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Exploring the applications of a pulsating jet hydrodynamic modulated voltammetric (HMV) system – Electrochemistry of nanostructured Pt electrodes and trace analysis

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ABSTRACT

The electrochemistry of nanostructured electrodes is investigated using hydrodynamic modulated voltammetry (HMV). Here a liquid crystal templating process is used to produce a platinum modified electrode with a relatively high surface area (Roughness factor, Rf = 42.4). The electroreduction of molecular oxygen at a nanostructured platinum surface is used to demonstrate the ability of HMV to discriminate between Faradaic and non-Faradaic electrode reactions. The HMV approach shows that the reduction of molecular oxygen shows considerable hysteresis correlating with the formation and stripping of oxide species at the platinum surface. Without the HMV analysis it is difficult to discern the same detail under the conditions employed. In addition the detection limit of the apparatus is explored and shown, under ideal conditions, to be of the order of 45 nmol dm^{-3} employing $[Fe(CN)_6]^{4-}$ as a test species.

1. Introduction

It is often the case, particularly for catalytic electrode reactions, that high surface area electrodes hold considerable benefit [1–5]. However, increasing the surface area of an electrode, while enhancing the catalytic reaction in question, will also increase background processes associated with the surface, double layer or oxide formation steps etc. [6–8]. This imposes some limitations in the number of electrochemical techniques which are able to interrogate the reactions occurring. This is particularly true if dynamic experiments are advantageous (for example those where it is desirable to scan the potential of a high surface area electrode rapidly). Here we show how hydrodynamic modulated voltammetry [9,10] (HMV) may be used to overcome some of these difficulties. This is a direct result of HMV offering the advantage of discrimination between solution phase Faradaic processes and non-Faradaic or surface bound Faradaic processes [11–14]. In particular we use HMV to investigate the important electrochemical reduction of molecular oxygen at a nanostructured [15] Pt electrode.

The fabrication and analytical applications of novel high surface area mesostructured microelectrodes produced by the 'true liquid crystal templating' technique have been widely reported, and these materials have been an area of interest for many authors [16–20]. Clearly the intrinsic high surface area of such electrodes can offer a significant advantage during the study of surface limited processes. However, the high surface areas can also be a disadvantage given the large currents associated with the electrochemical double layer, oxide and hydride processes. Consequently large background signals are associated with these electrodes. For example Birkin et al. showed that modified Pt microelectrodes, although catalytically interesting for oxygen reduction, required relatively slow sweep rates (of the order of 2 mV s^{-1}) in order to observe the appropriate voltammetry in the absence of detrimental distortion [1].

The modulation of flow to investigate the HMV response of a system is not new. There are many examples of this technique within the literature. In brief they can be divided into two basic strategies. In the first, flow to the electrode can be modulated in a periodic manner. This may involve modulation of the rotation rate of a rotating disk electrode or alteration of the flow to an electrode by 'chopping' or oscillating the flow in a suitable manner [13,14,21,22]. In the second, the modulation of the signal required is generated by the mechanical oscillation of an electrode [11,12,23]. Each of these systems has its advantages (for example the RDE system has known analytical solutions that may be applied to the system) and disadvantages (limited frequency regime and mechanical limitations) [11,24–27]. Here we employ an oscillating jet as the method of hydrodynamic modulation. This system produces an HMV signal from a stationary jet/electrode arrangement. Here the system relies on positioning an electrode above a

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pulsating jet. In this case a small mechanical oscillation of a large membrane produced the desired periodic fluid motion. Amplification of this fluid motion was obtained using a conical section which enhances fluid flow at the jet orifice [28]. This system was shown to be reproducible and suitable for HMV studies. One major advantage of this system is that it is relatively simple and can be deployed for a large range of different electrode substrates. This communication shows how such an approach may be applied to a high surface area electrode with significant catalytic interest and explores the detection limits achievable for a polished Pt interface.

2. Experimental

The general experimental arrangement used in this work has been reported previously [28]. Briefly this consisted of a ~3.5 cm radius membrane attached to the base of an inverted funnel. The funnel neck is then pulled into a 2 mm diameter jet orifice. In order to improve upon the previous performance of the system, the membrane was attached to a piston or disk like structure. This was designed to ensure complete motion of the membrane. A mechanical shaker (a Model V4, Signal Force, Data Physics Ltd.) was attached to the centre of the piston which was glued to a viton (500 μm thickness, Altec Products Ltd.) sheet which replaced the acetate membrane described in an earlier communication [28]. This sheet was attached to both the base plate and the inverted funnel to act as a flexible seal. A mechanical coupling incorporating a single axis accelerometer (Model 3100B, Dytran Instruments, Inc., sensitivity 99.3 mV g^{-1}) was included in order to access the magnitude of motion of the piston. The accelerometer signal was conditioned with an amplifier (Model 4105C, Dytran Instruments, Inc.) and recorded on an oscilloscope (Techtronixs, TDS 2014, 1GS/s, 100 MHz). The shaker was driven by an amplifier (Signal Force 30 W Power amplifier, Model PA 30E, Data Physics Ltd.) which was in turn supplied by a function generator (TGA12101 100 MHz Arbitrary Waveform generator, TTi Ltd.). In all cases the frequency of oscillation of the membrane, and hence jet, was 16 Hz. The electrodes employed (Pt, 0.5 mm diameter) were fabricated in-house and were sealed in glass (diameter 5.0 mm diameter). Positioning of the electrode with respect to the jet orifice was controlled using an XYZ stage (Zaber, 60 mm travel, resolution 0.1 μm, TLA 60A actuators connected to TSB 60-M stages). Data analysis (lock-in experiments) and positioning was attained through in-house written software (VB6) [29].

For flow visualisation, a 50 μm diameter Pt wire (Advent RM) was stretched across the neck of the flow apparatus. Here an inverted funnel with the same jet dimensions was employed. However, the tip of the jet was cut off, the Pt wire stretched across followed by reattachment of the tip of the jet. Electrochemical hydrogen bubble generation was driven by a DC power supply and imaged using a Photron APX RS high-speed camera.

The electrodes were hand polished to a mirror like finish, in a conventional manner, using alumina powder slurries (Struers, alumina 0.3 μm diameter) on microcloth (Buehler) polishing pads. A three electrode system (using a mercury/mercurous sulphate, MMS, or Ag reference and Pt counter electrodes) was employed in the experiments. Electrochemical data was acquired on an in-house constructed potentiostat interfaced to a PC through an ADC card (Computer boards type PCI-DAS1602/16). Software, to determine either conventional cyclic voltammetry or the HMV signal, was developed in-house. A pump (TCS, micropump, Model M100-S) was also included in the experimental arrangement (note that this was only used for the titration experiments). The pump employed in the titration experiments was used to mix the dead volume of the lower conical section of the cell with the upper compartment and hence ensure an even concentration of the titrant throughout the cell after each appropriate addition into the upper chamber.

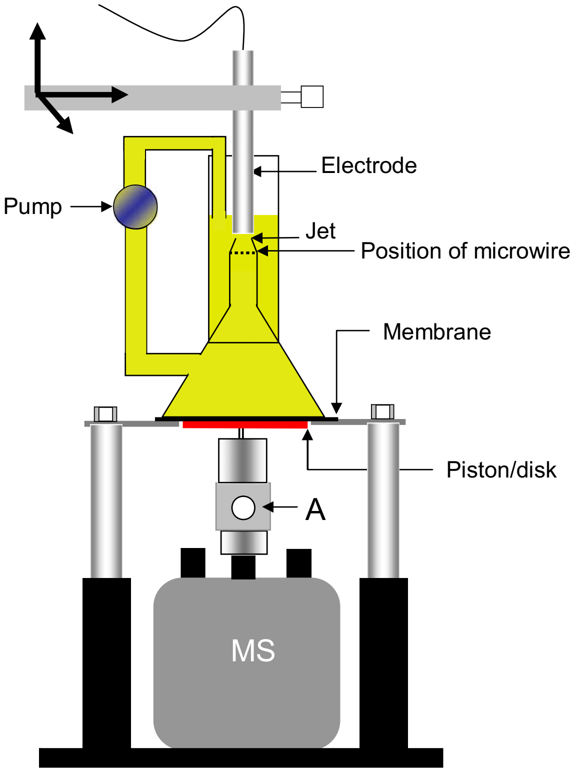

Fig. 1. Schematic representation of the HMV flow cell employed in this work adapted for titration experiments. Here a metal piston is added to the membrane arrangement reported previously [28]. An accelerometer (A) was included between the minishaker (MS) and the piston. The position of the electrode with respect to the orifice of the jet was controlled by an XYZ stage. Note the position of the microwire for the flow visualisation experiments is included in the figure.

A schematic of the improved flow apparatus including the position of the pump and the microwire (used for high-speed tracking experiments) is shown in Fig. 1.

Solutions were prepared using a Purite Select Fusion 160 (Ondeo) water purification system (resistivity typically >15 MΩ cm and a TOC <10 ppb). H_2SO_4 (98%, Fisher-Scientific), $Sr(NO_3)_2$ (99 + %, Sigma–Aldrich) and $K_4[Fe(CN)_6]$ (LRG, Fisher-Scientific) were used as received.

The Pt nanostructured electrode was deposited on a 0.5 mm diameter Pt disk electrode which had been previously electrochemically cleaned by cycling between +0.7 and −0.65 V vs. MMS at 200 mV s^{-1} in a 1 mol dm^{-3} sulfuric acid solution. The preparation of the mesoporous electrodes followed the procedure previously described [15,30]. Electrodeposition of the platinum films was achieved under potentiostatic and thermostatic control, the potential was stepped from +0.2 to −0.5 V vs. MMS. After deposition (9.12 mC), the electrode was removed from the cell and allowed to soak in deionised water, which was regularly replaced in order to remove the surfactant. Voltammetry of the electrode in sulfuric acid was used to determine the roughness factor (187 immediately after preparation) of the electrode as described previously [15,30].

3. Results and discussion

Fig. 2 shows two images gathered from high-speed camera investigations of the new 'piston cell'. Here a 50 μm diameter Pt