Electrochemically-modified Glassy Carbon Electrodes capable of incorporating Redox Species

Mark L. Bowers,*† Charles N. Durfor, and Barbara A. Yenser

GTE Laboratories Incorporated, 40 Sylvan Rd., Waltham, MA 02254, U.S.A.

Glassy carbon were electrochemically-modified by oxidizing in sulphate, carbonate, or phosphate media to yield electrodes capable of incorporating and concentrating cationic and aromatic redox species.

We report the formation and preliminary study of a new type of modified electrode, formed by electrochemical oxidation of glassy carbon electrodes (g.c.e.s) in sulphate, carbonate, or phosphate solutions. These electrodes are easy to make and readily incorporate and concentrate cationic and aromatic redox species leading to significantly enhanced surface equivalent concentrations. Chemically-modified electrodes capable of incorporating redox species have received considerable attention because it is possible to obtain tailor-made electrodes by selective immobilization of chemicals with properties desirable for catalysis and analysis. Present technologies require the deposition of a film (polymers or inorganic materials) onto a conducting or semiconducting base material prior to the uptake of redox couples,[1] and the formation of such electrodes often involves lengthy and complex syntheses, as well as the subsequent coating of the base material, which can result in electrode systems with poor stabilities.

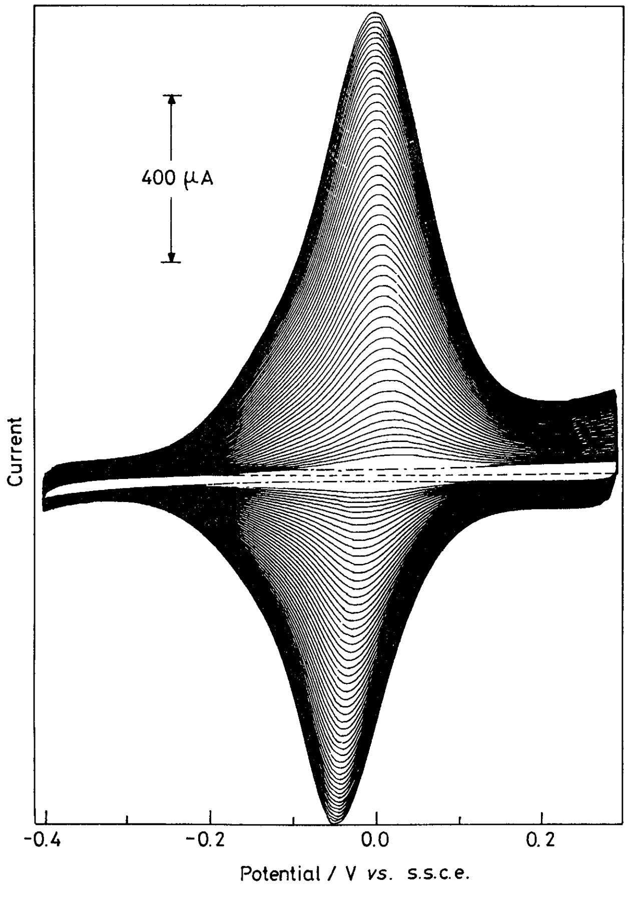

Figure 1. C.v.s. in 1 M H_2SO_4 at 100 mV/s. Background at an unmodified g.c.e. (- - -), background at a modified g.c.e. (–·–·–), and incorporation of riboflavin from 1 mM solution into a modified g.c.e, every fourth scan recorded, with scanning stopped before reaching saturation in the electrode (——).

Previously, anodic pretreatment of glassy carbon electrodes has often been used to enhance electrochemical activity.[2] A limited concentration of redox species has also been observed in some of these electrodes.[3] Generally, it is thought that the increased electrochemical activity is due to phenol-like surface groups introduced by the electrochemical oxidation.[4]

Glassy carbon electrodes were prepared by sealing a piece of glassy carbon (0.3 cm in diameter, Tokai or Carbone) in epoxy or heat shrink tubing, polishing with an Al_2O_3 suspension, rinsing, cleaning in an ultrasonic cleaner for ~15 s, and finally rinsing again with deionized water.[5] Most of the results reported here were obtained with electrodes modified in 8 M H_2SO_4 by cycling the potential between +0.6 and +2.3 V [*vs.* sodium chloride saturated calomel electrode (s.s.c.e.)] at 5 V/s for 10 min. A similar procedure was used for H_3PO_4– and $NaHCO_3$–m.g.c.e.s (modified glassy carbon electrodes) except that the phosphoric acid concentration was 4.9 M and the sodium hydrogen carbonate concentration was 0.5 M with the upper potential limit of +3.0 V. The subsequent cyclic voltammetric response of the sulphuric acid-modified electrodes revealed increased background currents (Figure 1).

Incorporation of positively charged and/or aromatic redox species was monitored by the increasing current peaks in the cyclic voltammograms (c.v.s). Typically, the electrode potential was cycled between several hundred mV positive and several hundred mV negative to the formal potential of the redox couple. Incorporation could also be achieved by simply soaking the m.g.c.e. in a solution of the redox couple. Sulphate-modified g.c.e.s were observed to incorporate the cations $Ru(bpy)_3^{2+}$ (bpy = bipyridine), $Ru(NH_3)_6^{3+}$, and $Cu(NH_3)_4^{2+}$; the neutral species ferrocene and hydroquinone; and the anions anthraquinone-2-sulphonate, all from 1 mM in 0.1 M KNO_3 solutions. Riboflavin was also incorporated in both the cationic (see Figure 1) and anionic form (at pH *ca.* 0 and 10.3, respectively). In contrast, the hydrophilic anions, $Fe(CN)_6^{4-}$ and $IrCl_6^{3-}$, failed to incorporate but still displayed responses similar to those at the unmodified g.c.e.

Incorporation into the m.g.c.e. occurred quickly at first and then more slowly as the concentration of the redox couple neared saturation in the g.c.e. Maximum loading of the electrodes took place within 3 h and approached *ca.* 10^{-7} mol/cm^2 (or nearly 10^4 equivalent monolayers) for the compounds $Ru(NH_3)_6^{3+}$ and riboflavin; somewhat smaller uptake was observed for the others. Longer cycling times (>10 min) while oxidizing the g.c.e. led to higher maximum loadings.

After transferring the electrode to pure supporting electrolyte solutions, most of the species left the electrode at a rate comparable to that at which they were incorporated. The decrease continued until nearly background c.v.s were obtained. An exception was riboflavin, which remained in the film indefinitely. The process of incorporation and loss could

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† *Present address:* Cambridge Research Laboratory, 195 Albany St., Cambridge MA 02139, U.S.A.

be repeated several times without any apparent degradation of the modified electrode. The electrodes could also be stored in air for days without loss of response. Peak potentials and peak separations were usually similar to those at the unmodified g.c.e. Plots of peak current *vs.* scan rate were linear from 1 to 500 mV/s for modified g.c.e.s showing that all the electroactive material has thin layer behaviour and, further, that charge transport within the electrode is not rate-limiting.[1a]

The formation of modified electrodes was attempted in a variety of other solutions ($HClO_4$, HCl, HNO_3, CF_3CO_2H, $LiCF_3SO_3$, tetraethylammonium *p*-toluenesulphonate, and NaOH), but only sulphate, hydrogen carbonate, and phosphate solutions formed a g.c.e. which would subsequently take up electroactive compounds. We also found that cycling the potential was necessary for the formation of good electrodes; however, the cycling could not extend into the negative solvent limit.

Glassy carbon has been used as an electrode material for a number of years and is regarded as a relatively inert and stable material under most conditions.[6] The structure of glassy carbon is considered to be a convoluted, tangled matrix of aromatic ribbon molecules[7] that form an impermeable solid. Our results suggest that this structure is altered at high anodic currents[8] resulting in a porous matrix with the uptake of sulphate, carbonate, or phosphate which may intercalate[9] between layers of the aromatic ribbons. The intercalated anions could then form the basis of a cation-exchange system.

The incorporation of relatively hydrophobic species may be explained by adsorption onto the exposed ribbon surfaces. This hypothesis is supported by preliminary secondary ion mass spectrometry and energy dispersive *X*-ray analysis of a sulphate-modified g.c.e. which shows that sulphur is included in the modified g.c.e.

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