The application of cyclic voltammetry and digital simulation for the examination of hydroquinone oxidation at a polycrystalline gold electrode in HClO₄

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The electrochemical behaviour of hydroquinone was examined using cyclic voltammetry at a polycrystalline gold electrode in 0.5M HClO₄. The peak-to-peak potential separation (ΔE_p) has been found to be 489 mV *vs*. SCE. The results indicate that the reductive peak coupled with the oxidative peak of hydroquinone is absent due to the presence of a chemical step following the electron transfer. The relevant chemical and electrochemical parameters were determined experimentally via cyclic voltammetry. A Theoretical study via electrochemical simulation based on oxidation behavior has been performed for the cyclic voltammograms obtained on the surface of an Au electrode. The kinetic data extracted from cyclic volta-mmograms was confirmed and verified with the help of digital simulation. The homogeneous and heterogeneous rate constants were estimated by comparing the experimental cyclic voltammetric resp-onses with the digital simulated results. On the basis of the electrochemical behavior we proposed an ECE mechanism for the electrochemical oxidation of hydroquinone. Digital simulation was used also to confirms the proposed ECE pathway of electrode reaction.

1. INTRODUCTION

It was established that hydroquinone (H₂Q) is an essential phenolic substance that is extensively used as a necessary coarse materials in the medicine industry, agriculture, and organic chemicals, with others [1]. Hydroquinones are essential electro-active species in the principles of electro-chemical research. Current methods for the investigation of hydroquinone are the electrochemical methods. The electrochemical manner is greatly valuable because of its adaptability, uncomplicated operation, good computerization, and environmental rapport [2]. In electro-catalytic

paths, in which an electrode surface is an electrifying catalyst, divergent electrode materials can change the electroch-emical reaction rate by divergent values, so new and effective catalytic electrode materials have constantly been a target of related research.

In the situation of examination of the electrochemical features of hydroquinone in the existence of acid medium [3-5] we became receptive in knowledge the mechanism of electrooxidation of hydroquinone in HClO4. Examination of the hydroquinone-quinone (H_2Q-Q) system, which has been considered the classical redox reaction [6, 7]

This article reports the electrochemical examination of hydroquinone at the polycrystalline gold electrode in acid solution via cyclic voltammetry and digital simulation. This work focuses on the determination of the kinetic parameters such as k^o, E^o, D, α, and k_c experimentally via different relationships using cyclic voltammetry. The obtained kinetic parameters were confirmed using the digital simulation method.

2. EXPERIMENTAL

2.1. Chemical reagents

Analytical grade chemicals were used without further purification. Aldrich HClO4 and 1,4-hydroquinone (H_2Q) were bought from Aldrich. De-ionized water was captured from a water purification apparatus. N2 gas was used to remove O_2 from the electrolyte solutions.

2.2. Instrumentation

Electrochemical experiments were accomplished in a conventional three-electrode cell. A saturated calomel electrode (SCE) was used as the reference electrode. The working electrode (a 1 mm diameter polycrystalline Au disc electrode) was polished using 1 lm of alumina and cleaned with water. The cyclic voltammetry experiments were done at various scan rates in the range of 50–2000 $mV.s^{-1}$.

A Digital simulation of the data was run using techniques of finite differences via the EG & G condesim software package. The algorithms for the simulation software were coded and implemented into the condesim software package.

3. RESULTS AND DISCUSSION

3.1 Cyclic voltammetry behavior of hydroquinone

Examination of the cyclic voltammetry behavior of H_2Q at a conventional polycrystalline Au electrode has been carried out in 0.5M HClO$_4$ solution at various scan rates and at ambient tempe-rature. Figure 1 exhibits the cyclic voltammetry curves of 3 mM 1,4-hydroquinone at a 50 mV s^{-1} scan

rate in 0.5 M HClO₄. As indicated, the cyclic voltammogram revealed the presence of the oxidation peak (A) coupled with the reduction peak (B), which disappeared at low scan speed, and another peak (C) due to the reduction of the electroactive species resulting from peak (B). From the CV indicated in figure 1 it can be viewed that at conventional polycrystalline Au electrode the peak-to-peak potential separation between a peak (A) and peak (B) are in the range of 124 - 165 mV vs. SCE. So, according to Nicholson [8], the obtained behavior reveals that the hydroquinone loss of two electrons at a conventional polycrystalline working Au electrode is strongly a moderate fast of the rate of electron transfer.
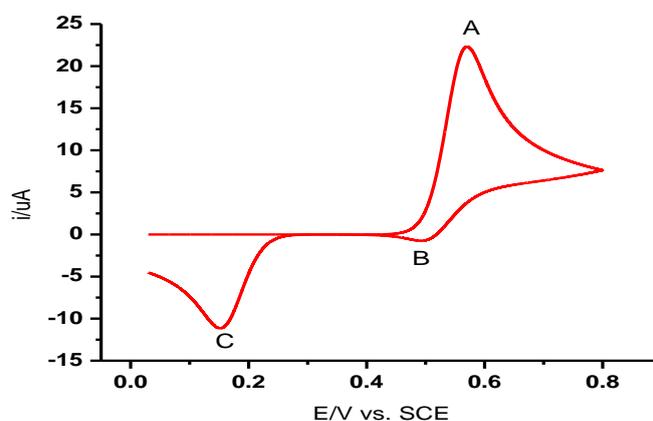

Figure 1. Cyclic voltammetry curve at a scan rate of 50 mVs⁻¹ for 3 mM hydroquinone in 0.5 M HClO₄ at a conventional polycrystalline Au electrode.

3.2. Effect of scan rate

Figure 2 indicates that the cyclic voltammograms of H2Q at different scan rates in 0.5 M HClO4 at a conventional polycrystalline Au electrode. It was noted that by increasing the scan rate the height of the oxidation peaks (A) and reduction peaks (B) increased and the peak separation between the forward oxidation peak (A) and backward reduction peak (B) increased. Also, it was observed that at a scan rate of 50 mVs⁻¹, the reduction peak (B) coupled with the oxidation peak (A) is absent, and at a scan rate greater than 50 mVs⁻¹, the reductive peak (B) appears and increases with increasing the scan rate.

This behavior confirms that the oxidative and reductive peaks of H2Q proceed as electron transfers followed by moderately fast chemical processes, i.e., the EC scheme. The peak (C) in the backward direction may be attributed to the reduction of the electro-active product. The cyclic voltammogram was recorded at two multiple scans to determine the nature of peak (C). Figure 3 displays an example of the H2Q at multi scan, which indicates the appearance of the oxidative peak (D) coupled with the peak (C). This behavior confirms the presence of simple electron transfer following the chemical process, i.e., ECE mechanism.
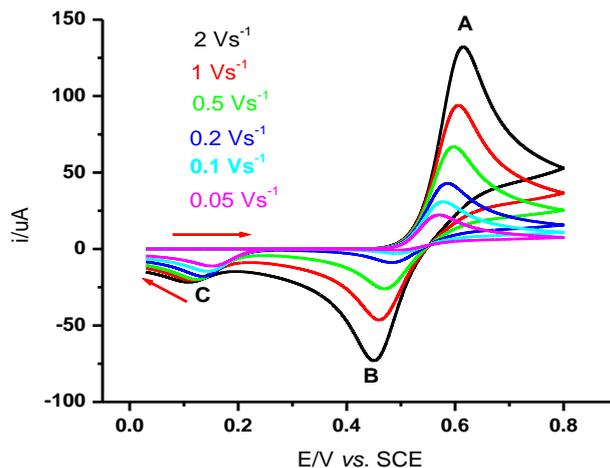
Figure 2: Cyclic voltammograms of H_2Q at in 0.5 M $HClO_4$ at various scan rates on a conventional polycrystalline Au electrode.
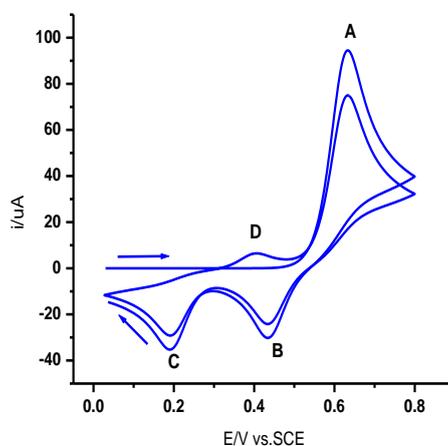

Figure 3: H_2Q Cyclic voltammograms at 1000 mVs^{-1} and two cycles in 0.5 M $HClO_4$ at a conventional polycrystalline Au electrode

Fig. 4A shows a linear relationship between i_p *vs.* the square root of the scan rate ($\upsilon^{0.5}$) over the whole range of 50 –2000 $mV.s^{-1}$, strongly suggesting that the redox reactions of H2Q are diffusion-controlled [9]. Plots of log i_p *vs.* log *v* have a slope close to 0.5, confirming that currents were diffusion-controlled (Fig. 4B). On the other hand, oxidation and reduction peak potential values were dependent on the scan rates, indicating the shift of the oxidation peak (A) to a more positive potential and the reduction peak (B) to a less positive potential, supporting the electrochemical processes of quasi-reversible character of the compound under consideration in the selected medium [10].
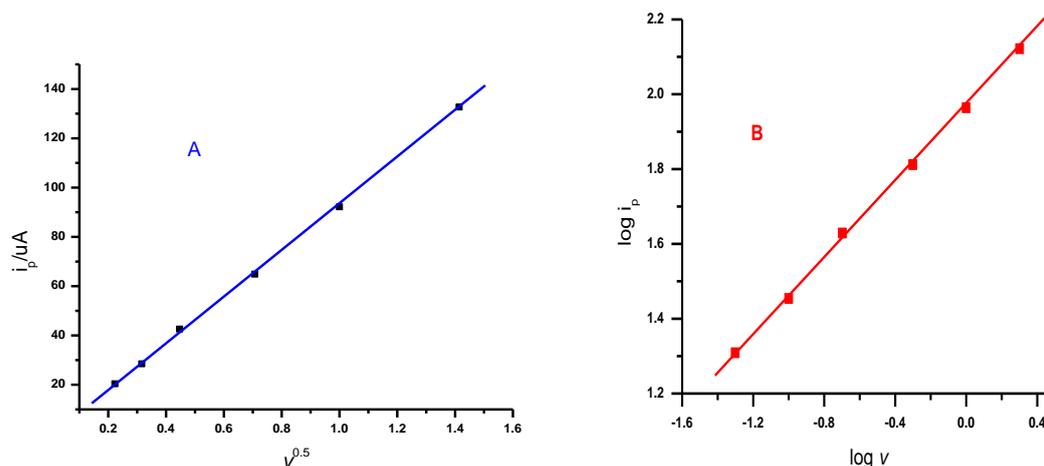
Figure 4. Linear relationship of i_p *vs.* $v^{1/2}$ of Fig. 3 (A); log i_p *vs.* log v (B).

Across time, there has been a small variance in terms of experimental calculation of the k^0 of an existing system. The predominant general method for the measurement of k^0 is cyclic Voltammetry (CV). Electrochemists generally use the methods established by Nicholson [11-13] for estimation of the k^0 values for the electrode reaction. A typical process is to investigate the peak-to-peak potential separation, ΔE_p (see Fig. 2) of a redox couple as a function of scan rate in a quasi-reversible system. This is achieved by constructing the working curve. The Nicholson method presents the dimensionless parameter, ψ, which is graphed opposite to the peak-to-peak potential separation, ΔEp, for a given scheme to generate a working curve. The dimensionless parameter thus shows electrochemical fastness (where ψ =20, the system is fast; where $\psi \leq 7$, the system is moderately fast) and is fitted to ΔEp to study electrochoemical regimes [8]. According to equation (1) established by Nicholson, the k^o value was determined and listed in table 1.

$$\psi = k^0 [\pi DnFv/RT]^{-0.5} \tag{1}$$

Where D is the diffusion coefficient of the hydroquinone materials, n is the number of electrons transferred in the electrochemical reaction, F is the Faraday constant, R is the molar gas constant, T is the absolute temperature, and π is a mathematical constant approximately equal to 3.14159. Equation (1) can be written in the following form:

$$\psi = k^o Z \tag{2}$$

where Z is equal to $[\pi DnFv/RT]^{-0.5}$.

As indicated before, the peak–to-peak potential separation, $\Delta E_{p'}$ is noticed to increase when the scan rate increases, indicating and confirming a moderate fast of the rate of electron transfer as a result of the rate of mass transport being approximately equal to the rate of electron transfer. In the case of the hydroquinone, the ΔE_p of 124 mV at a scan rate of 100 mV.s^{-1} increases to 165 mV when the scan rate is increased to 2000 mV.s^{-1}. Figure 5 displays the variation of peak separation with scan rate. These increases in peak separation with increasing the scan rate are transformed into ψ values, which are graphed against $[\pi DnFv/RT]^{-0.5}$ as shown in figure 6. The slope is then equal to k^0 as in Equation

(1); accordingly, the calculated value of k^o is equal to 3.18×10^{-3} cm.s^{-1} for the investigated hydroquinone species.

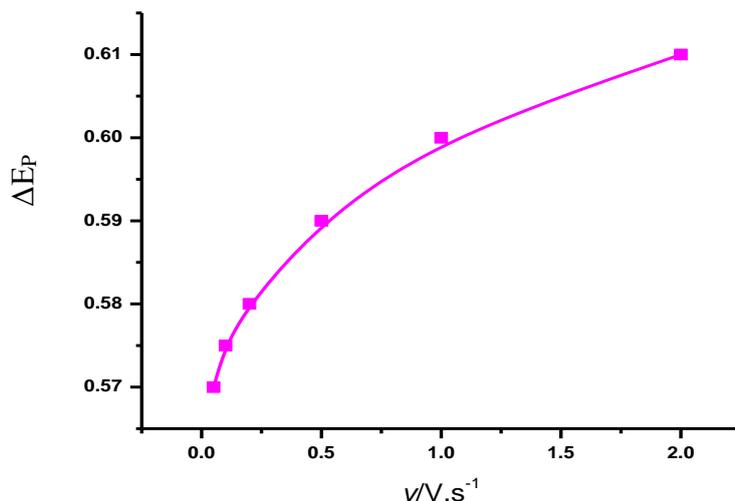**Figure 5:** Extracted from Figure 2, a plot of ΔE_p versus scan rate of hydroquinone at a conventional polycrystalline gold electrode in 0.5M HClO$_4$.
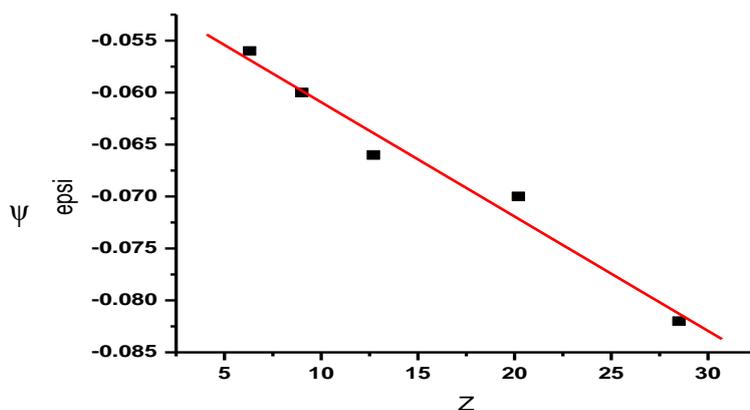

Figure 6 shows a plot of ψ versus Z of hydroquinone at a conventional polycrystalline gold electrode in 0.5M HClO$_4$

The value of the transfer coefficient was determined from the relationship (3) and is listed in table 2. Fig.7 and table 2 show the variation of $E_p - E_{p/2}$ with the scan rate. As indicated in table 2, the

$$E_p - E_{p/2} = 48/\alpha n_a \qquad (3)$$

magnitude of the half-peak width ($E_p - E_{p/2}$) increases with increasing scan rate. Also, the magnitude of the transfer coefficient reflects and confirms the moderate speed of electron transfer. Again, the magnitude of the ratio of the backward peak current (i_{pb}) divided by the forward peak current (i_{pf}), i.e., (i_{pb}/i_{pf}) is less than unity, confirming that the presence of electron transfer is followed by chemical step.

Table 1 Summarises the kinetic parameters of the electrooxidation of hydroquinone using cyclic voltammetry and digital simulation at a conventional polycrystalline Au electrode.

Parameters/ method	Technique		
	CV		Digital simulation
$k_s x 10^{-3}$ (cm.s^{-1})	3.40[a]	3.80[b]	3.50
α	0.32		0.38
E^o			
$D x 10^5$ (cm^2.s-1)	4.71[c]	5.26[d]	5.21
k_c (s^{-1})	---	---	0.89

(a) Value calculated from working curve, (b) calculated from equation (2), (c) calculated from equation (5), and (d) calculated from equation (6)

Table 2. Summarizes the values of the wave parameters of the electrooxidation of hydroquinone at various scan rates.

Scan speed (mV.s^{-1})	i_p/uA	$E_p - E_{p/2}$ /mV	ΔE_p/mV	i_{pb}/i_{bf}
100	28.5	31	124	0.23
200	42.6	46	132	0.35
500	64.9	57	141	0.49
1000	92.2	68	153	0.61
2000	132.7	74	165	0.71
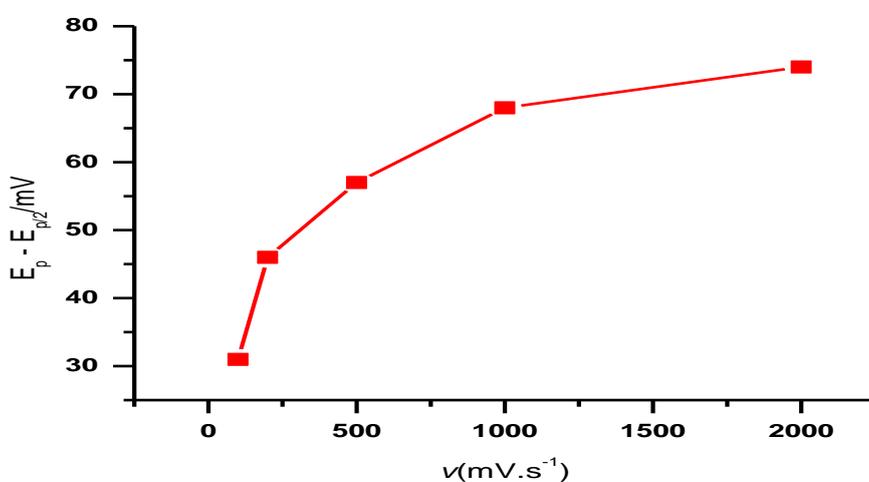
Figure 7. Plot of half-peak width (E_p-$E_{p/2}$) *vs.* scan speed of H$_2$Q at a conventional polycrystalline Au electrode in HClO$_4$.

As mentioned before, the peak current is seen to grow regularly according to the following Randles-Sevcik equation for a quasi-reversible reaction:

$$i_p = \pm 2.99 \times 10^5 n (\alpha n_a)^{1/2} AC^b D^{1/2} \upsilon^{1/2} \qquad (4)$$

where i_p is the peak current, and n, F, D, A, C, υ, R and T have already been defined. The value of the diffusion coefficient (D) was determined via eq. (4) from the slope of the i_p vs $v^{1/2}$ plot. The calculated value of D was listed in table 1. Equation 4 can be written in the following form [13]:

$$i_p = 3.099 I_{lim} (\alpha na)^{1/2} \upsilon^{1/2} \qquad (5)$$

where $I_{lim} = nFAC^b D^{1/2}$, n, F, D, A, C, υ, R and T have been illustrated before, α is the transfer coefficient and n_a is the number of electrons participating in the rate determining step. Accordingly, I_{lim} can be determined from eq. (5) as indicated in eq. (6):

$$I_{lim} = i_p / 3.099 (\alpha na)^{1/2} \upsilon^{1/2} \qquad (6)$$

So, the magnitude of the diffusion coefficient can be calculated by a combination between I_{lim} and i_p via eq. (6). The determined values of the diffusion coefficient from the above equation are listed in table 1.

3.3. Digital simulation

Digital simulation based on finite difference closeness has proven to be an excellent means for numerical explanation of electrode processes. The most extensively used implicit technique is the method of Crank-Nicolson [14], which is thoroughly stable. The considerable advantage of this method is that it can be used for many parameters with a significant decrease in accuracy. This means that rapid homogeneous chemical reactions that are paired with the charge transfer step can be measured without limitation. Wonderfully, applications of the Crank-Nicolson technique to electro-chemical problems are rare. The main purpose is that the suitable installation of the boundary conditions may generate some difficulties. This is particularly striking in the case of cyclic voltammetry, one of the most approved dynamic methods, of which only a few examples are illustrated in the literature [15, 16]. To overcome this disadvantage, we have used the condesim software package, which allows the implicit simulation of voltammetric curves with high accuracy.

Accordingly, to confirm and verify the nature of the electrode reaction for the electrochemical oxidation of hydroquinone at a gold electrode in 0.5M $HClO_4$, the data obtained from cyclic voltammograms has been tested by a commercial theoretical CONDESIM software programmed [17] to find the good-fit between experimental and theoretical cyclic voltammograms. The simulation was carried out assuming semi-infinite diffusion and planar electrode geometry. The parameter of the homogeneous chemical rate constant, k_c, was allowed to change through simulation of the cyclic voltammogram until a well-fitting between the theoretical and experimental cyclic voltammogram was obtained.

Based on the above, the digital simulation method is an important and successful tool for obtaining the kinetic parameters theoretically [18]. Accordingly, the electrochemical oxidation of hydroquinone in the present article was suggested and approved with the aid of diagnostic criteria for cyclic voltammograms. The transfer coefficient (α), diffusion coefficient (D), standard redox potential, and

the heterogeneous rate constants (k°) for the electrode process were estimated by the experimental methods then tested via digital simulation [19]. The best fit between experimental and theoretical curves consists of finding the electrochemical parameters that exhibit the minimum differences between the simulated and experimental data [10-21]. As shown in Figure 7, there is a good match between the theoretical and experimental voltammograms, confirming the accuracy of the elect-rochemical parameters calculated experimentally as well as knowing the nature of the mechanistic pathway, which suggests proceeding with the ECE scheme.
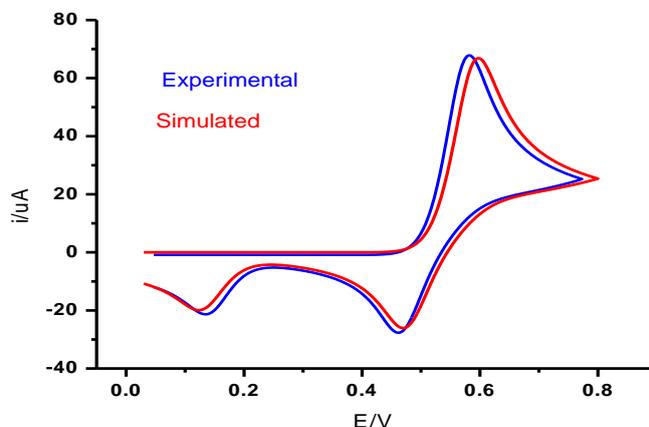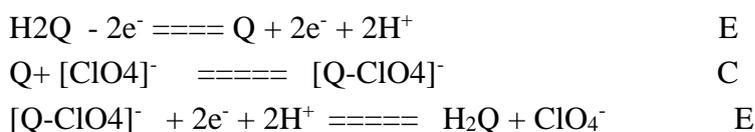

Figure 7. Experimental and Simulated and cyclic voltammograms of H_2Q at an Au electrode in 0.5M HClO4 and 500 mV.s^{-1}

So, the mechanism of electro-oxidation of hydroquinone in $HClO_4$ can be suggested to proceed as:

$$H2Q \ - 2e^- ==== Q + 2e^- + 2H^+ \qquad\qquad\qquad E$$
$$Q+ [ClO4]^- \ \ ==== \ [Q\text{-}ClO4]^- \qquad\qquad\qquad\qquad C$$
$$[Q\text{-}ClO4]^- \ + 2e^- + 2H^+ ===== \ H_2Q + ClO_4^- \qquad\quad E$$

5. CONCLUSION

The redox behavior of hydroquinone was investigated and demonstrated on a conventional gold electrode. The oxidation and reduction peak separation (ΔE_p) has been found to be in the range of 124 to 165 mV, indicating a moderately fast rate of electron transfer. Also, at low scan rate, the reductive peak coupled with the oxidative peak is absent and only appears at high scan rate. From cyclic voltammetry and digital simulation analyses, the electrode reaction was suggested to behave as an ECE process.

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