Chemically functionalised exfoliated graphite: a new bulk modified, renewable surface electrode

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Graphite particles are exfoliated and chemically functionalised to covalently attach electroactive molecules and subsequently pressed in the form of a pellet, without the use of a binder, to yield a bulk modified, renewable surface electrode material.

Research on the development and chemical modification of new electrode materials leading to improved catalytic and electro-analytical properties has received considerable attention in the last two decades.[1–14] Murray[1] has pioneered the area of chemically modified electrodes that includes modification of a variety of surfaces such as metals, metal oxides and to some extent carbon. Bulk modification of the material would lead to re-useable electrodes. Presently, the most popular bulk modified electrode is based on carbon paste. However, fouling and contamination of the surface and leaching of the modifier during operation pose significant hurdles in the long-term use of this material. Additionally, use of silicon oil as a binder leads to the deterioration of the material with time. Hence, it is pertinent to have covalently modified, renewable surface electrode materials based on inert binders that do not deteriorate with time. There have been a few attempts based on graphite–epoxy[12] and sol–gel silicate[9–11,13] matrices in this direction. It is very desirable to have the electrodes fabricated without any binder to have an unlimited storage and cycle life. Herein, we report, for the first time, the chemical functionalisation of exfoliated graphite particles and its use as a bulk modified, surface renewable electrode material. The electrodes are in the form of pressed pellets prepared without any binder.

Exfoliated graphite (EG) is an expanded graphite with low density and high temperature resistance.[14] The exfoliation of graphite is a process in which graphite expands by up to hundreds of times along the *c*-axis resulting in a puffed-up material. The compression of the EG results in a material of high lubricity and flexibility. The advantage of compression is that a high density porous substrate is formed with a surface area that is relatively high compared with other graphitic ad-sorbents.[15] Some of the demonstrated applications of this material include high temperature gaskets, seals, packings, thermal insulators, conductive resin composites, lubricant, catalyst supports and adsorption substrates.[14,16–18] Very few reports deal with the use of this material in electrochemical studies.[19–21]

Natural graphite of particle size 300–400 μm (Stratmin Graphite, USA) were soaked in a mixture of conc. H_2SO_4–HNO_3 (3:1, v/v) for 24 h. The material was then exfoliated by giving a thermal shock at 800 °C in air. The EG particles were treated with a mixture of conc. H_2SO_4–HNO_3 at *ca.* 100 °C for 4 h and the acid was later filtered off. The excess acid present on the material was neutralised with an alkali and the powder was subsequently washed with dilute HCl and excess distilled water. This oxidative pretreatment introduces and increases the number of oxygen containing functional groups on the EG surface. These functional groups thus introduced on to the graphite particles were reduced using $NaBH_4$ in methanol. The resulting –CH_2OH and –OH groups were attached to AQ or Fc using anthraquinone carboxylic acid or ferrocene acetic acid and *N,N'*-dicyclohexylcarbodiimide as a coupling agent. Soxh-let extraction with methanol for a prolonged period was carried out to make certain that the material does not contain any physisorbed reactants.

The graphite particles were chemically characterized at every stage by XRD, IR, XPS, elemental analysis and the morphology was followed by SEM. Electrochemistry was carried out using pellets pressed without the use of any binder. Fig. 1 shows the cyclic voltammograms obtained with anthraquinone modified EG electrode. The peak potentials are well defined and the value of ΔE_p ($E_p^c - E_p^a$) varies with the scan rate. The control voltammogram using EG electrode without the electroactive component does not show any redox activity as expected (Fig. 1, inset). The redox peak currents vary linearly with the scan rate showing that the redox species is bound to the surface of the electrode (Fig. 2). However, there is a tendency for the peak currents to saturate at higher scan rates (above 120 mV s^{-1}) which may be due to the proton transport limitation to the bound electroactive species. Additional experiments in buffers of different pH also confirm this. The formal redox potential varies with the solution pH and the slope of the linear plot corresponds to 59 mV decade^{-1} thus confirming that the process involves 2e$^-$ and 2H$^+$ as expected. The surface coverage was measured by integrating the area under the peak and was found to be 1.2×10^{-9} mol cm^{-2}. This value, however, is only a representative figure since the real surface area is different (owing to roughness created by the emery sheet) from the geometric area used for the calculation. The surface roughness is found to play a major role in the functionalisation and in turn the electro-activity of the modified material. Modified electrodes with smooth surfaces do not give rise to any peaks while an increase in surface roughness leads to better definition of the peaks. The cyclic voltammograms in Fig. 1 has roughness created using a 400 grit SiC paper. The SEM image (Fig. 3) shows the rough surface used in the present study. It is clear that roughening the surface results in an increase in the ratio of edge to basal planes. This points to the fact that the edge planes of the graphite are
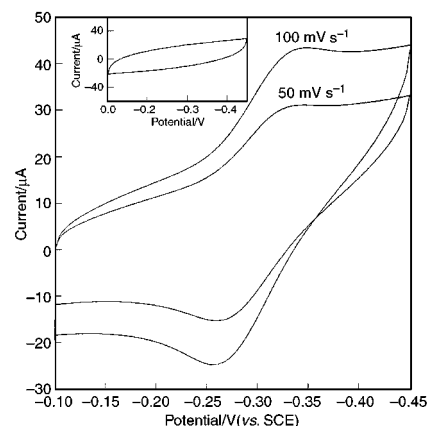
Fig. 1 Cyclic voltammograms of AQ modified EG electrode in acetate buffer, pH 3.5, at two different scan rates. The geometric area of the electrode is 0.08 cm^2. Inset: control cyclic voltammogram of the EG electrode prepared without AQ at a scan rate of 50 mV s^{-1}. Other conditions are as above.
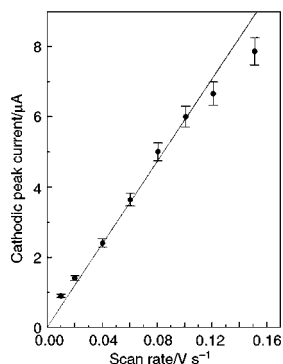
Fig. 2 Plot of reduction peak current *vs.* scan rate for AQ modified electrode in phosphate buffer, pH 7.

those that are functionalised with the redox moiety and are hence electrochemically active.

The bulk modification of the EG leads to reproducible electrochemical data. Mechanical polishing of the electrode exposes a new surface and different surfaces give rise to cyclic voltammograms that are very similar. The standard deviation in the peak currents for four successive polishings was < 5%. The fact that the quinone is chemically attached to the matrix and not physically adsorbed was confirmed by the following: non-modified EG particles were intentionally adsorbed with anthraquinone carboxylic acid and the resulting modified material was subjected to electrochemical measurements. Cyclic voltammograms show that the reduction of the adsorbed quinone occurs at −0.385 V while the chemically bonded quinone is reduced at −0.325 V at a scan rate of 10 mV s^{-1}. The difference in reduction peak potentials is expected to be due to combined effects of physical adsorption and the presence of –CO$_2$H group for the physisorbed material compared to the chemically functionalised EG. Second, the change in the reduction peak potentials with scan rate is much larger for the physisorbed quinone (120 mV for a change from 10 to 100 mV s^{-1}) than the chemically bound (30 mV for the same range) moiety. This reveals that the electrochemical reduction kinetics and the reversibility of the physisorbed quinone is sluggish compared to the chemically bound AQ. Third, quinones are known to get physically adsorbed on to the basal as well as edge planes and hence the voltammograms on the smooth surfaces (basal planes) are expected to show electrochemical activity.[22] Indeed, this is observed with the physisorbed quinone modified electrode. The chemically functionalised EG material did not show any activity on smooth surfaces and this again confirms the modification on the edge plane surfaces as revealed by the cyclic voltammograms.

The chemical modification is also confirmed by IR measurements. The IR spectrum of the unmodified graphite particles show the presence of phenolic and alcoholic –OH groups on the surface as confirmed by the XPS C 1s spectrum. Treatment with a conc. H$_2$SO$_4$–HNO$_3$ mixture is expected to result in the formation of graphite oxide in addition to other oxygen containing functional groups.[23] Experiments using various techniques have established that graphite oxide contains different amounts of tertiary C–OH groups, ether C–O–C groups, >C=O< double bonds as well as enol and ketone
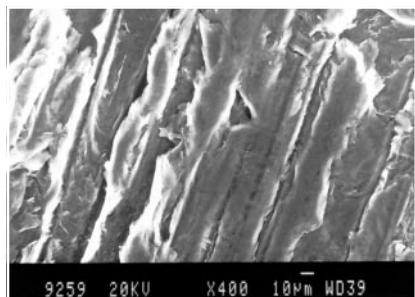
groups.[24] On NaBH$_4$ treatment, the functional groups that are formed on the EG particles, are reduced to –OH and –CH$_2$OH groups. Subsequent attachment of AQ or Fc through the –OH and –CH$_2$OH groups on the graphite would result in linkages of the type –COC(=O)AQ/Fc. Hence, the IR of the modified surface is expected to contain carbonyl functionalities from the quinone and the other ester type functionalities as described above. Indeed, the IR spectrum of the modified surface reveals the presence of these functional groups at *ca.* 1700 cm^{-1} for carbonyl and at *ca.* 1200 cm^{-1} for the CC(=O)–O stretch; the reduction in frequency for the latter is due to the conjugation of the phenyl ring. The modification is also confirmed by X-ray photoelectron spectroscopic studies. The deconvoluted C 1s spectrum of EG indicates the presence of graphitic, phenolic and carboxylic functional groups in the ratio of 77 : 4.4 : 18.7 while the AQ modified EG is found to contain graphitic, phenolic, carboxylic and, in addition, carbonyl functional groups in the ratio of 70.7 : 7.5 : 11.1 : 11.8. The presence of *ca.* 12% of carbonyl groups is a clear indication of the modification of EG by AQ. The ferrocene modified EG electrode shows a similar behaviour.

The exfoliated material is easy to prepare and is amenable to chemical modification. As demonstrated here, the electrode can be fabricated without the use of any binder, which is very advantageous. The electron transfer rate, however, increases with increasing number of edge sites. Detailed comparative studies on exfoliated graphite, modified exfoliated graphite, carbon paste and glassy carbon will be reported in due course.

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Fig. 3 SEM image of a rough EG electrode. Roughness created using 400 grit SiC paper.