

## Qualitative and Quantitative Determination of Silver in Silverex - Antimicrobial Cream Using Bentonite Modified Carbon Graphite Working Electrode

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*Authors' contributions*

*This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.*

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### Abstract

The results presented in this paper show that surface modified electrode technique can be used to qualitatively and quantitatively detect the presence of silver redox active moiety in silverex a topical broad spectrum antibiotic (SC).

The results indicate that when the silver containing topical cream is spin coated on the carbon graphite working electrode surface, the latter displays the properties of the immobilized SC.

When bentonite a clay montmorillonite characterized by the presence of octahedral and tetrahedral sites was used as host matrix, the electrochemical signal of the silver in SC was significantly enhanced. The enhanced redox activity is proposed to result from isomorphous substitution of the silver redox moiety in the octahedral layer leading to pre-concentration of the redox active moiety hence enhanced redox signal.

The voltammetric data obtained from bentonite modified carbon graphite working electrode yielded the surface coverage ( $\gamma$ ) for the silverex topical in the 20gm tube as  $1.43 \times 10^{-4} \text{ mol/cm}^2$ . From the data there was 0.25g silver in the 20gm silverex ionic gel, corresponding to 0.22% silver compared to manufacturers specification of 0.2%.

The results obtained from scan rate variation studies suggest that the STC is neither completely a surface attached species nor is its redox process diffusion controlled.

The p-Aminophenol has been shown to strongly influence the redox properties of STC and is proposed to act as an electro-catalyst by removing the oxidative stress associated with the oxidation-reduction of silver in SC.

The redox properties of SC are shown to be unaffected by change in supporting electrolyte solution pH, therefore does not depend on protonation-deprotonation equilibrium.

Polyaniline as a host matrix suppresses significantly the redox activity of the silver in the SC.

**Keywords:** Cyclic voltammetry; Surface Modified Electrodes; Electrocatalyst; Host-Matrix; Bentonite; p-Aminophenol.

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## 1 Introduction

A cream is a topical preparation usually for application to the skin. Creams can be classified into two broad categories- pharmaceutical products and cosmetic creams.

In general creams are applied to mucous membranes and are semi-solid emulsions of oil and water and are divided into two groups:

Oil-in-water (o/w) creams are used in cosmetics as they are less greasy and are easily washed away with water.

Water-in-oil (W/O) creams are composed of small droplets of water dispersed in a continuous oily phase. They are easily washed off using water hence are more cosmetically acceptable.

Creams are in general hydrophobic and are released readily from a water-in-oil cream than an oil-in-water cream. These creams are moisturizing providing an oily barrier which reduces water loss from the outermost layer of the skin.

In the work presented in this paper the surface of the carbon graphite working electrode has been modified using silver containing topical cream silverex. The silverex cream contains silver sulfadiazine (1% w/w).

Similarly, in this research, the surface of the carbon graphite working electrode was modified using bentonite, a clay montmorillonite known to have octahedral and tetrahedral layers. In the octahedral layer there are metal cations which can undergo isomorphous substitution [1-4].

The other host matrix used to modify the surface of the carbon graphite working electrode was polyaniline. It is one of the most attractive conducting polymers studied extensively by several research groups. This is as a result of it being easy to synthesize in addition to having a well behaved electrochemistry, and a reproducible electrochemical behavior [4-12].

## 2 Experimental Section

The electrochemical instrumentation used for generating the cyclic redox potential scans comprised of Princeton Applied Research (PAR) model 173 potentiostat/galvanostat and logarithmic current converter model 396 that controlled the current. This was used in conjunction with PAR model 175 Universal Programmer that generated triangular waves. The output signal was fed into PAR RE0089 X-Y recorder.

A three-electrode assembly in an undivided cell was used throughout this work. These consisted of a saturated calomel electrode (SCE) as the reference electrode, platinum wire as the auxiliary or counter electrode and carbon graphite, with a surface area of 0.38 cm<sup>2</sup> as the working electrode. The counter electrode contained inert platinum wire supported by a glass tubing 10 cm long.

### 2.1 Chemical reagents

Silverex a broad spectrum antimicrobial cream was used as received without further purification.

The monomer liquid aniline (Aldrich, 98%), was triply distilled until a colorless liquid was obtained. It was then stored under inert nitrogen gas. This distillation process was repeated for each fresh experiment. All the chemicals and acids were analytical grade and were used as received without further purification.

All solutions were prepared using high purity solvents. Distilled water was obtained from a Millipore water purification system.

All weighings were done using an analytical balance for maximum accuracy.

The bentonite (Athi River Mining Company Ltd., Kenya) has a mesh size ranging from 150 to 200  $\mu\text{m}$ , cation exchange capacity (CEC) 1.18 – 1.22 mM/g and pH range of 8.4 – 9.6. The density of bentonite is 1.25  $\text{g/cm}^3$ . It has average solvent retention capacity of 22.5% and 4.8% for water and organic solvents respectively. Its moisture content is 8.5%. It swells by a factor of 1.7 and 1.4 in water and organic solvents respectively.

It was purified as described by Gosh and Bard [3].

### 3 Results and Discussion

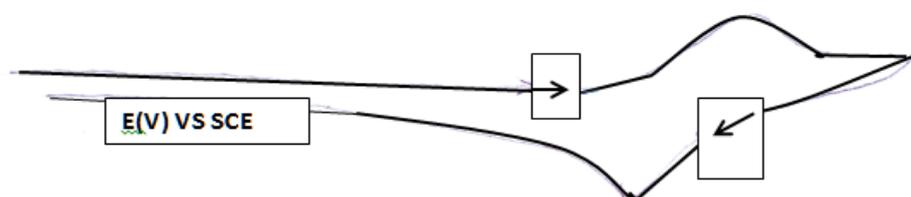
#### 3.1 Electrochemical Analysis of Silverex an Antimicrobial Cream (SC) on Carbon Graphite Electrode

The bare carbon electrode was prepared for usage by polishing it with a felt polishing cloth until a smooth glassy surface was obtained. This was then rinsed thoroughly with distilled water and allowed to dry at room temperature. This same procedure was followed every time bare carbon was used as the working electrode. The carbon graphite working electrode surfaces were modified as variously as described below:

In the case of silverex modified electrode, the working electrode was modified using the silverex antimicrobial cream. The silver containing topical broad spectrum antimicrobial cream was used as received without further purification. The carbon graphite working electrode was dip coated with the modification cream and the slurry on the surface was profiled giving a uniform film spread on the carbon graphite working electrode surface.

The electrode was then transferred to various electrolyte solutions containing 0.1M, 0.5M and 1.0M sulphuric acid. The potential of the electrode was cycled from -0.30V to 0.90V at a scan rate of 20mV/sec. The SC was not very stable and with the solution becoming cloudy suggesting that some of the SC diffused into the solution.

The resultant cyclic voltammetric response is shown in Fig. 1. below.



**Fig. 1. The cyclic voltammetric response obtained from SC modified carbon graphite working electrode, Potential range: -0.30V to 0.90V, Scan rate 20mV/sec in 1.0 M  $\text{H}_2\text{SO}_4$ .**

The resultant cyclic voltammogram had a poorly defined oxidation peak occurring at 0.25V, with a very broad poorly-defined reduction peak. The poorly defined oxidation peak and the absence of a reduction peak can be attributed to possible much favored chemical reaction between the silver in SC and the chloride ions to form a salt, as compared to the case of formation of salt with the bisulphate/sulphate ions.

Scan rate dependence studies for SC electrode in the electrolyte solution containing 1.0M hydrochloric acid yielded the values shown in Table 1.

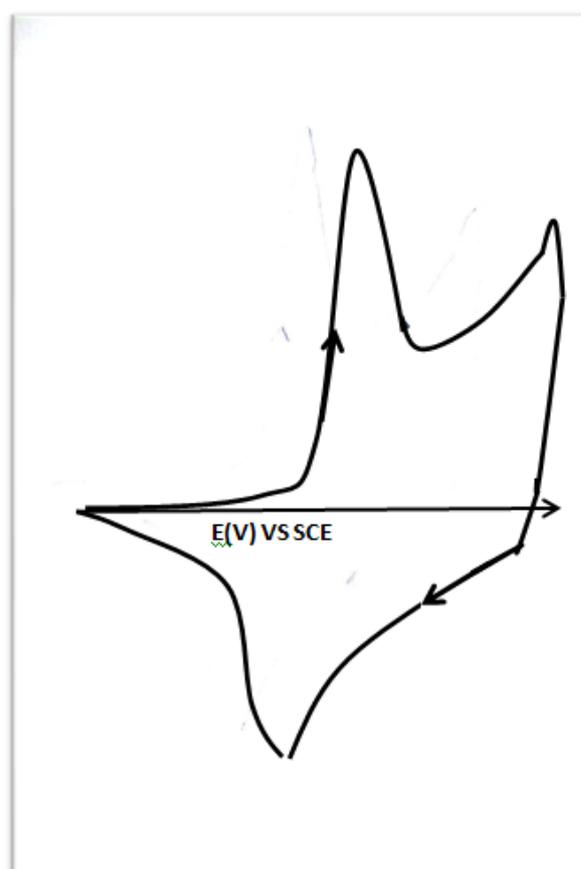
**Table 1. Variation of  $i_p$  versus  $v, \sqrt{v}$** 

Oxidation Peak Current, $i_p$ (mA)	Scan Rate, $v$ (mV/sec)	Square Root of Scan Rate, $\sqrt{v}$
0.006	10.0	3.16
0.008	20.0	4.47
0.024	50.0	7.07
0.036	100.	10.0

The values obtained from the scan rate studies clearly attest to the fact that, the oxidative peak current does not vary linearly (correlation coefficient  $< 0.900$ ) with either the scan rate or square root of scan rate. This is a pointer to the fact that the redox process in the SC electrode is not diffusion limited and the species has a loose surface attachment architecture.

### 3.2 Derivatization of the Carbon Graphite Working Electrode with Polyaniline

This was achieved by cycling the potential of the carbon graphite working electrode in a solution containing 0.01M aniline and 1.0M  $H_2SO_4$  from -0.20V to 0.85V at a scan rate of 20mV/sec. The polyaniline film was deposited with each cycle and had a well behaved electrochemistry in addition to being easy to synthesize. The relative film thickness or mount on the electrode correlates with the oxidative peak current. The redox efficiency of the process is related to the incremental increase in the anodic and cathodic peak currents. The resultant polyaniline cyclic voltammogram is shown in Fig. 2.



**Fig. 2. Polyaniline film on bare carbon graphite electrode**  
Potential range: -0.30V to 0.90V, Scan rate 20mV/sec

### 3.3 Bentonite Modified Carbon Graphite Electrode

#### 3.3.1 Modification of the Carbon Graphite Working Electrode with Bentonite

The carbon graphite electrode surface was modified using Bentonite, a clay montmorillonite having tetrahedral and octahedral site which play a key role in hosting isomorphously substitutable cations.

The choice of bentonite as a host matrix was guided by the fact that, it has an elaborate crystalline structure with octahedral site hosting isomorphously substitutable cations. The reasoning is further entrenched in the fact that, if the silver cation can occupy the octahedral site, and therefore, due to pre-concentration effects its redox signal is expected to be significantly enhanced.

The working electrode surface was modified using bentonite by dip coating the working electrode surface with the bentonite slurry in the same manner as described in the case of SC.

The bentonite modified electrode was then further modified with silverex. The electrode was then transferred to various electrolyte solutions containing 0.1M, 0.5M and 1.0M sulphuric acid. The potential of the electrode was cycled from -0.30V to 0.90V at a scan rate of 20mV/sec.

To prepare bentonite modified electrode a small amount of bentonite was put on a clean tile, and then electro-inactive adhesive was added and mixed with it thoroughly until thick slurry was obtained. The slurry was dip-coated on the surface of the freshly prepared carbon graphite electrode. The electrode was left to dry at room temperature for 24 hours; as a result we obtained a uniform dry bentonite on the surface of the electrode.

Composite mixtures for preparing composite electrodes involved mixing the substances in the required ratios on a weight/weight basis. This mixture was then dip-coated on the working electrode surface as already discussed.

The silverex was then dip-coated on the bentonite modified electrode. The silverex-bentonite electrode (SBE) was then transferred to a solution containing 0.1M, 0.5M and 1.0M HCl. The potential of the electrode was cycled from -0.30 V (constant) to 0.70 V, 0.75 V, 0.80 V, 0.85 V and 0.90 V at a scan rate of 20 mV/sec.

The cyclic voltammetric response obtained (see Fig. 3) shows a dramatic improvement in the redox properties of silverex, a non-reversible oxidation peak was obtained at 0.30V. The redox peak is well defined and sharp suggesting fast charge transfer kinetics in the faradaic process. The scaffolding observed during the reverse scan at 0.1 V is probably attributed to a nucleation process associated with metal deposition.

#### 3.3.2 Accuracy of Bentonite Modified Electrode As an Electro-gravimetric Tool

The charge under the oxidation peak in Fig. 3 was computed. The value for  $Q_{ox}$  for the silver peak was computed to be  $5.26 \times 10^{-7} Ccm^{-2}$  and the surface coverage  $\gamma$ , computed from the expression

$$\gamma = \frac{Q}{nFA}$$

Where  $n=1$  and  $F=96,500C/mol$

Yielded,

$$\gamma = 1.43 \times 10^{-4} mol/cm^2$$

Assuming  $1.1 \times 10^{-10} molcm^{-2} = 3.57 \times 10^{-5} g$  for hydroquinone in top-lemon cream detected using modified electrodes [13].

Therefore, in a 15g net weight tube:

$$\frac{5.26 \times 10^{-7}}{1.1 \times 10^{-10}} \times 3.57 \times 10^{-5} g = 0.188 g \text{ per } 15g \text{ net weight tube.}$$

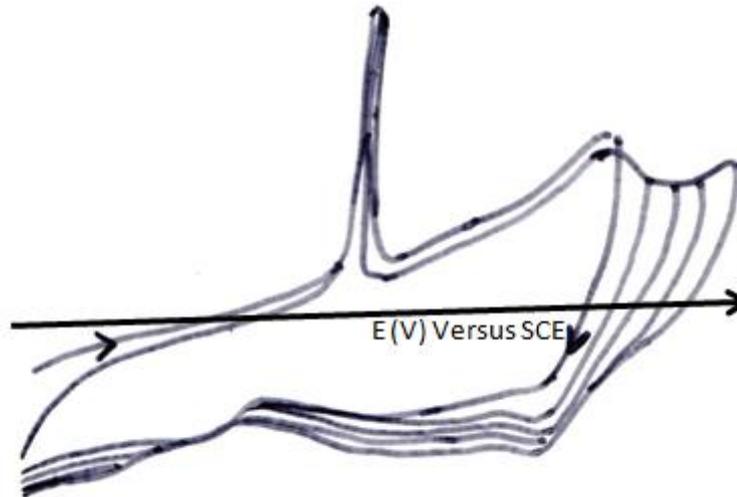
Therefore in a 20g net weight tube:

$$0.188 \times \frac{20}{15} = 0.25 g$$

$$\% \text{ silver} = \frac{0.25 g}{110.112 g} \times 100 = 0.22\%$$

This compares favorably with the purchased silverex ionic gel had a net weight of 20g and contained 0.2% silver nitrate according to manufacturer specifications.

This result confirms that, surface modified electrodes with the appropriate host matrix can accurately determine the quantity of the redox active moiety.



**Fig. 3. SC on Bentonite modified electrode**

Potential range: -0.30V (constant) to 0.70V, 0.75V, 0.80V, 0.85V and 0.90V. Scan rate 20mV/sec

The oxidative peak current versus scan rate and square root of scan rate yielded data shown in Table 2.

**Table 2. Variation of  $i_p$  versus  $v, \sqrt{v}$ . And values of  $E_{p,ox}(V)$**

Oxidation Peak Current, $i_p$ (mA)	Scan Rate, $v$ (mV/sec)	Square Root of Scan Rate, $\sqrt{v}$	$E_{p,ox}(V)$
0.0026	5.0	3.16	0.27
0.004	10.0	4.47	0.28
0.006	20.0	7.07	0.30
13.8	50	10.0	0.33

It is observed that there is a positive shift in the oxidation peak potential with scan rate. This is probably attributed to a changing internal geometry of the Bentonite lattice structure hosting the redox species and the ensuing entropy changes.

### 3.4 SC on Polyaniline Modified Carbon Graphite Electrode

The derivatization of the carbon graphite working electrode with polyaniline The Polyaniline Modified Electrode (PME) was now further modified by dip-coating of the SC on the PME to obtain a thin layer with a uniform surface. The PME/SC electrode had its potential cycled from -0.30V to 0.90V at a scan rate of 20mV/sec in electrolyte solutions containing 0.1M, 0.5M and 1.0M  $H_2SO_4$ .

We now observe broad misshapened peaks which appear to have an overlap of redox centres. The peaks appear to display a composite character which is probably resulting from a blend of redox interaction between polyaniline and silver redox centers. The redox activity of the polyaniline host matrix is significantly suppressed. This probably suggests that the redox centres are interacting in a non-complimentary manner. At a statistical thermodynamics level there is a possibility that the interaction interferes with the distribution and partition function associated with the energy levels in the host matrix.

When the potential window was varied from -0.30V (constant) to 0.70V,0.75V,0.80V,0.85V and 0.90V there was no significant change in the electrochemical profile and neither were there any indication that, the host matrix Polyaniline was degrading to the quinone/imine derivative as a result of the potential being cycled in an electrolyte not containing the aniline monomer and at far positive potentials.

When the PME-SC electrode was subjected to scan rate dependence studies in an electrolyte solution containing 1.0M  $H_2SO_4$  we observe a significant improvement in the oxidation reduction peaks which appear to be that of polyaniline with increasing scan rate. This suggests that, there are transient species associated with precursors to the polyaniline redox process which are captured at higher scan rates.

When the pH of the supporting electrolyte solution was varied, there was no corresponding change to the redox potentials suggesting a diminished role of protonation-deprotonation equilibrium in the overall redox process.

Scan rate dependence studies, once again yielded values whereby absolute linear correlation is not achieved with respect to the variation of oxidative peak current with either scan rate or square root of scan rate.

### 3.5 SC-p-Aminophenol Composite Modified Carbon Graphite Electrode

p-Aminophenol has been shown in previous work to remove the oxidative stress in redox active systems hence, improving the faradaic component of the total charge.

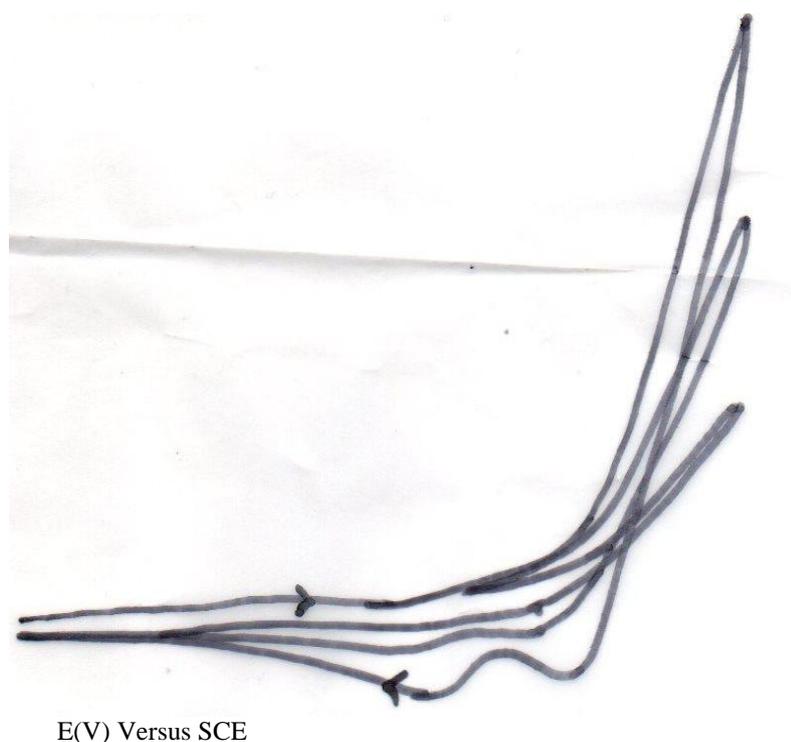
In this next set of experiments a composite was constituted by mixing SC and p-aminophenol and then using the composite mixture to modify the carbon graphite working electrode surface (SC-PAP electrode)

The SC-PAP electrode had its potential cycled from -0.30 V to 0.90V in a solution containing 0.1M, 0.5M and 1.0M  $H_2SO_4$ .

At a scan rate of 20mV/sec. the resultant cyclic voltammogram response is shown in Fig. 4. We observe two well defined reduction peaks at 0.4V and 0.65V. There are broad oxidative shoulders at 0.1V and 0.53V.

We propose that the reductive peak at 0.65 V is a redox center attributed to SC with the 599 mV positive shift in potential being attributed to the electro-catalytic role of PAP removing the oxidative stress associated with SC redox activity. Similarly the shoulder at 0.53 V showing a negative potential shift of 530 mV, once again can be associated with SC and electro-catalytic activity of PAP.

The carbon graphite working electrode was modified with SC and the electrode potential cycled in a solutions containing 0.01 M p-Aminophenol (constant) in 0.1M, 0.5M and 1.0 M  $H_2SO_4$  . The potential was cycled from -0.30 V to 0.90 V at a scan rate of 20mV/sec. In the cyclic voltammogram the oxidation and reduction peak potentials occurred at 0.70 V and 0.55 V respectively.



**Fig. 4. SC/p-Aminophenol modified electrode in 0.10M  $H_2SO_4$ , 0.5M  $H_2SO_4$ , 1.0M  $H_2SO_4$**   
 Potential range: -0.30(V). Scan rate 20mV/sec

Now unlike in the case where a composite mixture of SC/PAP was used to modify the electrode, the oxidation reduction peaks are now clearly defined. The oxidation peak has now shifted positively by 529mV and the reduction peak has also shifted positively by 100mV. It is apparent that when the PAP is in solution its electro-catalytic role leading to reduction in oxidation potential for SC is suppressed. This is not surprising given that in the composite formation where SC/PAP is used to modify the electrode surface, more active interaction between the SC and PAP redox centers. Similar experiment was repeated, but now in 0.1 M HCl supporting electrolyte and 0.01 M p-Aminophenol, with the potential being cycled from -0.30 V (constant) to 0.70 V, 0.75 V, 0.80 V, 0.85 V and 0.90 V at a scan rate of 100 mV/sec.

From the cyclic voltammetric response a misshapened non-reversible oxidation peak at 0.26V. The oxidation potential does not vary with increase in the positive potential limit. This suggests that, potential does not affect significantly the concentration of the redox active species.

When the concentration of HCl was varied to 0.1M and 0.5M keeping constant the concentration of p-Aminophenol at 0.01 M. There was no increase in the oxidation peak potential nor was there a shift in the oxidation potential. This is a pointer to the fact that the electrolyte solution pH hence, protonation/deprotonation equilibria does not affect the redox process.

The variation of peak current with scan rate does not yield linear plots when plotted versus scan rate or square root of scan rate. Therefore, the redox species is neither completely surface attached nor diffusion limited and this surface instability and poor faradaic features are reflected in the poor cyclic voltammetric response.

### 3.6 Modification of the Carbon Graphite Working Electrode with Polyaniline with p-Aminophenol

The polyaniline conducting polymer was electrodeposited on the carbon graphite working electrode by, cycling the potential of the carbon graphite electrode from -0.30V to 0.90V at scan rate of 20mV/sec in a solution containing 0.1M aniline, 1.0 M  $H_2SO_4$  and 0.01M p-Aminophenol.

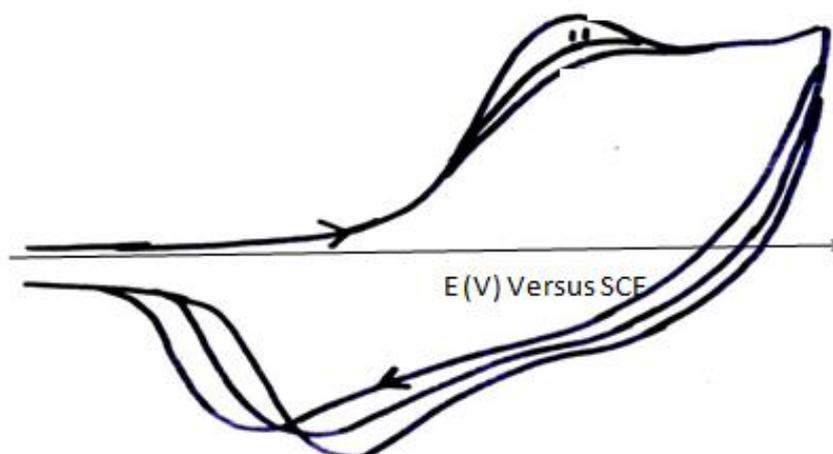
The polyaniline modified electrode was further modified using SC as already described elsewhere. The potential of the PAN/SC electrode was then cycled from -0.30 V to 0.70V at a scan rate of 20mV/sec. The reduction in the positive potential limit is to avoid electro-degradation of the polyaniline forming quinone/imine derivatives in a solution containing 0.1M, 0.5M and 1.0 M  $H_2SO_4$  and 0.01M *p* – Aminopropylamine (constant) in all the cases

We obtain oxidation/Reduction peaks at 0.45V ( 1.0M  $H_2SO_4$  ) , 0.72V ( 1.0M  $H_2SO_4$  ) 0.76V (0.5M  $H_2SO_4$ ) 0.80V(0.1M  $H_2SO_4$ )/0.3V, 0.56V, 0.75V (broad shoulder)

It is apparent that the redox process is dependent on  $[H^+]$  and is most likely associated with the polyaniline redox process. The peak at 0.45V is probably attributable to SC redox process. The reduction peaks are similarly associated with the polyaniline.

The presence of a nucleation loop at 0.23V a veiled pointer to metal deposition/and or related processes.

When the PAN/SC electrode was subjected to the same process but in electrolyte solutions containing 0.1M, 0.5M, 1.0 M  $HCl$  and 0.01M *p* – Aminopropylamine (constant), the resultant cyclic voltammetric response is shown in Fig. 5.



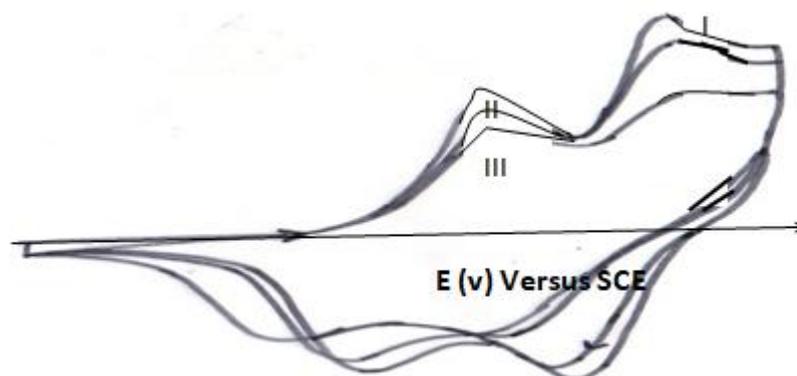
**Fig. 5.** SC on a polyaniline modified carbon graphite electrode in 1M  $H_2SO_4$  . Scan rate 20mV/sec

Unlike in the case of sulphuric acid we now obtain oxidation reduction peaks displaying more of polyaniline redox properties, in addition to them showing the typical pH dependence characterizing polyaniline redox process. There is no evidence of the nucleation loop. The redox activity of the SC is completely suppressed.

### 3.7 Modification of Carbon Graphite with Polyaniline/Bentonite Composite

A composite matrix of Polyaniline and Bentonite was prepared by the electrodeposition of polyaniline on a bentonite modified electrode, by cycling the potential of the Bentonite electrode in a solution containing 0.1M *aniline* and 1.0 M  $H_2SO_4$ . The scan rate was 20mV /sec and the potential cycle window ranged from -0.30V to 0.90V. See Fig. 6.

Once again we obtain oxidation reduction peaks with predominantly polyaniline redox features, with the SC redox process appearing to be totally suppressed.



**Fig. 6.** SC on a PANI/ Bentonite composite electrode in I-0.1M  $H_2SO_4$ , II- 0.5M  $H_2SO_4$  and III-1M  $H_2SO_4$   
 Potential range: -0.30 V to 0.90 V. Scan rate 20 mV/sec

## 4 Conclusion

The results presented in this paper, confirm the versatility of surface modified electrodes as an electro analytical tool capable of profiling the electrochemical activity of redox active moieties in Silver containing pharmaceutical cream (STC). The results obtained using bentonite modified electrode in the analysis of the quantity of silver in silverex attests to the versatility and accuracy of surface modified electrodes as electro-analytical tools. The non- interference of any other additives in the anti-microbial cream in the electro-analysis, points to the reliability of surface modified electrodes as redox specific. This technique can be extended in the profiling of other pharmaceutical products.

## Competing Interests

Authors have declared that no competing interests exist.

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