Dual-electrode measurements in a meniscus microcapillary electrochemical cell using a high aspect ratio carbon fibre ultramicroelectrode

CrossMark

Thomas S. Miller, Julie V. Macpherson, Patrick R. Unwin *

Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK

A B S T R A C T

The meniscus-based microcapillary electrochemical method (MCEM) allows electrochemical measurements to be made quickly and easily at a wide range of materials, simply by connecting up the sample of interest as a working electrode and bringing a capillary containing an electrolyte solution and quasi-reference/counter electrode into meniscus contact. In this work, microcapillary-based electrochemical methodology is advanced by introducing a very high aspect ratio carbon fibre ultramicroelectrode (CF-UME) allowing generation/collection and shielding (redox competition) measurements to be made. The experimental concept is demonstrated with the outer sphere (ferrocenylmethyl) trimethylammonium ion ($FcTMA^{+/2+}$) redox mediator on a single walled carbon nanotube (SWNT) network. It is then used to investigate electrochemical reactions on a complex electrode, i.e. a SWNT forest, which is not easily investigated using traditional techniques that would require the electrode material to be physically encapsulated. The technique is most powerful when used to probe the different mechanistic pathways of the oxygen reduction reaction (ORR). This aspect is illustrated through studies on platinum, glassy carbon and SWNT forest electrodes. By platinising the CF-UME, the electrode can be used as a local sensor for the intermediate H_2O_2 and the O_2 reactant, and it is possible to track the evolving consumption of these species near the working electrode during voltammetric measurements.

© 2014 Published by Elsevier B.V.

1. Introduction

Dual working electrode systems, as exemplified by rotating ring disk electrodes (RRDEs) [1], double channel electrodes [2], and several ultramicroelectrode (UME) formats [3–5] enhance the information content of a voltammetric experiment, either by using one (collector) electrode to detect the products and/or intermediates at a primary (generator) electrode or by setting the two electrodes in competition with each other, as in shielding [1] or equivalently, redox competition measurements [6,7]. We consider both types of measurements in this paper, but focus on the generator–collector (G/C) format.

In G/C measurements, a chemical species is produced at one working electrode (generator) by an n-electron redox reaction (e.g. $A + ne^- \rightarrow B$). A proportion of this species (B) is transported to a second working electrode where a reaction occurs, which may be the reformation of the initial species ($B \rightarrow A + ne^-$) or the production of a third species ($B \pm ne^- \rightarrow C$). Transport between the generator and collector electrodes occurs by diffusion [8] or convection/diffusion [8]. This approach has been used to probe reactions as varied as the oxygen reduction reaction (ORR) [9–12], reactions including coupled chemical processes [3,13–15] and trace level analyte detection [16] among many possible examples. G/C measurements have tended to involve the use of rather complicated experimental set ups, highlighted above, e.g. flow cells [3,10,11,17], the RRDE [18–20], scanning electrochemical microscopy (SECM) [13,14,21–23] or specialised electrodes [24]. This can restrict the type of electrode materials (and electrode preparations) that are open to study, especially for electrode materials that cannot readily be encapsulated in these formats.

The MCEM expands the range of electrode formats that can be studied without the need for electrode material encapsulation. Measurements are made by landing the meniscus of a solution-filled capillary, with a micrometer-scale aperture, on an electrode surface [25–29]. As the electrochemical cell is limited to the meniscus footprint, this type of approach has proven useful in areas where multiple measurements are to be made in different locations on a surface, for example in localised corrosion studies [30] or for the electrodeposition of metal nanoparticles (NPs) [25,27].

It also allows the user to make electrochemical measurements at targeted areas of a surface [26,28]. Importantly, this method negates the need for post-processing of electrode materials, e.g. through the use of lithography or encapsulation, saving time and ensuring the surface is free from any leftover residues which may hinder electrode processes [26].

In this work we demonstrate a simple method to combine the benefits of the MCEM with the analytical power of dual electrodes, through the use of very high aspect ratio carbon fibre ultramicro-electrodes (CF-UME). These can be readily produced, inserted into the capillary meniscus and used as a means of monitoring the processes at an electrode material targeted by the microcapillary cell, as we have demonstrated herein, through a variety of exemplar studies.

2. Materials and methods

2.1. Chemicals and reagents

The CF-UME was prepared by fully insulating a carbon fibre (CF) with polyoxyphenylene, via electropolymerisation, after which the end was removed with a razor blade, revealing the UME. The electropolymerisation solution consisted of methanol (99.5%, Fisher scientific) with the addition of phenol (99.0%, BDH laboratory supplies), 2-allyl phenol (98%, Aldrich), 2-butoxyethanol (99%, Lancaster), Triton X-505 (70%, Acros organics). CF-UMEs were modified with platinum NPs by electrodeposition from 5 mM potassium hexachloroplatinate (K_2PtCl_6, 99.99%, Aldrich) in 0.5 M $HClO_4$ (70%, Acros organics). Electrochemical measurements utilised the (ferrocenylmethyl) trimethylammonium ion ($FcTMA^+$), prepared as the PF_6^- salt via metathesis of $FcTMA^+I^-$ (99%, Stern Chemicals Ltd., UK) with $Ag^+PF_6^-$ (99.5%, Stern Chemicals Ltd., UK). This was dissolved in aqueous supporting electrolyte containing 50 mM KCl (>99%, Aldrich). The ORR (Pt and glassy carbon substrate electrodes) was investigated in a solution containing 0.5 M H_2SO_4 (96%, Aldrich), whereas on a SWNT forest the ORR was investigated using aqueous 50 mM KCl. All solutions were made using 18.2 MΩ cm (at 25 °C) Milli-Q (Millipore Corporation) deionised (DI) water.

2.2. Growth of SWNT networks and forests

SWNT networks were grown by catalysed chemical vapour deposition (cCVD) directly onto Si/SiO_2 (IDB Technologies Ltd, n-type, 525 mm thick with 300 nm of thermally grown oxide) from Fe NPs deposited from ferritin (Aldrich). SWNT forests were also grown by cCVD on silicon wafers (n-type, 525 μm thick, IDB Technologies Ltd, UK) which had been sputtered (Plassys (MP 900S)) with a 10 nm aluminium layer, which was oxidised in an oxygen plasma (K1050X plasma asher, Emitech, UK; O_2 pressure 6×10^{-1} mbar) and sputtered with cobalt (1 kV, 10 mA, 180 s; Quorum Technologies SC7640 sputter coater, fitted with a Co target, 99.95%, Testbourne Ltd., UK). Specific details of the cCVD growth and characterisation of these electrode materials have been given previously for SWNT networks [31] and forests [29,32].

2.3. Fabrication of CF-UMEs and their modification with platinum

The fabrication method used to produce polymer coated, high aspect ratio CF-UMEs has been reported previously [33]. Briefly, a ~2 cm length of 8 μm diameter carbon fibre (Goodfellow Ltd.) was electrically connected to a copper wire using conductive silver paint (RS) leaving half of the fibre protruding from the end. This was sealed in a glass capillary and the carbon fibre was coated in polyoxyphenylene via electropolymerisation (4 V vs. Ag/AgCl quasi-reference/counter electrode (QRCE), 30 min) and annealed

at 150 °C for 30 min. This produced an excellent insulating coating. The UME surface was exposed by removing the end of the coated fibre by cutting with a scalpel.

The CF-UME was modified with Pt by immersion in 5 mM K_2PtCl_6 in 0.5 M $HClO_4$. Potential cycling (50 mV s^{-1}) between 1.3 V and −0.05 V (vs. Pd-H_2 QRCE) was employed to drive Pt nucleation and growth for 10 cycles.

2.4. Microcapillary electrochemical method (MCEM)

As reported previously [25–27], with MCEM a borosilicate glass capillary (Harvard Apparatus, borosilicate glass, 1.2 mm O.D., 0.69 mm I.D.) was pulled (Sutter instruments P2000 laser puller) and polished flat to reveal an opening (50–100 μm diameter, measured accurately). After cleaning with DI water, argon was flowed through the microcapillary while the end was submerged in dichlorodimethylsilane (Fisher Scientific), which rendered the outer capillary surface hydrophobic. The capillary was then filled with the aqueous solution of interest and fitted with a QRCE (either AgCl coated wire or Pd-H_2 [34]), before it was manually approached towards the electrode surface to be studied using $x-y-z$ micropositioners (Newport 433 series). The capillary motion and meniscus landing was monitored using a camera (Pixe-LINK PL-B776U). Electrochemical measurements were made using a CHI instruments model CHI730A potentiostat.

2.5. Dual-electrode measurements

To perform dual-electrode measurements in the meniscus of the microcapillary, the CF-UME was mounted on a second $x-y-z$ micropositioner using a custom capillary holder to enable it to be positioned at a 45° angle with respect to the surface. Once the meniscus from the microcapillary had formed on the surface, the CF-UME was carefully inserted from the side (Fig. 1a–c). In a previous study using this type of CF-UME, the electrode was pressed against the surface under investigation until it deflected, after which it was slightly withdrawn with a micrometer to allow high precision positioning close to the substrate [33]. In this study, the CF-UME was inserted into the capillary meniscus which delimited the surface/CF-UME distance to be in the range 15–30 μm. The capillary radius (R_c) has been found to be a good approximation for the height of the meniscus from the surface both in this investigation and previously [26]. This means that the maximum possible height of the UME from the surface was R_c, or closer. In the main, electrochemical measurements were made by scanning the potential of the surface (working electrode 1) while the UME (working electrode 2) was held at a constant potential to act as a collector of a product or intermediate of the substrate (generator) electrode reaction. In some experiments 'shielding' measurements [1] were carried out where the UME and substrate electrodes competed for the same redox active species in bulk solution. In this case the UME was held at a potential to consume that species at a diffusion-limited rate, while the substrate electrode potential was scanned from a value where no electrode reaction occurs to one where it consumed the solution species at a diffusion limited rate.

3. Results and discussion

Fig. 1(d) shows a typical cyclic voltammogram (CV) for the one-electron oxidation of $FcTMA^+$ recorded at an 8 μm diameter CF-UME (Fig. 2). This CV shows the wave shape for fast electron transfer (ET) at a UME i.e. it shows steady-state behaviour and exhibits reversible ET ($|E_{3/4}-E_{1/4}|$ = 59 mV [35], where $E_{3/4}$ is the potential at which the current is ¾ of the diffusion limited value and $E_{1/4}$ is the potential at which the current is ¼ of the limiting