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Detection of hydrogen peroxide produced at a liquid/liquid interface using scanning electrochemical microscopy

Fei Li, Bin Su, Fernando Cortes Salazar, Raheleh Partovi Nia, Hubert H. Girault *

Laboratoire d'Electrochimie Physique et Analytique, Ecole Polytechnique Fédérale de Lausanne (EPFL), Station 6, CH-1015 Lausanne, Switzerland

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ABSTRACT

Scanning electrochemical microscopy (SECM) was used to monitor *in situ* hydrogen peroxide (H_2O_2) produced at a polarized water/1,2-dichloroethane (DCE) interface. The water/DCE interface was formed between a DCE droplet containing decamethylferrocene (DMFc) supported on a solid electrode and an acidic aqueous solution. H_2O_2 was generated by reducing oxygen with DMFc at the water/DCE interface, and was detected with a SECM tip positioned in the vicinity of the interface using a substrate generation/tip collection mode. This work shows unambiguously how the H_2O_2 generation depends on the polarization of the liquid/liquid interface, and how proton-coupled electron transfer reactions can be controlled at liquid/liquid interfaces.

1. Introduction

The interface between two immiscible electrolyte solutions (ITIES), is well-suited to carry out proton-coupled electron transfer reactions [1–3], i.e., protons can be provided from the aqueous side, and lipophilic electron donors or acceptors can be located in the organic side. Furthermore, by controlling the polarization of the interface, it is possible to control the rate of either proton or electron transfer across the interface. Recently, we have investigated oxygen reduction by lipophilic donors in 1,2-dichloroethane (DCE) in contact with aqueous acid solutions and shown that the final product of this biphasic reaction was hydrogen peroxide (H_2O_2) in water [4].

Herein, scanning electrochemical microscopy (SECM) was employed for the detection of H_2O_2 generated at a water/DCE interface. SECM is a well-established technique with a key advantage of localizing and detecting interfacial electrochemical reactions [5] and has been widely employed to detect H_2O_2 produced by the oxygen reduction reaction (ORR) on various solid substrates [6–8]. In this work, the water/DCE interface was formed between a DCE droplet containing DMFc supported on a solid electrode and immersed in an acidic aqueous solution. The SECM tip was positioned close to the water/DCE droplet interface in the top aqueous solution. With this configuration, the polarization of the water/DCE interface to drive the proton transfer to allow oxygen reduction with DMFc on the organic side of the interface was found to be concomitant with the amperometric detection H_2O_2 by the SECM tip biased at a potential for the oxidation of H_2O_2. The different SECM parameters, including the tip-interface distance and interfacial Galvani potential difference, have been optimized for an efficient H_2O_2 detection.

2. Experimental

All chemicals were used as received. The organic supporting electrolyte was bis(triphenylphosphoranylidene) ammonium tetrakis(pentafluorophenyl)borate (BTPPATPFB) [9]. All aqueous solutions were prepared with Milli-Q reagent water (Millipore, > 18.2 MΩ/cm) and the DCE (Synthesis Grade, SDS) was saturated with water prior to use.

All the electrochemical measurements were carried out on a CHI 900 SECM (CH Instruments, Austin, TX) at room temperature with air-saturated solutions. A 5 μL DCE droplet was deposited on the surface of a 2 mm-diameter silver/silver tetrakis-(pentafluorophenyl)borate (Ag/AgTPFB) electrode [10], which was inserted into a Teflon cell and 1.5 mL aqueous solution was added on the top of it to overlap the droplet, a water/DCE interface was thus formed. The voltammograms at this interface were obtained in a three-electrode configuration (Fig. 1a) with the DCE droplet-covered Ag/AgTPFB electrode as the working electrode (WE), a Ag/AgCl wire and a Pt wire positioned in the aqueous solution as the reference electrode (RE) and counter electrode (CE), respectively. The electrochemical cell is depicted as follows:

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* Corresponding author. Tel.: +41 0 21 6933151; fax: +41 0 21 6933667.
E-mail address: hubert.girault@epfl.ch (H.H. Girault).

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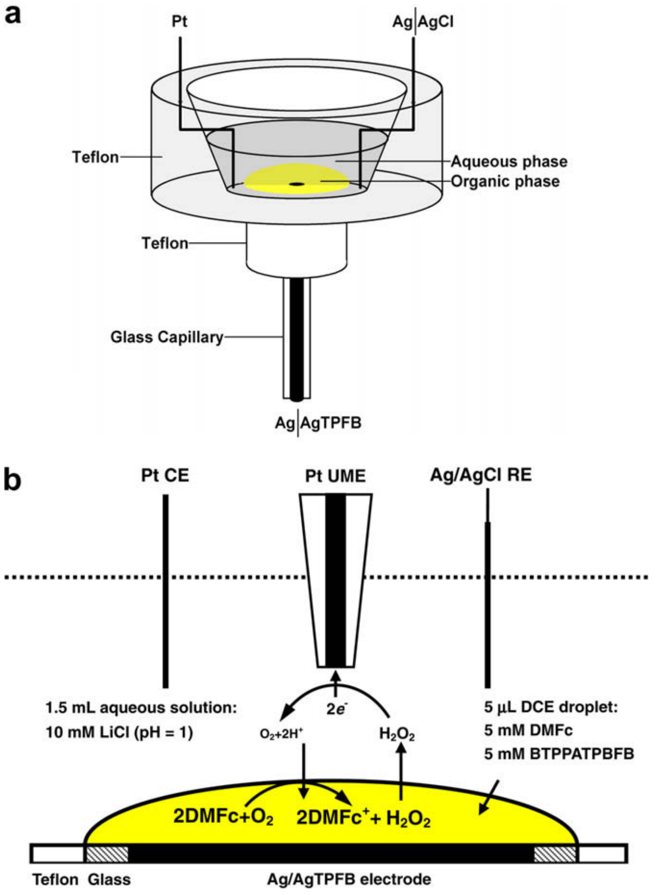

Fig. 1. Schematic diagrams of (a) a three-electrode cell and (b) its combination with SECM in a SG/TC mode.

$$\text{Ag}\left|\text{AgCl}\right|\begin{matrix}100\text{mM HCl}\\ 10\text{mM LiCl}\end{matrix}_{\text{(aqueous)}}\left\|\begin{matrix}5\text{mM DMFc}\\ 5\text{mM BTPPATPFB}_{\text{(DCE)}}\end{matrix}\right|\text{AgTPFB}|\text{Ag}$$

Cell 1

The Galvani potential difference across the water/DCE interface ($\Delta_o^w\phi$) was calibrated by the ion transfer of tetraethylammonium (TEA^+) [11]. The ionic current resulting from the transfer of cation from the aqueous to DCE phase is defined as a positive current.

The combination of SECM with the droplet was achieved by positioning a 25 μm-diameter Pt microelectrode tip [12] ($RG = r_g/a$ was about 3, where r_g is the radius of the glass insulator plus the radius a of the disk-shape microelectrode) on the top of the droplet, as illustrated in Fig. 1b. The Pt microelectrode was first brought to a known distance from the droplet on the basis of feedback current measurements. The tip current due to H_2O_2 oxidation was then monitored using the substrate generation/tip collection (SG/TC) mode [5], whereby the Galvani potential difference across the water/DCE interface was scanned or biased at a constant value through applying a potential at the substrate electrode and the tip potential was simultaneously scanned or fixed at a H_2O_2 oxidation potential. The tip and substrate potentials were independently controlled by the SECM bipotentiostat.

3. Results and discussion

Fig. 2a shows the cyclic voltammograms obtained at the water/DCE droplet interface supported on an Ag/AgTPFB electrode. The dotted curve represents the cyclic voltammogram in the absence of DMFc, which shows a potential window limited by the transfers of Cl^- and H^+ from aqueous to DCE phases on the negative and positive sides, respectively [11]. In Cell 1 including 5 mM DMFc in the DCE droplet, a current increase was observed at positive potentials (solid curve), which is similar to that observed at a water/DCE interface using a four-electrode setup [4] and the current increase stems from a proton transfer followed by O_2 reduction with DMFc to produce H_2O_2 (Fig. 1b). Moreover, an ion transfer voltammetric wave of decamethylferrocenium ($DMFc^+$) produced by O_2 reduction can be visualized in Fig. 2b, if extending the negative side of the potential window by replacing the aqueous supporting electrolyte anion Cl^- with more hydrophilic SO_4^{2-}. These facts prove that the oxygen reduction by DMFc can be realized with the present droplet methodology using a three-electrode setup, which also suggests a potential polarization range, namely 0.25 ~ 0.45 V, for the following SECM detection of H_2O_2.

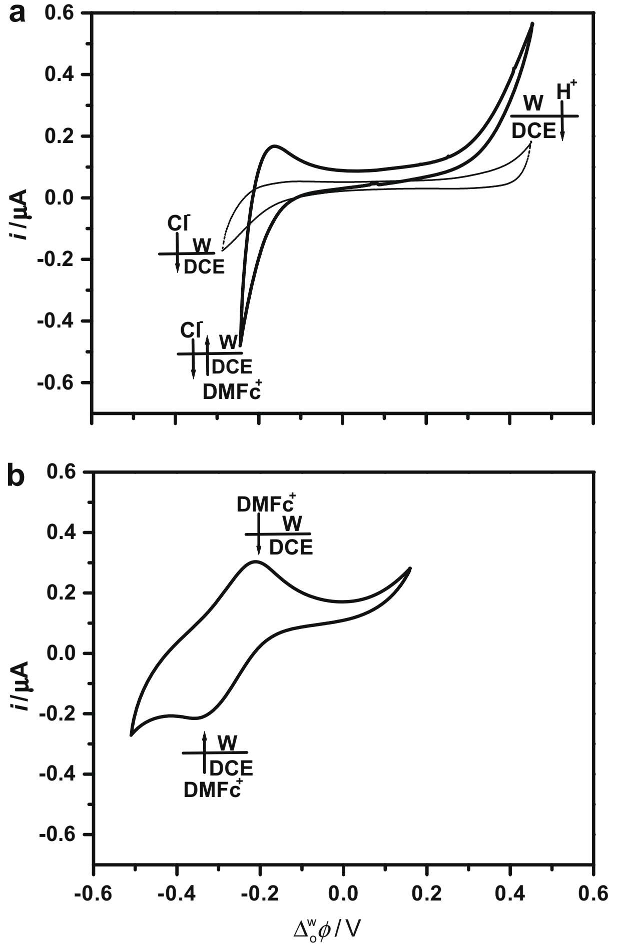

Fig. 2. Cyclic voltammograms measured with: (a) Cell 1 in the absence (dotted curve) and presence (solid curve) of 5 mM DMFc in DCE and (b) Cell 1 but using Li_2SO_4 (10 mM) and H_2SO_4 (pH 3) instead of LiCl and HCl in the aqueous phase. Scan rates 20 mV s^{-1}.

To perform the SG/TC measurement to detect H_2O_2 generated at the water/DCE interface, the tip potential and tip-interface distance must be optimized. First, the tip potential was determined as 0.6 V (oxidation potential of H_2O_2) by recording a linear sweep voltammogram (LSV) with the Pt microelectrode in an acid aqueous solution containing 0.1 mM H_2O_2 (figure not shown here). The tip-interface distance was determined by moving the Pt microelectrode slowly to the water/DCE interface with a tip potential (E_{tip}) of 0.6 V and the Galvani potential difference across the