Journal of Electroanalytical Chemistry 649 (2010) 37–41

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Flow-through Electrochemical Surface Plasmon Resonance: Detection of intermediate reaction products

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ARTICLE INFO

Article history:
Received 13 November 2009
Received in revised form 19 December 2009
Accepted 29 December 2009
Available online 6 January 2010

In honour of Professor Lipkowski on occasion of his 65th birthday

Keywords:
Electrochemical Surface Plasmon Resonance
Radical
Hydroquinone
Benzoquinone
Cyclic voltammetry
Chronoamperometry

ABSTRACT

The electrochemical reaction of hydroquinone–benzoquinone (HQ–BQ) system in acetonitrile was studied by a flow-through Electrochemical Surface Plasmon Resonance (EC-SPR) technique. The semiquinone radical anion ($BQ^{\bullet-}$) was detected as a large negative SPR shift for the first time by the hyphenated technique. The real time SPR signal shows the entire reaction process of the $BQ^{\bullet-}$ including generation, transformation and disappearance. The lifetime of the $BQ^{\bullet-}$ in the reaction was extracted by comparing the SPR signals along the flow stream. The study demonstrates that the flow-through EC-SPR is a powerful tool for monitoring not only surface bindings, but also solution phase chemical reactions. In addition, it is especially suitable for detecting unstable intermediate reaction products, which are difficult to measure using conventional analytical methods.

1. Introduction

Surface plasmon resonance (SPR) is very sensitive to various processes taking place on or near a metal surface [1–6]. The metal surface where SPR is created can also serve as a working electrode for electrochemical measurements. Combining electrochemical and SPR measurements has led to the development of Electrochemical SPR (EC-SPR). To date, EC-SPR has been used in the analysis of trace metal ions [7–10], detection of surface bound redox species [11–15], electrochemical polymerization [16–22] and biosensing [23–25,14]. These studies are mainly focused on adsorption/desorption processes or changes in the adsorbed species. SPR is also sensitive to the charge density in the metal film [12], which has been employed recently by us to develop a surface impedance imaging technique [26]. In addition to applications based on the SPR dependence on the intrinsic dielectric properties of the metal films and molecular adsorption on the metal films, SPR measures local refractive index in the bulk solution near the metal film [27]. Here we describe a flow-through EC-SPR and its application for detecting intermediate reaction products.

The electrochemical reaction of hydroquinone–quinone system has been widely studied as one of the most classical organic redox reactions in chemistry, biochemistry and electrochemistry [28–36]. The system is often used as a model to test new electrode materials, new electrochemical techniques, or new solvents. In addition, the electrochemistry of quinones is important for understanding biological electron transfer processes such as the photosynthesis, oxidative phosphorylation [37], cytotoxic functions and paradoxically antitumor activity [38–41]. Quinones and their redox products, such as semiquinone anions and quinone dianions, have been studied with various techniques, i.e., with electrochemical methods such as polarography [42–44] and with ultraviolet/visible [45,46] and infrared spectroscopy [47–51]. However, due to the similarity of the signals, these techniques are difficult to distinguish the short-lived semiquinone anion radicals and the final redox products.

In the present work, we have investigated the redox reaction of hydroquinone–benzoquinone (HQ–BQ) system in acetonitrile with a novel two channels flow-through EC-SPR setup. This setup can measure either the electrochemical and SPR signals, or both of them simultaneously. More importantly, it allows one to monitor the electrochemical, or/and SPR signals at different locations along the flow path, which opens the door to many new applications. For example, one can generate an electrochemical reaction at upper stream and detect the reaction products at downstream. This unique capability makes it possible to separate the proton and electron transfer processes, as well as the reaction intermediates and

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doi:10.1016/j.jelechem.2009.12.027

final products. In the case of HQ–BQ system, we were able to detect semiquinone anion radical, $BQ^{\bullet-}$, as a very large negative SPR signal, which can be easily differentiated from the positive SPR signal of the reaction products. The lifetime of $BQ^{\bullet-}$ can be estimated from the SPR data collected at different positions of the flow. To the best of our knowledge, this is the first time to obtain radical information in bulk solution by SPR, and our results demonstrated SPR as a new tool for detecting radical reactions.

2. Experimental

2.1. Reagents

Acetonitrile (99.8%) and hexaammineruthenium (III) chloride ($Ru(NH_3)_6Cl_3$) were purchased from Sigma–Aldrich. Hydroquinone (⩾99%), *p*-benzoquinone (⩾99.5%) and tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) (⩾99.0%) were purchased from Fluka.

2.2. Instrument and electrodes

BI-2000 SPR Instrument (Biosensing Instrument Incorporation) was used for the experiments. The instrument was equipped with a EC-Dual-Flow Analysis Module which include a dual-channel flow-through cell. Each channel is 2.0 mm wide, 0.5 mm high and 5 mm long, with a fluid volume <5 μL. The flow control system allows one to either operate the two channels in parallel or in series. A gold film coated glass coverslip was used as the working electrode (WE), along with a glassy carbon counter electrode (CE) located directly above the regime of the gold film measured by the SPR, and a Ag/AgCl reference electrode (RE) located in the middle of the flow channels (Fig. 1). A microAutolab type III potentiostat (Metrohm Autolab company) was used for controlling the potential and recording the potential and current.

2.3. Preparation of the sensing surface

22 × 22 mm #1 BK7 glass microscopy coverslips (VWR #48366067) were first cleaned with deionized water and absolute ethanol, followed by 3 min cleaning in an oxygen-plasma cleaner (Harrick Scientific Corporation). The cleaned coverslips were coated with 2 nm chromium and 47 nm gold by a sputter coater (Quorum Emitech Corporation, model K675X). Prior to each experiment, a gold film was cleaned with deionized water, absolute ethanol and blown to dry with nitrogen, and then briefly annealed with a hydrogen flame to remove possible surface contamination. To decouple the EC signal with the SPR signal, each gold chip was divided by cutting lines crossing the chip surface into four electrically isolated quadrants (Fig. 1) before mounting it under the EC-SPR cell.

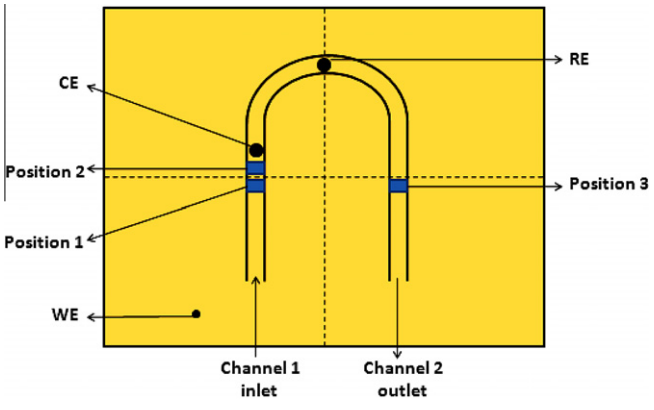

Fig. 1. A schematic drawing of the flow channels and the electrodes on the gold coated sensing chip (top view). The two channels are connected into a U-shape. The width, height and length of each channel are 2.0 mm, 0.5 mm and 5 mm, respectively. The WE contacts the sensing chip with a contact pin; the RE and CE are on the top of the flow channel shown at the figure. The solution flows into the cell through channel 1 and flows out through channel 2. Position 1 is at the WE location; positions 2 and 3 are at downstream locations. For 100 μL/min flow rate, it takes 0.1 s and 5 s for a sample to flow from position 1 to positions 2 and 3, respectively.

2.4. EC-SPR measurement of HQ–BQ redox reaction

The EC-SPR measurement was carried out according to the following steps: (1) Load acetonitrile solution (containing 0.1 M Bu_4NPF_6, 50 mM HQ, and 50 mM BQ) into two 10 mL carrier syringes and begin pumping the solution at 100 μL/min through the flow cell. (2) Place the o-ring around the RE head and insert the RE into the RE collar attached on the flow cell. (3) Once the solution nearly fills the RE well, place the RE collar with RE electrode and o-ring into the RE well of the flow cell. (4) After the system stabilizes and equilibrates with the flowing solution, EC-SPR experiment begins with the serial flow mode (from channel 1 to channel 2).

3. Results and discussion

3.1. Cyclic voltammetry of hydroquinone–benzoquinone system

The oxidation of HQ and the reduction of BQ were characterized by cyclic voltammetry (CV) in bulk electrolyte solution (Fig. 2). The typical chemically irreversible two-electron oxidation peak (I) of hydroquinone (Scheme 1(1)) was observed at potential 1.5 V [30]. It has been reported that the reduction of quinones in acetonitrile takes place in two steps, each involving one-electron transfer [34] (Scheme 1(2)). The first one-electron reduction corresponds to the formation of semiquinone anion $BQ^{\bullet-}$, which has a peak at −0.74 V, and the second one results in the formation of benzoquinone dianion BQ^{2-} at −1.18 V [49]. Base on these studies, we assign the reduction peak (II) at −0.75 V in the CV shown in Fig. 2 to the one-electron reduction of BQ to $BQ^{\bullet-}$. The radical anion $BQ^{\bullet-}$ is unstable and undergo chemical reactions in the presence of proton donors. HQ acts as a weak proton donor and can protonate $BQ^{\bullet-}$ [30,31] (Scheme 1(3)). The oxidation peak (III) in Fig. 2 is the reverse reaction of the reduction of $BQ^{\bullet-}$ to BQ (Scheme 1(2)).

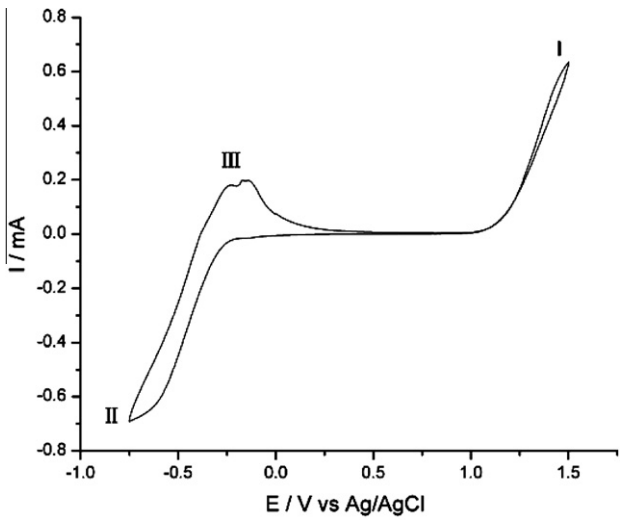

Fig. 2. Cyclic voltammetry of 50 mM HQ and 50 mM BQ in acetonitrile containing 0.1 M Bu_4NPF_6. Potential scan rate: 0.1 V/s. Flow rate: 100 μL/min.