The aqueous electrochemistry of carbon-based surfaces –
investigation by scanning tunneling microscopy

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Abstract. Electro-oxidation of carbon-based materials will lead to conversion of the solid to
CO₂/CO at the anode, with H₂ being produced at the cathode. Recent voltammetric
investigations of carbon nano-tubes and single crystal graphite have shown that only edge sites
and other defect sites are electrochemically active. Local oxidation of diamond-like carbon
films (DLC) by an STM tip in moist air followed by imaging allows correlation of
topographical change with electro-chemical conditions and surface reactivity. The results may
have implications for lithographic processing of carbon surfaces, and may have relevance for
electrochemical H₂ production.

1. Introduction
Carbon-based solids, ranging from amorphous graphite to crystalline diamond, are used widely in
industry. Diamond-like carbon (DLC) also forms the basis for many advanced applications (e.g.,
coatings, high temperature electronics, etc.) [1]. Boron-doped DLC has attracted interest as an electrode
surface [2,3]. Carbon-based structures, inspired by C₆₀ nanotubes and their derivatives, will figure in
future nano-technologies. A recent study has investigated the electro-oxidation of coal-slurries [4] in
the context of enhanced efficiency of H₂ – production.

The surface chemistry and electro-catalytic properties of carbon nanotubes as compared with other
carbon-based electrodes have attracted interest in recent times due to reported attractiveness as sensors
[5-8]. The use of voltammetry as the principal, non-local, tool is the common theme in most electro-
chemical investigations. Thus any interactions that lead to modifications of carbon surface can only be
inferred.

Scanning tunneling microscopy (STM), with the probe tip acting as a local traveling electrode, is an
ideal tool for investigating the structural and topographical response of carbon surfaces to
electrochemical conditions.

It has been shown [4] that electrochemical gasification of coal/water slurries can generate CO₂ and H₂
at the anode and cathode, respectively. Elsewhere we show that the mechanism constitutes a method for
lithographic patterning of DLC [9]. In the case of conducting DLC the film exhibits conversion to
gaseous species, either in bulk water or when the probe tip is located inside an adsorbed aqueous film.

The likely respective reactions can be written as

Anode (oxidation): DLC + 2H₂O = 4H⁺ + 4e⁻ + CO₂      (1)

Cathode (reduction): 4H₂O + 4e⁻ = 2H₂ + 4OH⁻      (2)

where the overall reaction can be written as

DLCₙ⁺(s) + 2H₂O(l) → CO₂(g) + 2H₂(g)      (3)

2. Experimental details
Electrically conductive IB-DLC films were produced by an ion beam assisted (IB) variation of the chemical vapour deposition route. Specimens from the same route have been investigated in earlier studies [10, 11]. High density and purity polycrystalline graphite originated with the UK reactor research program. Highly oriented single crystal pyrolytic graphite (HOPG) was obtained from a supplier of SPM instrumentation. Clean a-b faces were prepared by cleavage with adhesive tape.

Analysis was carried out with a JEOL JSTM-4200 instrument. It has the attribute of allowing analysis within a bell jar; the ambient can be controlled, ranging from \(10^{-3}\) Pa vacuum to atmospheric pressure with known relative humidity (R.H.), monitored by a hygrometer placed within the analysis envelope. The sample can be biased with respect to the tip while scanning in various modes. Etched Pt/Ir tips were used for STM lithography and analysis, and constituted the cathode during electrochemical exposure. In some cases the outcomes of electrochemical exposure was confirmed by SEM imaging.

XPS survey and detailed scans were carried out with steps of 1.0 and 0.1 eV, and for pass energies of 100 and 20 eV, respectively. Angularly resolved analysis was carried out in order to confirm that oxygen was confined to the surface.

Arrangements for local and non-local electrochemical exposure are shown in figure 1. The tip is shown in the local electrode mode inside the adsorbed layer of moisture (solid line), and non-local mode (in excess of 100 \(\mu\)m distant in bulk water from the surface) (broken line). In the former case the approach of the tip to the surface was made in the constant current mode. Once ‘contact’ is made with the adsorbed fluid phase, the meniscus bridge forms part of the circuit. The Faraday current will then dominate (the STM will de facto remain in a constant current mode, with the tip-to-surface distance defined by the length of the bridge). The bridge will promote localization even though the tip will be well outside the tunnelling range. In the latter case the fluid ‘cell’ consisted of a droplet of distilled and deionised water. Due to the high Faraday current the current sensing circuit will saturate even at a low bias voltage. The exposure will be delocalised, and no estimate can be made for the delivered power. The outcomes of experiments with the tip as a non-local electrode are of principal interest as a tool for masked lithography [9]. The field of view was scanned subsequent to electrochemical exposure in order to detect alteration. The sample was biased positively during lithographic alteration. Generation of gas bubbles was observed optically, but the close proximity of the electrodes precluded collection of gas samples from the separate electrodes and identification of the gaseous species.

3. Results

3.1. Electrochemical exposure

Images are shown in figure 2a and b for mask-less pattern generation in the electrochemical exposure mode with the STM tip as a local traveling electrode. An uneven distribution of reactive surface sites is apparent. Imaging by SEM at an angle of 76° (not shown), showed that the pit shape and size could be described by a box of dimensions 3x2x0.1 \(\mu\)m\(^3\). The spatial resolution obtainable by electro-oxidation
in the local mode is illustrated in figure 3. Similar results obtained by STM [12] and contact mode AFM [11] have been reported previously, although the role of adsorbed moisture was then not appreciated.

Figure 2a. STM image of electrochemical patterning of a DLC surface. The array of pits was generated at 60% RH, at 8V and 6 nA. The dwell time at each pit was 1 s.

Figure 2b. SEM image of the array of pits. Regions of low reactivity are evident, and are correlated with features in the STM image. Field of view is ca. 100x70 μm².

Figure 3a. STM image of line of pits 20 nm apart. Conditions: 78% R. H., 4.5 V bias, 10 nA tip current, and 10 ms exposure per pit.

Experiments similar to those in figures 2 and 3 were undertaken for HOPG and graphite. The results were consistent with a-b planes being electrochemically inert, and with edge sites being reactive [5,6].

3.2. XPS analysis.

XPS analysis was undertaken to gain insight into the surface reactivity of carbon phases. It has been argued elsewhere [5,6] that chemisorption of oxygen is an indicator of reactive sites. Survey scans in figure 4 show that chemisorbed oxygen was present at trace level on HOPG, while being present at 7.8 and 12.6 at.% of surface sites on graphite and DLC, respectively (table 1). The surface concentration of oxygen is likely to be understated due to the attenuation length, AL, for C 1s electrons being ca. 1 nm while that for O 1s electrons being marginally less [13]. Detailed scans were carried out for the O 1s structures of the graphite and DLC specimens. Results are shown in figure 5. Peak positions and shapes proved to be identical to within the resolution of the measurements, with a binding energy of 533.2 ± 0.1 eV. The O 1s binding energy was consistent with oxygen being present as a hydroxyl [14], or as a non-bridging species [15].
Figure 4. Survey XPS spectra for HOPG, polycrystalline graphite and DLC, top to bottom. The spectra have been offset along the vertical axis for clarity.

Figure 5. High spectral resolution spectral data for the O 1s level for graphite (continuous line) and DLC (broken line).

| Sample  | C (at. %) | O (at. %) |
|---------|-----------|-----------|
| HOPG    | 100       | <0.1      |
| graphite| 91.3      | 7.8       |
| DLC     | 84.9      | 12.6      |

3.3. Dependence on bias and exposure time

Parallel trenches were written at different bias to a DLC surface. The contour line in figure 6 shows the dependence of depth as a function of bias, for constant humidity, tip current and dwell time. There was a clear trend to increasing rate of conversion with bias. Electro-oxidation at 68% R. H., and for a relatively short exposure time, was not resolvable for a bias of 3 V. However, at longer exposure times and higher R. H. resolvable conversion of DLC has been observed at a bias as low as 2 V.

4. Discussion

The present study and other work [5-8,16] show that the surface chemistry affects the rate of electro-oxidation of carbon-based materials. For instance, the a-b planes of HOPG have proven to be electrochemically inert, presumably due to lack of reactive sites in the sp²-bonded surface. On the other hand, edge sites are reactive. Likewise, IB-DLC exhibits regions of low reactivity, as shown in figure 2. In this case the differential reactivity may arise from ‘phase regions’ where extent of short-range order and relative changes in the ratio of local sp²/sp³ will affect the outcome. Additional work, currently underway, will be required to describe the systems in greater detail.

The present study illustrates the merits of STM as a local electrochemical probe whereby structural and topographical features and changes can be linked directly to the kinetics and thermodynamics of electro-oxidation processes. In a technical context STM, or AFM carried out with a conducting probe, allows patterning of carbon-based materials on the nano-scale, either by a relatively slow serial route in the local probe mode, or by a much faster parallel route in the non-local probe mode [9].

The data in figure 2 permits a rough calculation of the energy required to oxidize a carbon atom, and thus to produce two molecules of H₂. Approximately 2.5x10¹⁰ carbon atoms were removed from a pit in the pattern in response to an energy deposition of 5x10⁻⁸ J. Thus the work required per atom was of
order $2 \times 10^{-19}$ J (of order 1 eV). The back-of-the-envelope estimate suggests that the process is surprisingly efficient, and merits further investigation as a means of hydrogen production.

Figure 6. (Left) STM image of trenches arising from local electro-oxidation of DLC at 6, 3, 4, 5 and 6 V bias (left to right), at 68% R. H., and for a tip current of 10 nA. The exposure time for each trench was ca. 0.5 s. (Right) Contour line drawn left to right through the pattern.

5. Conclusions
The outcomes of the study may have implications for technologies exploiting carbon-based materials as building blocks for meso/micro-structures, when DLC-type films are used as passivative/protective layers or as patterned active elements. Likewise, further work may show that electro-oxidation of carbon could be an efficient method for producing hydrogen gas [4].

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