Application of Surface Modified Electrodes as a Nano-detection Tool in the Qualitative and Quantitative Assesment of Hydroquinone in a Cosmetic Cream

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Authors' contributions

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

ABSTRACT

The results presented confirm that when the surface of the carbon graphite working electrode is modified using the beauty crème the modified electrode displays the electrochemical properties of the immobilized cream.

The oxidation/reduction peak potentials for the hydroquinone in the cosmetic cream occurred at 0.61V/0.21V.

Electrochemical calculation from the oxidative charge for the hydroquinone redox process gave a surface coverage of 1.1×10^{-10} mol/cm^2 corresponding to an electro-gravimetric weight of 3.57×10^{-5} g for hydroquinone in the beauty cream, which corresponds to 0.121×10^{-9} g for hydroquinone in the 12g of the beauty cream.

It was also observed that, the hydroquinone in the beauty cream inhibits the polyaniline electro-degradation process at far positive potentials.

The results also indicate that modification of the carbon-graphite working electrode with bentonite; affect significantly the redox processes associated with hydroquinone in the beauty cream, the oxidation/ reduction peaks occur at 0.58V/0.28V. The effect of the bentonite host matrix is attributed to pre-concentration of electroactive species in the montmorillonite matrix.

The observed changes in the redox profile of the hydroquinone in the beauty cream in sodium chloride supporting electrolyte can be attributed to cationic and anionic effects associated with the sodium cation and the high charge density of the chloride anion.

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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.

Most creams are semi-solid emulsions of oil and water and are divided into two groups:

Oil-in-water (O/W) creams: These are characterized by droplets of oil dispersed in a continuous phase. These creams are used in cosmetics as they are less greasy and are easily washed away with water.

Water-in-oil (W/O) creams: These on the other hand, 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 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 [1].

Top Lemon cosmetic cream is a skin lightening complexion cream purchased from retail outlet without any prescription requirements. They are indicated to give a smooth extra Lightening complexion. The Top-lemon crème has active antiseptic component which clears spots and blemishes. Top –lemon especially has no composition data, and no detailed pharmacology and pharmacokinetics information.

Hydroquinone is a phenolic compound that is widely used in cosmetics. It is an environmental pollutant. This compound is harmful to both humans and animals even in very low concentrations. Therefore, it is necessary to develop an electro-analytical too that is sensitive and selective for the determination of hydroquinone in cosmetics. The overwhelming publications in this area are captured in references [2-13].

In this paper we present results where the surface of the carbon graphite working electrode has been modified using the Top lemon beauty cream. The electrode is shown to display the electrochemical properties of the immobilized cosmetic. The redox properties of the moieties in the Top-lemon cream confirm the presence of hydroquinone.

In addition further modification of the carbon graphite working electrode surface with bentonite (clay montmorillonite) and polyaniline (conducting polymer) as host-matrices [14-17] are shown to significantly alter the redox properties of Top-lemon cream.

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 a carbon graphite as the working electrode. The counter electrode contained inert platinum wire.
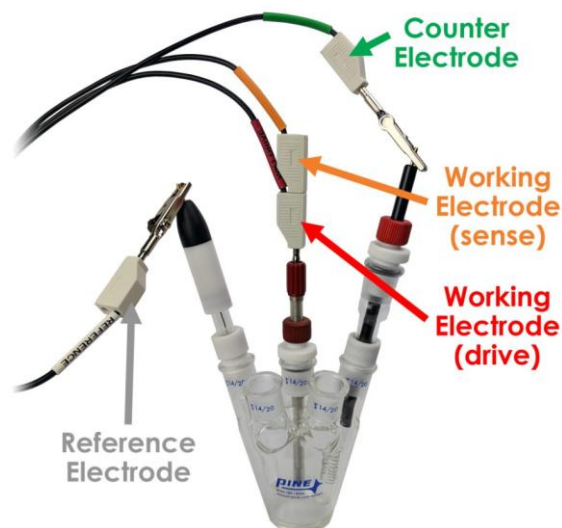

Fig. 1. The three- electrode electrochemical cell consisting of working, reference and counter electrodes
(Source: internet illustrations)

2.1 Modification of the Carbon Graphite Working Electrode Surface

The bare carbon electrode was prepared for usage by polishing it until a smooth 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 working electrode was modified using Top-lemon cream.

Conducting polymer-polyaniline and clay montmorillonite-Bentonite were used as host matrices.

The Top-lemon 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 smeared giving a uniform spread on the carbon graphite working electrode surface.

To prepare bentonite modified electrode a small amount of this clay 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 smeared uniformly on a smooth surface of a freshly prepared carbon electrode. The electrode was left to dry at room temperature for 24 hours; as a result we obtained a 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 smeared uniformly on the working electrode surface as already discussed.

Polyaniline, was prepared by electrodepositing polyaniline on a freshly polished bare carbon electrode by cycling the potential from -0.2V to 0.80V in a solution containing 0.1M aniline and 1M H_2SO_4. This is the optimum electrolyte composition for electrodepositing aniline. The scan rate was set at 20mV/s while the current scale was at $10\,mA/V$. The sensitivity of the recorder was set at 50 mV/cm.

2.2 Chemical Reagents

The Top-lemon beauty 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 an inert gas nitrogen. 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. Two types of acids as supporting electrolyte were used namely sulphuric acid (Gowa), and hydrochloric acid (Gowa). Other chemicals used include acetonitrile, and sodium chloride (sigma)

All solutions were prepared using high purity solvents. Distilled water was obtained from a Millipore water purification system. In the non-aqueous studies, acetonitrile (HPLC grade, Fischer) was used as received.

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 µm, cation exchange capacity (CEC) 1.18 – 1.22 mM/g and the density of bentonite is 1.25 g/cm^3

3. RESULTS AND DISCUSSION

The carbon graphite working electrode was polished as already discussed elsewhere giving a glossy finish. The cosmetic crème was applied on the carbon graphite working electrode giving a thin layer with a uniform surface. This electrode was then put in an electrolyte solution containing 1M Sulphuric acid. The potential of the working electrode was cycled from -0.3 V to 0.9 V at a scan rate of 20 mv/s. The cyclic voltammogram

The total oxidative and reductive charges were computed. The values obtained were 8.0 x10^{-6} coul/cm^2 and 7.6 x10^{-6}coul/cm^2. The values obtained indicate that the oxidative and reductive charges are nearly equal suggesting that the process is quasi reversible. The surface coverage Γ for the oxidative process was computed from the equation

$$\Gamma = \frac{Q_{ox}}{nFA}$$

Where Q_{ox} is the oxidative charge, n is the number of electrons, A is the electrode surface area.
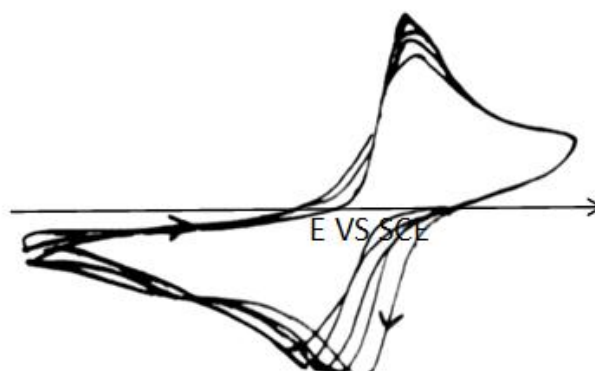
Fig. 2. The cyclic voltammetric response for Top-lemon in supporting electrolyte solutions containing 0.1 M Nacl and 1.0M Nacl. Potential window: -0.3V to 0.9V, scan rate 20 mV/sec

It is proposed that this redox process represents the hydroquinone redox process. This redox peaks resembles that observed when polyaniline is oxidized at far positive potentials leading to its degradation yielding Quinone/imine derivatives [17].

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$$\Gamma = \frac{Q_{ox}}{nFA}$$

Where $\mathbf{Q_{ox}}$ is the oxidative charge, n is the number of moles of electrons, F is the Faraday constant and A is the surface area of the electrode. The value computed for the surface coverage was $1.1 \times 10^{-10} \, mol/cm^2$ giving an electro-gravimetric weight of $0.121 \times 10^9 g$ from calculations based on the total cream spread surface area and the electrode surface area the amount of hydroquinone in the 15g cream in the tube was $3.57 \times 10^{-5}g$

The Top lemon modified electrode was then subjected to scan rate dependence studies. A plot of oxidative peak current versus square root of scan rate yielded a linear plot suggesting the process is diffusion limited.

The effect of pH was studied by cycling the potential of the Top lemon modified electrode from -0.3V to 0.90V at scan rate of 10mv/sec in electrolyte solutions containing 0.125M, 0.25M, 0.50M, 1M and 2M Sulphuric acid.

An extensive shift in the reductive peak potentials towards positive potentials is observed as the pH is lowered as shown in the Table below.

Table 1. Effect of pH on the redox potentials

Redox potential	pH
0.14	0.9
0.16	0.6
0.19	0.3
0.12	0.0

The change in reduction potential versus pH i.e., $\frac{\Delta E_{red}}{pH}$ is approximately $120 \, mV/pH$. This confirms that this process is a $2H^+/\overline{e^-}$ which is in agreement with the Quinone/imine redox process observed in polyaniline [17].

3.1 Top Lemon Modified Carbon Graphite Electrode in Sodium Chloride Supporting Electrolyte

The supporting electrolyte was now changed to 1M Nacl, and the potential of the Top lemon modified carbon-graphite electrode cycled from -0.30V to -0.90V at a scan rate of 10mv/s. The cyclic voltammetric response shows an oxidation peak at 0.13V and 0.58V (as shown in Fig. 2)

There is a single reduction peak at -0.01V. There is a significant difference in the redox response of the Top lemon modified carbon graphite electrode in Nacl supporting electrolyte as compared to the case of sulphuric acid supporting electrolyte discussed previously. These differences can be attributed
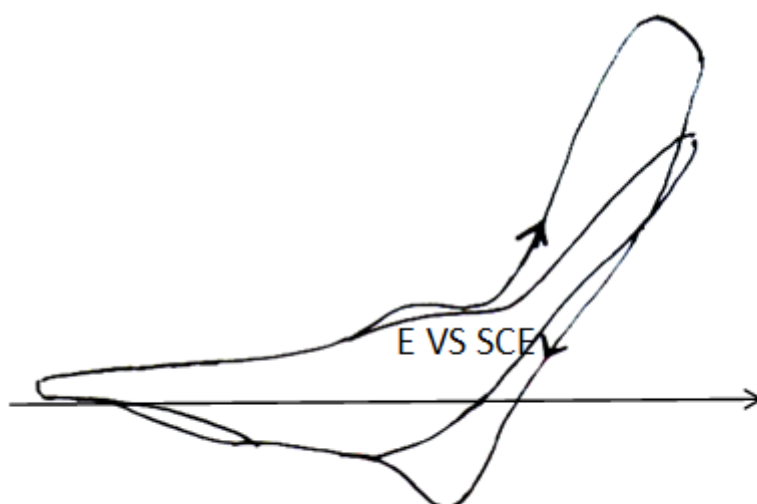
Fig. 2. The cyclic voltammetric response for Top-lemon in supporting electrolyte solutions containing 0.1 M Nacl and 1.0M Nacl. Potential window: -0.3V to 0.9V, scan rate 20mV/sec

To the difference in the cations and anions of the supporting electrolyte. A key difference being, the charge densities i.e. charge density of the chloride is higher than that of Hydrogen sulphate (HSO_4^-) or sulphate (SO_4^{2-}). The cations, sodium ions (Na^+) and hydrogen ions (H^+), though belonging to the same group in the periodic table, also have significant difference in the ionic radii and mobility. The charge density and the ionic radii, definitely affect the redox process and this is reflected in the redox potentials.

The potential window of the Top lemon modified carbon-graphite electrode was then varied from -0.30V to 0.70V, 0.75V, 0.80V, 0.85V and 0.90V. It was observed that there was no change in the oxidation/reduction peak potentials. This observation is a veiled pointer to both structural and entropic stability of the redox center/sites in the Top lemon.

3.2 Top lemon on Polyaniline Modified Electrode

Polyaniline was electrodeposited on the carbon graphite electrode by cycling the potential of the carbon-graphite electrode from -0.30V to 0.90V, at a scan rate of 20mv/s in a solution containing 0.1M Aniline and 1.0M Sulphuric Acid. The polyaniline electrode was then modified with Top lemon by dip coating and the resultant cyclic voltammogram is shown in Fig. 3.
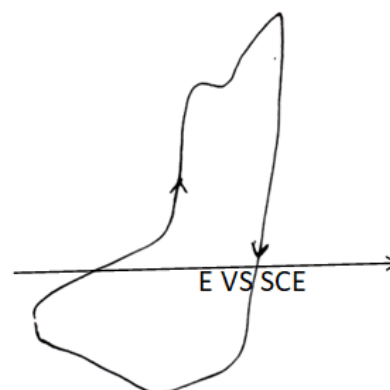

Fig. 3. Top-lemon on polyaniline electrode in electrolyte solution containing 1M sulfuric acid. Potential window: -0.3V to 0.9V. Scan rate 20mV/sec

It is observed that there are two oxidation peaks occurring at approximately 0.33V and 0.57V at a scan rate of 5mv/s. As the scan rate is increased, the oxidation peak potentials shift by approximately 100mv. On the other hand, there is only one reduction peak which occurs at 0.42V, at a scan rate of 5mv/s. Similarly, on varying the scan rate, the reduction peak shift towards negative potentials by approximately 100mv. This is not the same for the oxidation peak potential, which shifted positively as the scan rate was increased.

A plot of the anodic peak current, versus square root of scan rate, yielded linear plots with a correlation coefficient of 0.98. This implies that the process is diffusion limited as expected.

When the potential window of the Top lemon modified electrode was varied in a solution containing 1M Sulfuric Acid and 0.1M aniline, from -0.30V to 0.90V at a scan rate of 10mv/s from -0.30V to 0.70V, 0.75V, 0.80V, 0.85V and 0.90V at a scan rate of 10mv/s, it is observed that there is no change/variation in the oxidation/reduction peak. In the cyclic voltammogram the oxidation/reduction peak potentials for polyaniline occurs at 0.31V and 0.04V respectively, while the quinonic peaks associated with polyaniline appear at 0.53V and 0.40V respectively.

It was expected that, when the polyaniline electrode was modified with Top Lemon, and the potential cycled in the electrolyte solution, containing aniline, polyaniline will continue being electrodeposited. This was not the case, instead, an oxidation peak and a broad reduction peak are occurring at 0.39V and 0.15V respectively.

These results, when compared to the case of Top Lemon on bare carbon graphite, where oxidation and reduction peaks for the Top-lemon redox process occurred at 0.60V and 0.21V respectively, suggest that there was a significant alteration in both the polyaniline and Top lemon redox processes.It is proposed that this redox behavior is the result of the formation of a composite structure, where the redox centers of polyaniline and Top Lemon interact substantively. This assertion is based on the fact that if the structure was a bi-layer, then the polyaniline and Top lemon redox processes would have been independent of one another, /and or redox junctions characterized by charge rectification would have been observed.

Fresh polyaniline electrode was electrogenerated and further modified with Top lemon. This electrode was then transferred to various supporting electrolytes containing 0.1M, 0.25M, 0.5M, 1.0M and 2M Sulphuric acids (H_2SO_4). It is observed that as the [H⁺] is increased, the redox profile/faradaic processes improved leading to well defined reduction peaks. This improvement in the reduction peak profile as [H⁺] is increased mathematically mimics a homogenous function of 1st degree, where the factor ( )and the thermodynamic function is the potential of the redox center. This potential is related to the Gibbs function ($\Delta G = nFE$)

Therefore, applying the Euler Theorem;

$$\alpha n M = \sum_{i=1}^{n} \left(\frac{\partial M}{\partial n_i} \right)$$

Where n is the concentration of the redox centers, and M is the Gibb's free energy , α is a function of the redox potential, hence; correlates to the population of the redox centers. Further refinement yield

$$[H^+]nM - \sum_{i=1}^{n} n_i \bar{M}$$
$$[H^+]M = \sum_{i=1}^{n} \frac{n_i}{n} \bar{M}$$
$$M = \frac{1}{[H^+]} \sum_{i=1}^{n} X_i \bar{M}$$

Where,   is [H⁺] and X_i is the mole fraction of the identical redox centers, Hence,

$$M = \frac{1}{[H^+]} \sum_{i=1}^{n} \left(\frac{\partial M}{\partial n_i} \right)$$

Therefore, for the individual identical redox centers; 1, 2, 3, then…………etc.

$$M = \frac{1}{[H^+]} \left\{ X_1 \left(\frac{\partial M}{\partial n_1} \right) + X_2 \left(\frac{\partial M}{\partial n_2} \right) + X_3 \left(\frac{\partial M}{\partial n_3} \right) + - - - - - - \right\}$$

Note that, M Gibbs function is proportional to the redox potential and that it is assumed that the effect of $[H^+]$ on the faradaic processes is linear and the redox potential is assumed to be an average of the potentials of the many individual redox centers, i.e, bulk property.

In further experiments, the Top Lemon on PANI modified electrode had its potential cycled from -0.30V to 0. 90V in a solution containing 0.1 aniline and 1.0M Sulfuric acid. The electrode was subjected to a scan rate dependence studies, a plot of anodic peak current versus scan rate yielded a linear plot suggesting that, the Top Lemon is surface attached. This observation brings to light the influence of the polyaniline host matrix on the surface properties of Top Lemon. This is confirmed by the fact that, when Top Lemon is attached on bare carbon-graphite electrode, the redox process is diffusion-limited.

It is apparent from this dual behavior of Top-lemon that there is interaction akin to physical adsorption between the Top Lemon redox sites with those of polyaniline when the polymer is switched from the insulating to the conducting state.

This is further confirmed by the redox peaks observed in the cyclic voltammogram, which

displayed composite properties for both the polyaniline and Top Lemon. The composite oxidation and reduction potential occurred at 0.31V and 0.13V respectively.

When the Top lemon on polyaniline modified carbon-graphite electrode had its potential cycled from a constant 0.30V to varying positive potential limits (0.70V, 0.75V, 0.80V, 0.85V and 0.90V) in a solution containing 0.5M Sulfuric acid, there was no variation in the oxidation-reduction peak potentials [18-20].

In addition it is important to note that traditionally, PANI, when cycled to far positive potentials in acid solution, in the absence of aniline monomers electro-degrades to form Quinone-imine derivatives.

In this case, there was no evidence of electro-degradation of polyaniline despite being the host matrix. Therefore, it is possible that the presence of the Top Lemon inhibits or significantly reduces the oxidative stress in polyaniline hence slowing down the electro-degradation process.

3.3 Analysis on a Bentonite Modified Electrode

The carbon-graphite electrode was modified with bentonite as already discussed in the previous sections. The bentonite modified electrode was further modified with Top lemon and the potential cycled from -0.2V to 0.85V at a scan rate of 20mv/s in 1.0M sulphuric supporting electrolyte solution. The resultant cyclic voltammogram is as shown in Fig. 4.

We observe an oxidation peak at 0.58V and a broad reduction peak at 0.28V. The oxidation and reduction peak potentials vary with scan rate, suggesting a time dependent redox process. This is a veiled pointer to the instability of the Top lemon redox sites on the bentonite host matrix probably as a result of both structural and entropic effects.
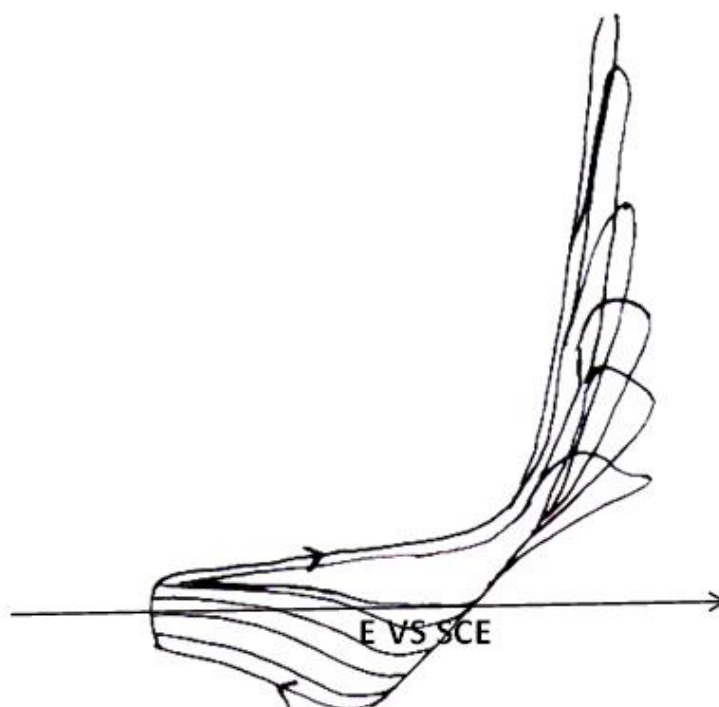

Fig. 4. Cyclic votammeric response of Top-lemon on a bentonite modified electrode in 1M sulfuric acid supporting electrolyte solution. Potential window: -0.3 V to 0.9V, scan rate 20mV /sec

4. CONCLUSION

The results presented in this paper, confirm the versatility of surface modified electrodes as an electro analytical tool in profiling the electrochemical activity of redox active moieties in Top-lemon cream.

The detection of quinone derivatives has traditionally been based on conventional chemical methods hence the detection of these derivatives using surface modified electrodes opens a new analytical frontier.

The use of host matrices such as electronically conducting polymers (polyaniline) and bentonite (clay montmorrilonite) and the resultant enhancement in the electrochemical signal associated with the redox moieties in the crèmes due to pre-concentration and a combination of structural and entropic effects in this host matrices is a plus in the use of surface modified electrodes in the Nano-detection of hydroquinone in cosmetic creams.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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