

Surface electrochemistry of inorganic complexes

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Study of the surface electrochemistry of inorganic complexes provides a means to investigate the redox behaviour of femtomole quantities of metallic complexes adsorbed onto an electrode, commonly graphite. These species undergo reactions induced by electron transfer to create products which remain on the electrode and can be studied directly. Reactions can also occur with solution species in contact with the electrode, also to generate products adhering to the electrode. Further, these surfaces can behave as electrocatalysts for the oxidation or reduction of target species. Aspects of these various reactions and processes are presented here.

The purpose of this presentation is to summarize some of the work that we have been undertaking in surface electrochemistry over the last few years and to illustrate the various applications that this technique offers. We will not deal in great depth with each of the areas but rather indicate the power of this technique to gain insight which might be more difficult to obtain by other technologies. One of the beauties of the technique is the recognition that when one places a monolayer of some species on the electrode, usually pyrolytic graphite, one obtains a new electrode which is essentially a molecular electrode described by the chemistry at the molecule itself. The underlying chemistry of carbon is usually not relevant to the study except in those circumstances where one wishes to draw distinction between the electrochemistry of some diffusing species occurring by permeation through to the carbon surface and that occurring at the molecular surface

A number of characterization experiments are carried out to ensure that the species we are studying is actually bound to the surface and is not diffusing thereto from the bulk solution. Fundamentally there are two ways of proving this. One is to note that the scan rate dependence of the surface wave will have current proportional to scan rate and not to the square root of the scan rate, which is the case with the diffusing species. It is important however to carry out such a scan rate study over a sufficiently wide range of scan rates that one can statistically distinguish between a square root dependence and a non-square root dependence. The other rather simple idea is that once the compound is adsorbed onto the surface the electrode can be removed from the solution used to adsorb the material and then this electrode can be placed into an electrolyte which no longer contains the active species. If one still sees strong waves associated with the active species then they necessarily must be adhering to the electrode, i.e. we are looking at surface electrochemistry.

The presentation is divided into four sections which illustrate four or more different attributes of surface electrochemical methods.

i) - The Copper Phenanthroline Story

In summary, this story demonstrates that while several species may be in equilibrium in solution, it is possible under suitable circumstances to study each component of the equilibrium independently on an electrode surface. In this particular case, we are interested in the equilibria which occur between copper ions

and phenanthroline. In solution, there is an equilibrium between three complexes containing 1:1, 2:1 or 3:1 phenanthroline:copper. If one disturbs this equilibrium in solution, then obviously there would be a redistribution of the mix of species. In the solid state, on the surface of an electrode, this does not happen during the lifetime of the experiment. It is fortunate that the individual stepwise stability constants for the three copper species are such that it is possible to make aqueous solutions which are close to 100% of the 1:1 or the 2:1, or the 3:1 phen:Cu species depending upon the molecular ratios used (ref. 1). If a very carefully cleaned, ordinary pyrolytic graphite electrode is dipped into each of these solutions, it is possible thereby to deposit on the graphite surface each one of these individual species more or less exclusively (ref. 2). In this section, we indicate the methodology used to convince ourselves that indeed each of the three copper phenanthroline complexes can be studied individually on the surface of the electrode and also to show that they have rather different chemical properties.

In general, in the surface electrochemical method, the dipping of an electrode into a solution of an organic material usually containing aromatic rings, leads to the deposition of the organic material cleanly on the electrode surface. In some cases, one obtains a monolayer and in other cases a multilayer. The amount of material deposited on the electrode can be assessed from the charge under the surface waves assuming that one knows the number of electrons per molecule and the area of the electrode.

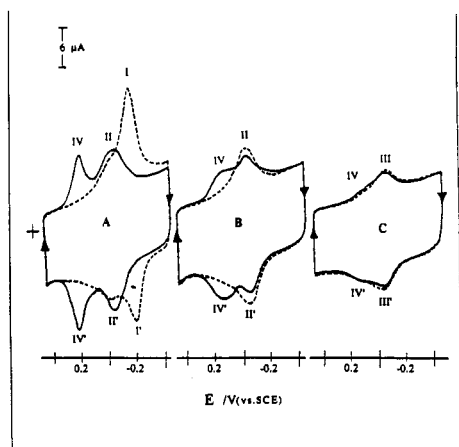


Figure 1 Availability of coordination sites also indicated by addition of cyanide ion (5×10^{-5} M CN^-). Dotted lines before addition of cyanide, solid lines following addition of cyanide.

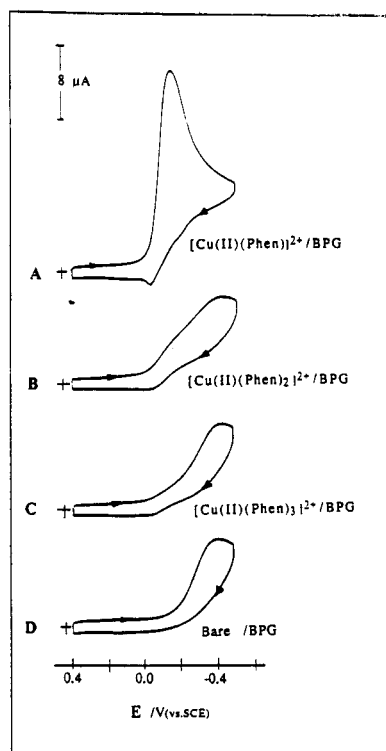
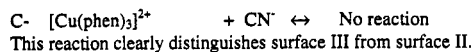
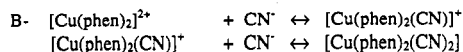
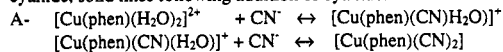
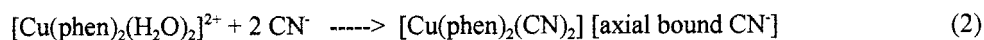
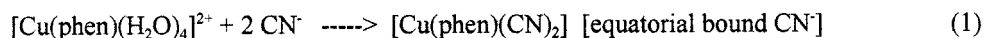


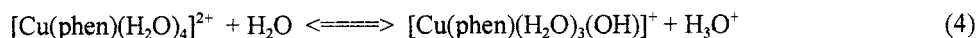
Figure 2 Effect of Oxygen on the three Copper surfaces. Only the $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$ surface responds to oxygen, presumably because of the availability of in-plane aqua sites which can be exchanged by oxygen.

Figure 1 shows the surface voltammograms of each of the individual species scanned through the Cu(II)/Cu(I) redox process. It is evident that the 1:1 surface behaves very differently from the 2:1 surface and is therefore easily distinguished. The 3:1 surface however does not differ a great deal from the 2:1 and this study alone would not convince us that the 3:1 surface was in fact uniquely different from the 2:1.

Approximately the same amount of phenanthroline is deposited on each of these three electrodes so that the areas under the peaks reflect the ratios of the amount of copper in the three systems and those ratios from top to bottom are 1:1/2:1/3 as would be predicted. However, this is also not totally convincing since it is difficult to control the amount of phenanthroline on the surface. Rather, we use the chemistry at the surface as an alternative means to distinguish them. If one adds extremely small amounts ($5 \times 10^{-6} \text{ M}$) of cyanide ion to the solution into which the electrode is dipped, one observes major changes in the surface electrochemistry of the 1:1 and the 2:1 species clearly indicating cyanide binding to form different cyanide species (Fig. 1). However there is essentially no reaction between cyanide ion and the 3:1 surface. This can be understood in terms of the following equilibria.



Of course, the lack of reaction for the 3:1 surface is a negative experiment, conclusions from which should be drawn cautiously, but this was repeated many times and one can be sure that there is a real difference in behaviour between the 2:1 and 3:1 surface species. Given equations 1 to 3, it is certainly clear that cyanide ion would bind to the equatorial sites of the 1:1 complex displacing water molecules readily whilst it would bind weakly to the 2:1 surface occupying axial sites. However, unless it can displace phenanthroline, it is unable to bind to the 3:1 surface thereby explaining the lack of reactivity. There have been previous reports of the existence of the 1:1 and the 2:1 species on the surface but no reports of the existence of the 3:1 (ref. 2b)(ref. 3)]. Other studies which have been carried out with these surfaces include the pH dependence of these surface waves. Wave 1 shows a pH dependence of approximately -60 mV/pH indicative of reaction 4 occurring at the equatorial sites.



Consistent with the presumed very weak binding of water to the axial sites of the 2:1 species and no binding of water in a 3:1 species, the waves 2 and 3 show only a very shallow dependence on pH.

Copper phenanthroline complex surface species are known to be electrocatalysts for the electrocatalytic reduction of oxygen to water (ref. 3). Figure 2 shows the response of bare pyrolytic graphite and the 1:1, 2:1, 3:1 species towards an oxygen environment. It is clear that only the 1:1 species is electroactive towards oxygen. Analysis by the traditional Koutecky-Levich methods confirms that the process for the 1:1 species is indeed the four-electron reduction to water. This surface will also reduce hydrogen peroxide at the same potential and in this case the Koutecky-Levich analysis indicates a two-electron reduction process as anticipated.

One of the problems with using electrochemistry for the detection of various target materials, is the fact that they are often easily poisoned by undesired reactions. As we have seen, cyanide ion will poison a copper electrode by binding very strongly thereto. However, we can make use of this phenomenon as a means of detecting the cyanide ion. Thus if micromolar quantities of cyanide are added to a solution containing the 1:1 surface species on an electrode, in the presence of oxygen, the oxygen reduction wave decreases in height in a manner proportional to the concentration of cyanide in solution. By this means, it is possible (Fig. 3) to identify the concentration of cyanide in solution at micromolar levels. One can similarly identify other species which bind strongly to the electrode, specifically, in this case, the sulfide and thiocyanate ions, and Fig. 4 shows the behaviour of the surface in the presence of these ions. Quite clearly, when these species bind to the copper on the surface, they prevent oxygen binding by occupying sites which the oxygen atoms would otherwise occupy (ref. 2a).

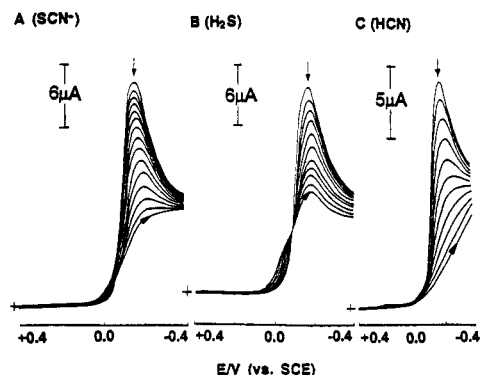


Figure 3 Cyclic voltammograms of a BPG electrode coated with $[\text{Cu}(\text{phen})]_{\text{ads}}^{2+}$ in 0.28 mM O_2 solutions containing various quantities of (A) SCN^- from (top) 0.0 M to (bottom) $1.3 \times 10^{-3} \text{ M}$ in the concentration interval $1 \times 10^{-6} \text{ M}$, (B) H_2S from (top) 0.0 M to (bottom) $1.3 \times 10^{-5} \text{ M}$ in concentrated interval $1 \times 10^{-6} \text{ M}$, and (C) HCN from (top) 0.0 M to (bottom) $14 \times 10^{-6} \text{ M}$ in the concentration interval $2 \times 10^{-6} \text{ M}$. Supporting electrolyte (pH 5.3), steady-state scan, potential scan rate 20 mV s^{-1} .

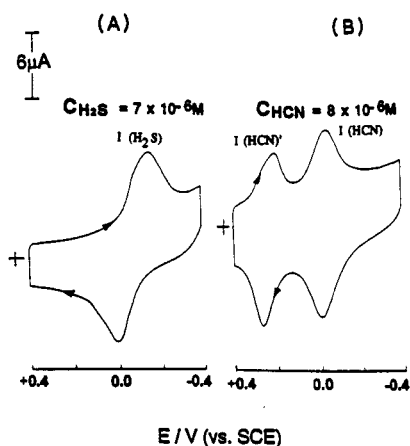
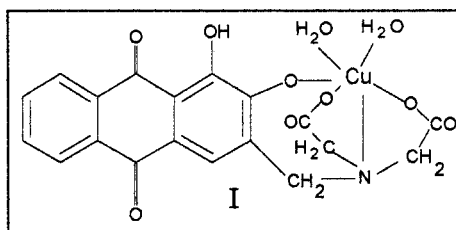


Figure 4 Cyclic voltammograms of a BPG electrode coated with $[\text{Cu}(\text{phen})]_{\text{ads}}^{2+}$ in the presence of (A) $7 \times 10^{-6} \text{ M H}_2\text{S}$ and (B) $8 \times 10^{-6} \text{ M HCN}$. Supporting electrolyte (pH 5.3), equilibrium scan, potential scan rate 150 mV s^{-1} .

ii) - The Copper Complexone System (ref. 4)

In this section, we illustrate the ability to carry out quite complicated chemistry on the electrode surface, and show how one can apparently isolate small molecular units inside a larger molecular unit using this approach. This is a type of matrix isolation carried out on an electrode surface. The copper complexone species is an anthraquinone derivative (I) containing side chains capable of forming a complex with copper in which four other ligating groups come from the anthraquinone component and there are two vacant sites which are presumably occupied by water. The free ligand undergoes a two-electron, two-proton reduction with conversion of the quinone to the diol as shown in Fig. 5a (waves I, I'). This is a reversible well-behaved process. When the copper complex is adsorbed onto the surface, two additional waves are observed which can be associated with the reduction of $\text{Cu}(\text{II})$ to $\text{Cu}(0)$, (wave II') and its re-oxidation by a two-electron process (wave II) (Fig. 5b).



The identity of waves 2 and 2' as two-electron processes is confirmed by the fact that the area under these curves is the same as the area under the ligand reduction process which is known to be a two-electron two proton process. The pH dependencies of these waves are all consistent with proton coupled processes in which the number of electrons and the number of protons involved are the same (wave I, I' slope -62 mV/pH ; wave II, II' slope -50 mV/pH).

Thus reduction at wave II generates the zero valent copper atom which is now localized inside the framework of the anthraquinone ligand. It does not evidently interact at all with the ligand since the ligand reduction potential occurs slightly more negative of wave II at identically the same potential as it does in the free ligand. We therefore have generated a surface where a copper atom is sitting nestled inside the anthraquinone in either its quinonoid or diol oxidation state. This is a form of matrix isolation on the solid electrode surface. Clearly there may be opportunities here for the reaction of this bare copper atom with various reagents in a fashion not previously investigated. We have not explored the chemistry of this bare copper in any detail as yet but we have exposed it to sulfide ion.

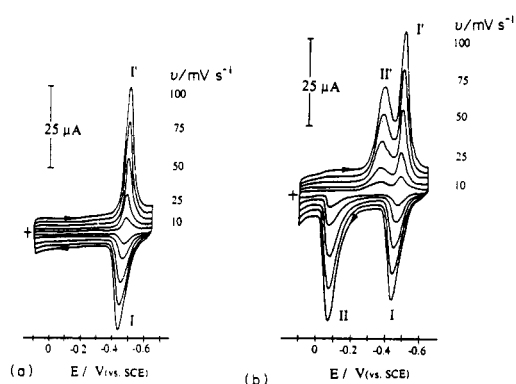


Figure 5 (A) Cyclic voltammetry of AC (7×10^{-10} mol cm $^{-2}$) adsorbed on a BPG electrode (area 0.17 cm 2). The freshly polished electrode was first soaked in 1×10^{-4} M AC solution for 10 s, and was then washed and transferred to pure supporting electrolyte (0.1 M NaClO $_4$ + 0.1 M (CH $_3$ COOH + H $_3$ BO $_4$ + H $_3$ PO $_4$) + NaOH, pH 5.3) to record the voltammograms. (B) Cyclic voltammetry for a Cu II AC|C electrode. The electrode used to record cyclic voltammetry in (A) was exposed to 1×10^{-3} M CuSO $_4$ solution for 10 s, and was then washed and transferred to pure supporting electrolyte solution to record the voltammogram. Equilibrium scan. Potential scan rate as indicated on the figures.

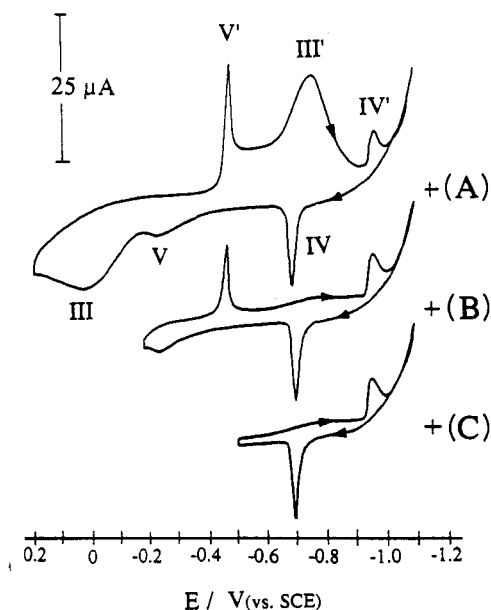
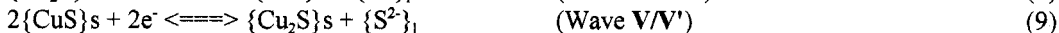
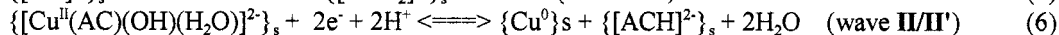


Figure 6 Cyclic voltammetry of a graphite electrode on which 1.3×10^{-9} mole cm $^{-2}$ Cu 0 had been deposited electrochemically, measured in 1×10^{-3} M Na $_2$ S solution buffered at pH 5.3. Before exposure to the sulfide solution, the bare BPG electrode was polarized at a potential scan rate of 20 mV s $^{-1}$ from 0.2 to -1.1 V in 5×10^{-5} M CuSO $_4$ solution buffered at pH 5.3, washed and transferred to the sulfide-ion-containing solution to record the voltammograms; (A) from -1.1 to 0.2 V and then back to -1.1 V; (B) from -1.1 to -0.18 V and the back to -1.1 V; (C) from -1.1 to -0.5 V and then back to -1.1 V. Potential scan rate, 20 mV s $^{-1}$.

When this surface is exposed to sulfide ion, the surface behaviour changes dramatically. Fig. 6 (top) shows the chemistry of the bare pyrolytic graphite electrode and the complexone coated surface towards sodium sulfide in the bulk electrolyte. A significant number of new waves are observed. One of the characteristic problems in surface electrochemistry when one sees a series of oxidation and reduction waves is to determine the relationships between them, i.e. which waves are coupled together corresponding to the oxidation and reduction of related species. The usual way to accomplish this is to change the potential at which the electrode is switched in scan direction (switching potential) and see which waves appear and disappear as a consequence. We see this experiment in Fig. 6 where it is clear that wave III and III' must relate to the same species as do waves IV, IV', and V with V', although not all of the confirmatory experiments are shown here.

Of course, these various pairs are not simple reversible processes in which a given species is oxidized or reduced. If they were completely reversible, then the corresponding components for oxidation and reduction would appear at the same potential. That they are widely separated is a clear indication that some chemistry, either following or preceding the electrochemical reaction, must be occurring. We do not have the space here to argue the nature of each of each species. Suffice to say that they were determined, on the one hand, by further electrochemical studies of these surfaces, but also by comparing the chemistry of these surfaces with the considerable literature precedent for the chemistry of copper sulfide species. In this fashion, the various waves were identified as shown in equations (5-9): {NB The free ligand has three dissociable protons; when Cu is lost, the phenolic oxygen is protonated}[Subscript s- surface, subscript l, - liquid phase]



iii)- Nanoarchitecture: Binding Additional Species at the Electrode Surface: The Surface Bound Ferro(i)cyanide Ion (ref. 5)

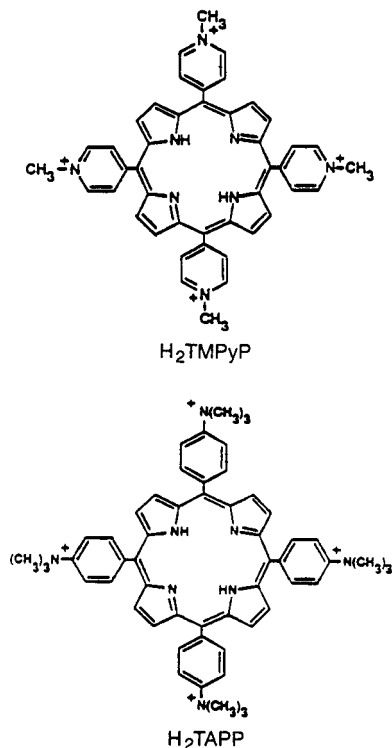


Figure 7 Molecular structure of 5,10,15,20-tetrakis(1-methyl-4-pyridyl)-21H,23H-porphine (H₂TMPyP) and 5,10,15,20-tetrakis[4-(tri-methylammonio)phenyl]-21H,23H-porphine (H₂TAPP).

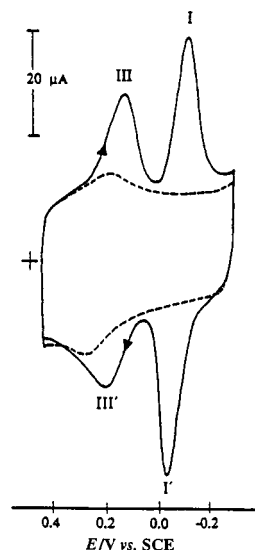


Figure 8 Cyclic voltammograms of a bare BPG electrode (---) and a BPG electrode coated with 2.9×10^{-10} mole cm⁻² of H₂TMPyP (—) in a solution of 0.01 M HClO₄ + 5×10^{-5} M Na₃[Fe(CN)₆] (pH = 2) Potential scan rate: 300 mV s⁻¹.

It is possible to bind very highly positively charged porphyrins at the electrode surface. Figure 7 shows the formulae of two such porphyrins which contain peripheral positive charges for a total charge of 4+. When these species sit on the electrode surface, this charge must be neutralized. The counter anions will normally be the anion available in the electrolyte in contact with the electrode. However, the question arises as to what might happen if you expose such a surface to redox active anions. To pursue this idea, potassium ferricyanide was added to an electrolyte solution to which these electrodes were exposed. Figure 8 shows the resulting chemistry for the tetramethylpyridinium porphyrin complex H₂TMPyP. The intense wave labelled I,I' corresponds to a two-electron reduction of the positively charged porphyrin which one observes in the absence of ferricyanide ion in the electrolyte solution. The hatched line shows the response of a bare BPG electrode to ferrocyanide ion in solution. These small waves correspond to diffusion controlled oxidation and re-reduction of the ferricyanide species, [Fe(CN)₆³⁻]/[Fe(CN)₆⁴⁻] process. When one exposes the surface bound porphyrin electrode to the ferricyanide solution, then a new pair of waves III and III' is generated. These correspond to the same Fe(III)/Fe(II) redox process but now attached to

the surface. They are much more intense than the diffusion waves because the local concentration of ferrocyanide at surface is much higher than in the diffusion experiment. They are also shifted from their positions in solution indicative of the binding energetics of the species to the surface. The areas of the waves can be shown to be consistent with the binding of four ferrocyanide ions, for every three porphyrins on the surface, and upon reduction the binding of one ferrocyanide for every porphyrin on the surface. In this experiment therefore, we have generated a composite ion pair electrode in which both components of the ion pair are redox active. It is clear that this idea can be extended to bind much more complicated systems to the electrode either by ion pair electrostatics or by direct chemical binding through, for example, coordination of a species in the solution to a metal centre on the electrode.

This is a competitive reaction in the sense that if one exposes this electrode to other ions such as chloride, sulfate, etc. there will be a competition for the bound ion between the ferrocyanide and the competing electrolyte ion. This series of experiments were undertaken (some are shown in Fig. 9) in which the relative concentrations of the ferrocyanide ion and the counter ion such as chloride were varied. As can be seen, if the concentration of chloride or sulfate is very much greater than that of ferrocyanide, then it replaces the ferrocyanide on the surface and the ferrocyanide wave diminishes in current intensity. Similar experiments can be investigated by changing the concentration of the porphyrin on the surface. In this fashion, it is possible to derive equilibrium binding constants for the ferrocyanide ion. These were reliable and reproducible and suggest that indeed all the surface species are fully electroactive.

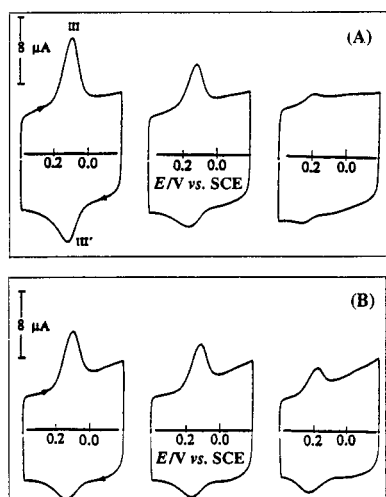


Figure 9 Cyclic voltammograms of a BPG electrode coated with 2.6×10^{-10} mole cm^{-2} of H_2TMPyP in a 2×10^{-5} M $\text{Na}_3[\text{Fe}(\text{CN})_6]$ solution containing various concentrations (A) NaCl (left, middle, right: 0.08, 0.2, 1.0 M NaCl, respectively) and (B) Na_2SO_4 [same concentrations as noted in (A), of Na_2SO_4]. Potential scan rate; 150 mV s^{-1} .

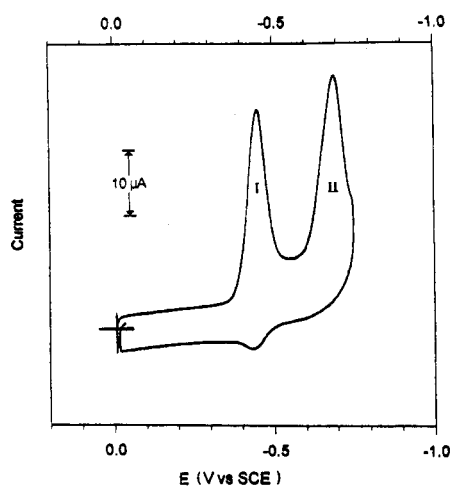


Figure 10 Cyclic voltammogram of TPPZ/BPG electrode in 0.1M H_3PO_4 (pH 2); N_2 saturated conditions; Pt wire counter electrode; scan rate 100 mV/s . First scan ongoing to positive potential.

These experiments then demonstrated the ability to build up structures on the surface by chemical processes.

iv) - The Tetrapyrrolylpyrazine (TPPZ) Story (ref. 6)

In this last section, another of the fundamental properties of the surface electrochemical experiment is explored. In this case, we demonstrate that the surface species undergoes a series of chemical reactions generating new species on the surface. One can think of this in terms of a species **A** on the surface which we might designate **A/BPG** being converted to species **B**, and then **C**, and **D**, etc. By controlling the conditions in the electrolyte and the potential at which the electrode is polarized, one can study the

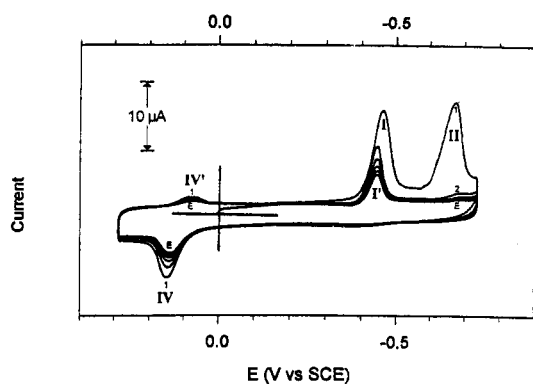


Figure 11 Cyclic voltammogram of TPPZ/BPG electrode in pH 2 Buffer solution; argon-saturated conditions; scan rate 100 mV/s. 1: first scan ongoing to positive potential; 2: second scan after first scan; E: equilibrium scan after 6 total scans.

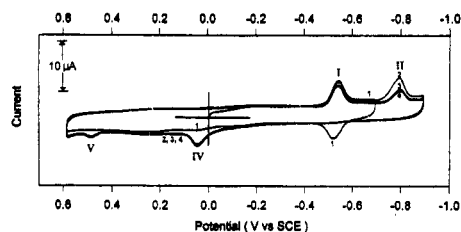


Figure 12 Cyclic voltammetry of IVTPPZ/BPG electrode in pH 2 Buffer solution; argon-saturated conditions; scan rate 100 mV/s. Result after holding just positive of wave V for one minute and rezeroing. 1: scan ongoing to positive potential; 2: second scan after first scan and the negative limit is switched to just negative of wave II; 3: third scan after second scan; 4: fourth scan after third scan.

Figure 10 shows the surface electrochemistry of the TPPZ molecule. The chemistry being observed is a two-electron, two-reduction process to form the 1,2 dihydrotetrapyridylpyrazine (1,2 DHTPPZ) (wave I) followed at a more negative potential by a second wave (wave II) which is also two-electron, two-proton reduction, to form the 1,2,3,4-tetrahydrotetrapyridylpyrazine (1,2,3,4 THTPPZ). Wave I is reversible if the potential is switched positive of wave II but no anodic return waves corresponding to waves I and II are seen when switched negative of wave II.

Regarding the voltammogram in Fig. 10, one can now stipulate that at potentials positive of wave I, we have a TPPZ/BPG electrode. Between wave I and wave II, we have a 1,2 DHTPPZ electrode (DHTPPZ/BPG) and at potentials negative of wave II, we have a 1,2,3,4 THTPPZ electrode (THTPPZ/BPG). The THTPPZ/BPG electrode is stable to re-polarization back at least to 0 volts and if we scan negatively at this point, no waves will be seen in the regions 0 to -0.7 V, i.e. both waves I and II will have disappeared. However, if the scanning is continued towards more positive potentials, re-oxidation of this surface does occur to generate now the 1,4-tetrahydropyridylpyrazine, 1,4 DHTPPZ (not 1,2 DHTPPZ) at wave IV. This chemistry (at a different pH from that shown in Fig. 10) is shown in Fig. 11 where wave IV and IV' correspond to the oxidation of 1,2,3,4 THTPPZ to 1,4 DHTPPZ and its re-reduction back to 1,2,3,4 THTPPZ. This pair of waves is stable upon cycling. If the cycle is now switched back to beyond wave II, then since 1,2,3,4 THTPPZ is already on the electrode, waves I and II are again absent. In Fig. 12, we demonstrate how if the potential is extended even to more positive potentials than wave IV then a new wave V appears which corresponds to the re-oxidation of 1,4 DHTPPZ back to TPPZ. We have now regenerated TPPZ on the electrode and therefore as we scan negatively once again, waves I and II are recovered. This system therefore represents an elegant example of how by controlling the potential and potentiodynamic properties of each of these electrodes A/BPG, B/BPG, C/BPG, etc. in some detail. In solution voltammetry, this is by no means an easy objective. If a solution species A reacts at the electrode surface to generate a new species B, then this species will slowly diffuse away from the electrode and therefore although its surface behaviour can often be identified to some degree, one cannot easily study the behaviour of these product species in detail. In the surface experiment, the new species is trapped on the surface and therefore within the potential range for its existence, it can be studied readily.

In solution phase TPPZ is known (ref. 7) to reduce to 1,4-dihydrotetrapyridylpyrazine, 1,4DHTPPZ which then rearranges slowly to 1,2-dihydrotetrapyridylpyrazine 1,2DHTPPZ; Further reduction to the 1,2,3,4-tetrahydrotetrapyridylpyrazine 1,2,3,4THTPPZ and the octahydrotetrapyridyl pyrazine is also observable. The basic chemistry, therefore, involves a succession of two electron/ two proton reduction processes: This system is then a good candidate for studying a series of redox species on a graphite electrode.

the scan width on the electrode, one can essentially generate a series of different molecular surfaces whose properties could be studied. We could for example expose each of these surfaces to some solution species to see how they respond. The chemistry of this TPPZ system is in fact rather more complex than we have discussed here since at pH 2 there is a further reaction in which 1,4 DHTPPZ is converted to yet another species, C', which is reduced at wave I'. This will be discussed in more detail in a future publication. At pH 8.7, this reaction is strongly inhibited.

The "beauty" of the surface electrochemical study is the ability to investigate the electrochemistry of all these species independently on the electrode surface. Thus in addition to studying TPPZ/BPG we can independently study the electrochemistry of 1,4DHTPPZ/BPG, 1,2DHTPPZ/BPG, 1,2,3,4THTPZ/BPG and C'/BPG since each of these species is constrained to the electrode surface rather than being formed in small amounts in bulk solution.

v) Conclusions

We have demonstrated that the use of surface electrochemistry provides a very convenient way of investigating the electrochemistry and electrocatalytic properties of a range of materials in a facile fashion. It is possible to carry out various kinds of electrochemical experiment on the surface including, as we have shown, the formation of additional structures, the formation of matrix isolated species and the study of a range of different decomposition or rearrangement products as in the last case. While the electrochemical data shown here involve exclusively cyclic voltammetry, there is no reason why other electrochemical techniques cannot be used to obtain definitive information. In our studies, we have used various forms of carbon as the support, such as ordinary pyrolytic graphite or highly oriented pyrolytic graphite because these usually provide a molecular organization which facilitates good electrochemistry. However, one could certainly use other electrodes and transparent electrodes such as indium tin oxide would be beneficial since one could then obtain UV spectroscopic data which are much more difficult to obtain on a graphite surface. Other techniques which might be used however are grazing angle infrared absorption.

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