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Carbon–epoxy electrodes: unambiguous identification of authentic triple-phase (insulator/solution/electrode) processes†

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A novel electrode consisting of crystals of an electroactive organic solid immobilised into a carbon–epoxy electrode has been subjected to insonation, which facilitates the clear characterisation of triple-phase processes occurring at the insulator/solution/electrode interface.

The voltammetry of solids has seen much recent impetus stimulated by the pioneering work of Scholz *et al.*[1] who 'mechanically' or 'abrasively' attach solids to the surface of electrodes. This has permitted the analytical voltammetry of a whole range of compounds[1] as well as the study of ion insertion. Typically the solid under study is immobilised by embedding it in an electrode surface such as paraffin-impregnated graphite,[1] basal plane pyrolytic graphite,[2–4] pencil-lead,[5] metal electrodes (usually platinum[6] and gold[3,7] or boron doped diamond surfaces.[8] All these require abrasive immobilisation of the solid indicator species but can lead to the crushing of crystals of certain samples. After immobilisation the electrochemical oxidation and reduction can occur by two mechanisms: (a) *via* electron transfer at the triple-phase boundary formed between the electrode, the solid and the solution in which the former are immersed or (b) *via* the embedded solid dissolving into the solution and subsequently reacting on the electrode interface. The voltammetric distinction between these two processes is difficult and would ideally employ hydrodynamic approaches. However, this is impossible since the solid is typically only 'loosely' immobilised onto the electrode surface and once placed into a conventional flow cell or on a rotating disc the hydrodynamic nature of the system would shear the solid from the electrode surface. In this note we advocate the use of carbon–epoxy composite electrodes as a means of solving such problems; the solid is effectively 'glued' into place so permitting hydrodynamic interrogation and hence unambiguous mechanistic resolution.

In the following a carbon–epoxy composite electrode is reported and studied under both stationary and hydrodynamic conditions. Voltammmetric data is compared with that obtained from an immobilised basal plane pyrolytic graphite (BPPG) electrode under analogous conditions. An unambiguous assignment of a triple-phase boundary process is made.

The chemical selected for study was *N*,*N*′-diphenylphenylenediamine (DPPD) which is of interest in the detection of thiols and hydrogen sulfide.[9]‡ The electrochemistry of DPPD has been examined previously at platinum electrodes whereby the oxidation is shown to undergo a two-electron electrochemically reversible process.[10,11] The resulting voltammetric behaviour is analogous to that of the well known aniline/polyaniline electrochemistry.[10]

The manufacture of carbon–epoxy electrodes is described first; in order to ascertain the optimal current of the DPPD indicator species the ratio of carbon powder and DPPD was varied and a cyclic voltammogram in 0.1 M HCl (scan rate = 100 mV s^{-1}) of each electrode recorded. The optimal response was for a weight to weight ratio for epoxy : carbon : DPPD of 1 : 1.6 : 1.4, which provided a clear voltammetric response characteristic of DPPD oxidation without over-compromising the conductivity of the electrode. The electrodes were initially polished with sandpaper, followed by alumina of decreasing particle size down to 1 μm. The reproducibility of this polishing technique was examined by repeated measuring of the oxidation peak current obtained from a cyclic voltammogram (0.1 M HCl) of an electrode after polishing as described above. The oxidation peak currents were found to be 565 ± 41 μA giving a standard error of 7.3%, showing that this process results in the generation of a fresh reactive surface capable of undergoing the same chemistry and producing the same signal as the previous exposed surface, and is thus one of the main advantages inherent in the modified carbon–epoxy electrode. The regeneration of the surface allows the device to be used as a single shot device

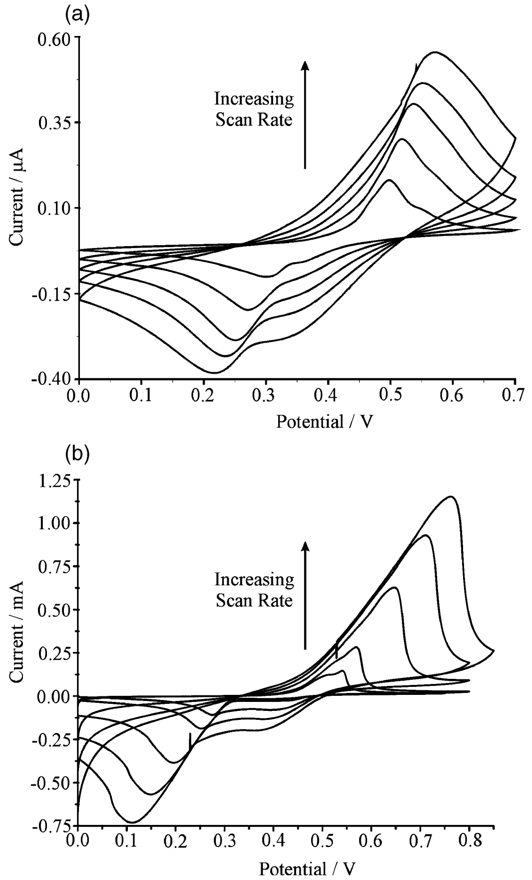

Fig. 1 The effect of varying scan rate (5–200 mV s^{-1}, 0.1 M HCl) on the voltammetric response of (a) the DPPD modified carbon–epoxy (weight to weight ratio; epoxy : carbon : DPPD = 1 : 1.6 : 1.4) and (b) a BPPG electrode abrasively immobilised with DPPD.

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† Electronic supplementary information (ESI) available: AFM image of the carbon–epoxy electrode. See http://www.rsc.org/suppdata/cc/b2/b201506b/

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Table 1 The effect of ultrasound on the peak currents (μA) obtained from the two immobilisation processes

Electrode Type	Peak current before ultrasound	After 5% ultrasound (310 W cm^{-2})	After 10% ultrasound (310 W cm^{-2})	After 15% ultrasound (310 W cm^{-2})
Carbon epoxy	619 ± 10	601 ± 6	656 ± 10	709 ± 15
Immobilised BPPG	1930 ± 60	1390 ± 99	N/A	N/A

capable of being mechanically polished such that it can be used again. The voltammetric responses of the DPPD electrode in a solution containing 0.1 M HCl at various scan rates are detailed in Fig. 1(a). These reveal an oxidation wave at + 0.61 V (*vs.* SCE, 100 mV s^{-1}) and a corresponding reduction wave at + 0.22 V (*vs.* SCE, 100 mV s^{-1}), showing that there is solid DPPD present in the DPPD carbon–epoxy electrode which can be oxidised easily to form the di-cation species either *via* chloride ions inserting through the triple-phase boundary to restore neutrality in the charge or otherwise by the dissolution of DPPD followed by conventional voltammetric discharge.

Next the electrochemical response of the DPPD electrode was examined under the 'extreme' hydrodynamic conditions of insonation. Cyclic voltammograms (0.1 M HCl, 100 mV s^{-1}) obtained at the carbon–epoxy electrode were recorded before, after and during insonation of the system. The voltammetric responses were analogous to those observed above under 'silent' conditions even after ultrasound of 310 W cm^{-2} (5–15%) was applied to the electrode. The magnitude of the oxidation and reduction peak currents were not affected and voltammetric scans taken under insonation produced no change in the voltammetric waveshape. This is confirmed by analysis of the peak current data; Table 1 compares the average oxidation peak current obtained before and after ultrasound for the carbon epoxy electrode which reveals a slight increase in the peak current attributable to electrode activation due to the removal of used species from the electrode surface. Insonation has been shown to produce extreme levels of mass transport (with diffusion layers as thin as 0.7 μm in certain cases):[12] the insensitivity of the voltammetric response clearly rules out the dissolution/oxidation mechanism (where a substantial reduction of the peak current would be expected) so supporting the triple-phase boundary alternative.

Atomic force microscopy was utilised as a means of probing any surface porosity of the carbon–epoxy electrode; the results (see ESI†) revealed a non–porous surface with globular deposits of carbon interspersed amongst the epoxy binder.

In order to validate the voltammetry at the carbon–epoxy electrode, DPPD was abrasively attached to a basal plane pyrolytic graphite (BPPG) electrode[2,3] by gently rubbing the DPPD onto the electrode surface using fine filter paper, with the mass of the immobilised DPPD species recorded. Cyclic voltammetric results obtained for differing scan rates (5–200 mV s^{-1}, 0.1 M HCl) are detailed in Fig. 1(b). It can be seen that the voltammetric response obtained shows a close similarity to that observed in Fig. 1(a) with the DPPD carbon–epoxy electrode. This concurs with the fact that there is solid DPPD present in the DPPD carbon–epoxy electrode that can be oxidised easily at the surface of the electrode.

As before the robustness of the immobilized layer was examined under ultrasound. The corresponding peak current data obtained are compared in Table 1. These reveal that unlike for the carbon–epoxy electrode the peak current drops significantly after ultrasound is applied to the electrode surface and can in this case be attributed to the removal of the DPPD species from the electrode surface.

These results reveal how the carbon–epoxy electrode allows a clear strategy for the identification of the involvement of the triple-phase boundary in solid state voltammetric experiments.

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Notes and references

‡ *Experimental*: all reagents were obtained from Aldrich and were of the highest grade available and used without further purification. All solutions and subsequent dilutions were carried out using deionised water from an Elgastat (Elga, UK) UHQ grade water system with a resistivity of not less than 18 MΩ cm. All results were obtained at a temperature of 22 ± 2 °C. Electrochemical measurements were recorded using an Autolab PGSTAT 30 computer controlled potentiostat (Eco-Chemie, Netherlands) with a standard three-electrode configuration. A modified carbon–epoxy (see above) or basal plane graphite (BPPG) electrode acted as the working electrode. Platinum wire wound into a spiral provided the counter electrode with a saturated calomel reference electrode (SCE, Radiometer, Copenhagen) completed the cell assembly.

Sonoelectrochemical investigations were conducted using a 20 kHz transducer with a 3 mm stepped titanium probe placed 8 mm directly above the face of the working electrode. The ultrasonic intensity was determined calorimetrically according to the procedure of Margulis *et al.*[13] to be 310 W cm^{-2} (5–15%) The probe was electrically isolated from the test solution through the combined use of a PTFE spacer and connecting screw.

Surface Morphology was obtained using a Topometrix TMX 2010 Discoverer atomic force micrscopy (AFM) operating in the tapping mode with SFM probes (Type 1520-00) and a 75 μm scanner (Type 5590-00).

Electrode construction: The constituents involved in the making of the electrode were carbon powder (1–2 μm, Aldrich) and epoxy (12% hardener Durcisseur MA2). These were mixed thoroughly, forced into a plastic pipette tip (4 mm) in which a bare wire was wound to produce the electrical connection and left to set for 24 h to form a hard and durable electrode substrate. A series of electrodes were fabricated in which the proportions of carbon to epoxy were varied in order to find the best composition in terms of both durability and conductivity. In order to obtain information on the best carbon : epoxy ratio the resistance from the attached wire to the electrode surface was initially measured and cyclic voltammograms illustrating the electrode response to the ferrocyanide/ferricyanide (1 mM, pH 7 aqueous phosphate buffer) redox couple were recorded. The resistance data showed that the least resistive carbon : epoxy weight to weight ratio is 4 : 1. However, it was observed that the mechanical integrity was compromised and the substance was too fragile to be useful as an electrode substrate, therefore a 3 : 1 weight to weight ratio of carbon : epoxy was used throughout the rest of the studies.

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