemically inert working electrode is commonly used. Whereas for studying ion transfer processes the interface between two immiscible electrolyte solutions [Scholz] is applied. Yet, the last interface can be an entity where the electron transfer occurs too, or both electron and ion transfers take place simultaneously. The common experimental arrangement for studying charge transfer across liquid interfaces comprises of four electrodes [Wang], though arrangement with three-electrode are also known [Mirceski].

The electron transfer across an interface between solid electrode and electrolyte solution is predominantly studied by means of three-electrode configuration [Holze]. The electrolytic cell used consists of a working, reference and counter electrode, being all immersed into an electrolyte solution (Scheme 1A). Numerous modifications of the basic configuration have been developed over decades, which are mainly focused on modifying the working electrode in terms of its surface, dimensions, and geometry [Bard].
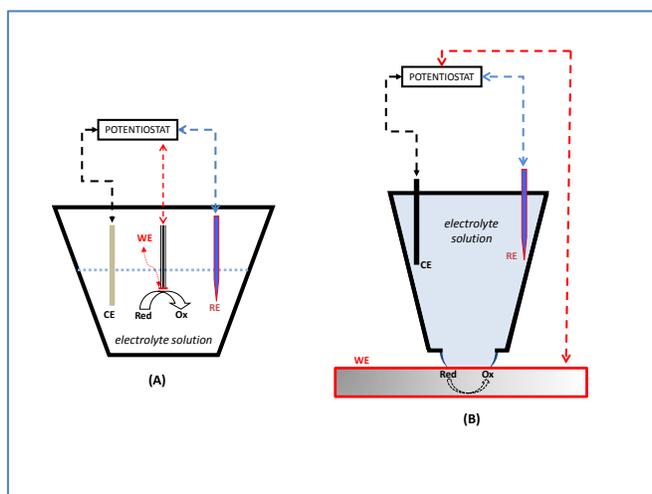
Scheme 1.(A) A conventional electrolytic cell where all three electrodes, the small *working electrode* (WE), the large *counter electrode* (CE), and the robust *reference electrode* (RE) are immersed in the electrolyte solution. **(B)** Electrolytic cell ending with a capillary orifice with a diameter of 1 mm, through which an electrolyte solution droplet is formed, being in a contact with externally positioned macroscopic working electrode.

Yet, there is a need of an experimental arrangement in which the working electrode cannot be immersed in the electrolyte solution together with the other electrodes. Examples are found in the corrosion science where the in-situ examination of a surface of a macroscopic object is required, without being able to prepare a working electrode of the studied material as in the conventional electrochemical experiment. Thus, an experimental arrangement as depicted in Scheme 1B can be easily envisaged, in which the working electrode is externally positioned relative to the electrolytic cell. Principally, the same arrangement is found in a plethora of techniques known as electrochemical microcell techniques [Andreatta], some of which are related with scanning electrochemical microscopy, as one of the most advanced electrochemical techniques [Polcari]. Electrochemical microcell techniques utilize a capillaryof micrometer or nanometer dimensions containing the electrolyte solution to form an interface with the working electrode; thus, electrochemical reactions studied are governed by mass transfer phenomena typical for microelectrodes [Scharifker]. Though electrochemical microcell techniques are very powerful experimental systems, their implementation is still a state of the art, demanding experimental sophistication and proficiency in manipulation with instrumentations.

The present study aims to demonstrate that the application of the experimental arrangement depicted in Scheme 1B is possible with a macroscopic interface between the externally positioned working electrode and the inverted electrolytic cell. A collection of voltammetric experiments is presented to prove the feasibility of this approach, enabling a versatile application in a range of fields of electrochemistry, such as electroanalysis, in particular solid particles and gas sensing, corrosion studies, metal deposition, etc.

2. EXPERIMENTAL ANALYSES

Experimental analyses have been performed with homemade electrochemical cell, schematically depicted in Fig. 1B, combined with potentiostat PalmSens2, driven by PSTrace software, using Ag/AgCl/3 mol L^{-1} KCl and a platinum wire as a reference and counter electrode, respectively. The cell ends with a capillary with an orifice with a diameter of 1 mm. A droplet of the electrolyte solution formed at the end of the capillary is in contact with the externally positioned electrode, made of a graphite paste deposited on a flat glass surface, or paraffin impregnated graphite electrode (PIGE) in a form of a macroscopic rod. The droplet of the supporting electrolyte of the inverted cell covers partly either the flat graphite paste electrode or the basis of the cylindrical PIGE electrode.

All chemicals used were of analytical grade purity (Sigma-Aldrich). All solutions were prepared with water obtained from Arium® mini Plus purification system from Sartorius. All experiments have been conducted at room temperature, by applying cyclic voltammetry (CV). The other experimental conditions are given in the figure captions.

3. RESULTS AND DISCUSSION

A typical response recorded with the inverted electrochemical cell of a dissolved electroactive species under conditions of CV is depicted in Fig. 1A (curve 1), showing oxidation of hexacyanoferrate(II) ions, dissolved in 0.1 mol/L KCl supporting electrolyte at the graphite paste electrode. A well developed cyclic voltammogram is obtained, typical for a quasireversible electrode reaction, with a peak potential separation of about 150 mV and the peak current ratio close to 1, revealing an excellent operation of the inverted electrochemical cell. In comparison with the conventional experiment (curve 2 in Fig. 1A) differences are seen only in the intensity of the response, due to different electrode surface are, which for the inverted cell, depends on the dimension and spreading of the droplet on the working electrode surface. The peak potential difference obtained with the inverted cell is slightly larger than

in the conventional experiment due to the slight effect of the uncompensated resistance, mainly dictated by dimensions of the capillary orifice. Increasing the scan rate up to $v = 100$ mV/s results in increasing of the peak-currents and the peak potential separation (data not shown), as typical for the quasireversible electrode reactions [Compton]. Yet, at $v > 100$ mV/s the uncompensated resistance is becoming significant, thus optimisation with respect to the diameter of the capillary orifice and the distance between the working and reference electrode should be considered in designing the inverted electrochemical cell.

Fig. 1.(A) Comparison of cyclic voltammograms recorded with inverted (**1**) and conventional cell (**2**) for the oxidation of 1 mmol/L $K_4[Fe(CN)_6]$ dissolved in 0.1 mol/L KCl aqueous solution at the scan rate $v = 20$ mV/s. **(B)** Cyclic voltammograms of $K_4[Fe(CN)_6]$ recorded at different spots of the working electrode. The other conditions are as in panel (A). Cyclic voltammograms of microparticles deposited on the working electrode surface of viatmin K **(C)** and elemental copper **(D)** in contact with a phosphate buffer (pH = 1.8) at $v = 50$ mV/s.
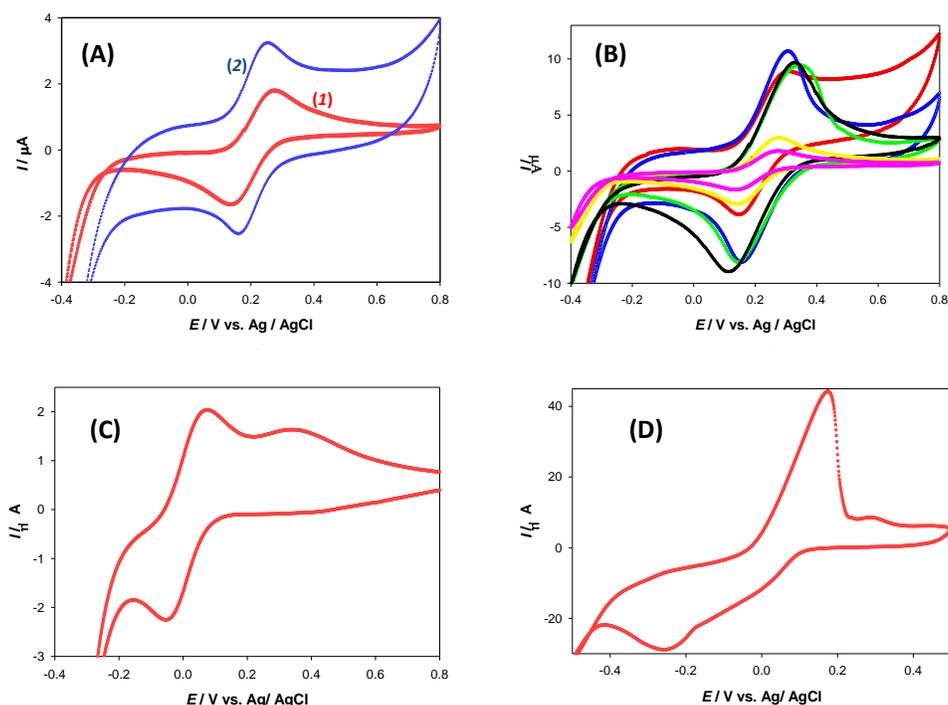
More importantly, the inverted cell can be used as a scanning probe for sensing surface morphological variation of the working electrode, i.e. the surface of any substrate acting as a working electrode. To this end a heterogeneous working electrode surface has been formed with a graphite paste of different thickness and surface morphology, while cyclic voltammograms have been recorded at different regions of the electrode. As clearly shown in Fig 1B the cyclic voltammograms are highly sensitive to the surface morphology. The differences arise due to specific wettability and spreading of the electrolyte droplet over the electrode surface, the rate of the electrode reactions, and the ohmic resistance effect. Cyclic voltammograms with a larger current intensity imply larger contact area of the electrolyte droplet and the electrode, whereas the smaller peak potential difference indicates faster electrode reaction and less influence of the ohmic resistance.

Besides being used as a scanning probe the inverted electrochemical cell as can be effectively applied for electroanalytical purposes and sensing of electroactive species immobilized on the electrode surface. For instance, it is particularly intriguing to develop electroanalytical methods for detection and quantification of solid species insoluble in a particular supporting electrolyte. Using vitamin K, a model experiment has been designed to demonstrate the capability to detect solid, hydrophobic particles, randomly distributed over the surface of the graphite paste electrode in a form of microcrystals. Positioning the inverted cell over particular region of the electrode enriched with a cluster of vitamin K microcrystals (presumably not exceeding the amount of a nanogram of a single microcrystal cluster), a well developed cyclic voltammogramcan be recorded, as shown in Fig. 1C. The

quasireversible nature of the electrode reaction in contact with the aqueous buffer solution is due to reversible redox chemistry of the quinone-like structure of water insoluble vitamin K [Sýs].

Fig. 2. Inverted electrochemical cell used as a gas sensor. Typical cyclic voltammograms recorded with the inverted electrolytic cell using paraffin impregnated graphite working electrode in contact with 0.1 mol/L HCl aqueous solution at $v = 50$ mV/s in the absence **(1)** and in the presence of gaseous H_2O_2 **(2)**. For **(2)** the 10 mL of 30% solution of H_2O_2 have been brought in the vicinity to the droplet of the inverted cell (approximately at the distance of 10 cm). The inset shows a scheme of the inverted electrochemical cell emphasizing the three-phase boundary region where the gaseous phase, the working electrode and the supporting electrolyte meet.
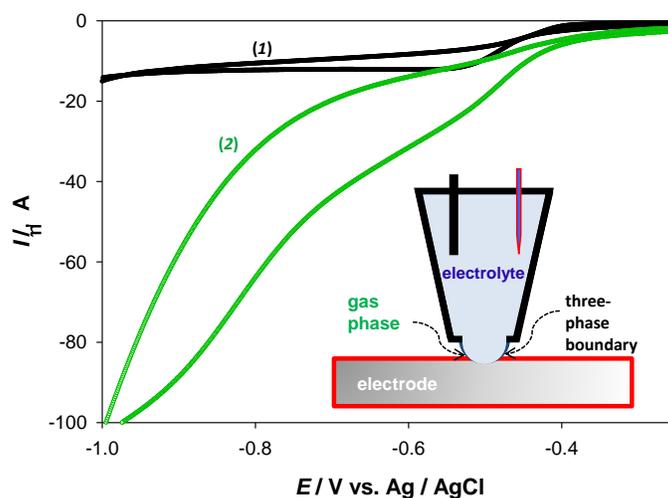
Besides detection of water insoluble organic species, the inverted electrochemical cell can be used for patterned metal deposition, or for detection of metal nanoparticles immobilized on the electrode surface. Figure 1D illustrates the detection of copper nanoparticles deposited on the graphite paste electrode, following the methodology of anodic stripping voltammetry [Boussemart]. The initial scan in the anodic direction of the cyclic voltammogram results in electrochemical dissolution of copper nanoparticles to the corresponding metal ions (i.e. the anodic, sharp stripping peak in Fig. 1D), whereas the reverse cathodic scan reflects electrochemical reduction of copper ions formed in the vicinity of the working electrode. Importantly, the intensity of the response for the case of microcrystal detection (Fig. 1 C and D) does not depend on the contact area of the droplet rather than on the amount of the electroactive microcrystals.

Finally, the inverted electrochemical cell is highly suited experimental arrangement for electrochemical detection of gaseous species. To this aim of particular importance is the three-phase boundary line of the inverted cell, where the droplet electrolyte, the gas phase and the working electrode meet, as depicted in the inset of Fig. 2. Clearly, working in ambient conditions, the gaseous phase is represented by the air, thus any electrochemical experiment is conducted in the presence of oxygen. Even by previous degassing of the supporting electrolyte from the dissolved oxygen, as soon as the droplet electrolyte is formed, the gaseous oxygen is being dissolving in the droplet, saturating rapidly the small volume droplet. More importantly, at the three-phase boundary line where the working electrode, the supporting electrolyte and the gaseous phase meet, the electrochemical reaction of the gaseous species can readily takes place, even in the case when of low soluble gases. Consequently, curve 1 in Fig. 2 illustrates clearly the irreversible reduction of oxygen at the PIGE electrode at about of -0.500 V, recorded with the inverted electrochemical cell. In the presence of H_2O_2 vapour formed in the vicinity of the droplet, a strong voltammetric signal due to irreversible reduction of hydrogen peroxide emerges, as depicted by the curve 2 in Fig. 2. The H_2O_2 vapours have been produced by evaporation of 10 mL of 30% H_2O_2 brought approximately at 10 cm distance from the droplet of the inverted cell, under ambient conditions.

In conclusion, the presented preliminary set of experiments clearly demonstrates the simplicity and versatility of the inverted electrochemical cell for studying redox species dissolved in the electrolyte solution (thus used as a scanning

probe) or immobilized on the working electrode in a form of solid particles. More importantly, the inverted cell has a promising application in the area of gaseous detection, in particular detection of gaseous H_2O_2, which is of exceptional importance for medical applications [Meier] and for detection of hydrogen peroxide based explosives [Krivitsky].

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