Journal of New Materials for Electrochemical Systems 20, 025-030 (2017)
© J. New Mat. Electrochem. Systems

Electrochemical Behavior and Convoluted Voltammetry of Carbon Nanotubes Modified with Anthraquinone

Mohamed A. Ghanem[1,*], Ibrahim S. El-Hallag[2] and Abdullah M. Al-Mayouf[1]

[1]Electrochemistry Research Group, Chemistry Department, College of Science, King Saud University,
Riyadh 11451, Kingdom of Saudia Arabia
[2]Chemistry Department, Faculty of Science, Tanta University, Tanta, Egypt

Received: August 23, 2016, Accepted: January 15, 2017, Available online: April 23, 2017

Abstract: *The validity of convolution voltammetry for determination accurate values of diffusion coefficient (D) and electrons number (n) consumed in electrochemical reaction has been explained by applying the technique to a carbon nanotubes chemically modified using functional groups of anthraquinone(AQ). The analysis with macrodisk electrode was facilitated due to the presence of minor contribution of nonfaradaic current, so moderate values of sweep speed can be used without subtraction of residual current to quantify the diffusivity of electro-active species.The values of D and* nC^b *were determined simultaneously and demonstrated using convoluted procedure. The obtained results indicate that the convolution voltammetry provides advantages over constant state methods (plateau) such as micro-disk electrode voltammetry and rotating disk electrode voltammetry, as it is not limited by the method of diffusion (planar or radial), which remove the limitations of solvent viscosity, geometry of electrode, and voltammetric sweep speed.*

Keywords: Convolution voltammetry, diffusion coefficient, digital simulation, heterogeneous rate constant

1. INTRODUCTION

Electrode surface modification is widely used to overcome the slow kinetics and to reduce the overvoltage of many electrochemical processes. Carbon nanotubes (CNTs) represent an important class of nanomaterial that having high surface area, unique electronic properties, substantial mechanical strength and good chemical stability. Therefore carbon nanotubes were extensively investigated and modified with a variety of organic functionality for application of modified electrodes [1-5]. Electron mediators used in modified electrodes are important because they are significantly reducing the overpotential required for electro-oxidation of the substratein addition of improving the sensitivity and selectivity of the sensor signal.Adaptable path to attach monolayers of organic compounds covalently with different functionality to the surfaces of GC and CNTs was described by Ghanem *et al.*[6-9] via a collecting of solid phase synthesis and electrochemical grafting [10]. There is no any study carried out on convolution voltammetry at electrodes modified with organic functional groups such as anthraquinone (AQ)). So, in this article we explain and discuss the convolution voltammetryof AQ chemically attached to the surface of CNTs and making precise and low cost analytical method for the determination of the diffusion (D), concentration in the bulk (C^b), and number of electrons (*n*) consumed in the electrochemical reaction.

2. EXPERIMENTAL

NanoLab (Boston,MA) provides a multiwall carbon nanotube (CNTs) which consist of multiple rolled layers (concentric tubes) of graphene with diameter of 20 – 30 nm of bamboo like structures. Potassium ferro-cyanide was bought from Aldrich. The synthesis of other chemicals were described and established in literatures [10].The immobilization of the 4-(N-Boc-aminomethyl) spacer into the exterior of the CNTs was carried out via the reduction of the corresponding $C_6H_4CH_2NHBoc$ diazonium salt chemically at 25 and 60 °C through treating 100 mg of CNTs in acetonitrile solution which containing 10 mM of 4-(N-Boc-aminomethyl) benzene diazonium tetra fluoroborate. The mixtures of the reaction were kept under reflux overnight with constant stirring. Then, the filtration of solution was carried out and followed by washing of the CNTs under consideration with ethanol, acetone, and finally

---

*To whom correspondence should be addressed: Email: mghanem@ksu.edu.sa
Phone: :+996 0114670405

with water, and dry in the oven at 40 °C. For the elimination of the Boc-group, the linker modified CNTs were treated with 4.0M HCl in solution of dioxane for one hour and under stirring at ambient temperature.The separation of CNTs were performed via centrifuge and washing with DMF, ethanol and triple distilled water respectively. The AQ functional group attachment, the perpetration of the electrodes and the experiments of electrochemical reaction were performed as explained in literatures [6-10]. Modified CNTs was loaded on GC electrode by immersing 2.0 mg of CNTs in DMF solvent (1.0 ml) using ultrasonic agitation; a micropipette was used for casting an aliquot of CNTs suspension on the GC (geometric area =0.070 cm^2) electrode and left to dry at ambient temperature.

3. RESULTS AND DISCUSSION

In case of simple electron transfer process for species A, the expression of Fick's Second Law is describes as:

$$[\partial C_A/\partial t]_x = D_A[\partial^2 C_A/\partial x^2]_x \qquad (1)$$

The above equation may be solved at the electrode to gives

$$I_1(t) = (C_A^{\,b} - C_A(t)).[\ nFAD^{1/2}A] \qquad (2)$$

The electrode area is represented by the symbol A and I_1 is, termed the semi-integral current symbolized by I_1 and is defined as:

$$I_1(t) = \pi^{-1/2}\int_0^t [i(u)/(t-u)^{1/2}]du \qquad (3)$$

As shown the $I_1(t)$ contains the diffusional and current part i(u) from t=0 and reduces the contributions to $I_1(t)$ by scaling each current segment i(u) by a factor dependent on the time interval (t-u). Also it follows that under condition of pure diffusion-controlled [i.e., $C_{(0,t)\,=\,0}$], $I_1(t)$ exhibits its limiting value, $I_{\lim}$:

$$I_{\lim} = nFAC\sqrt{D} \qquad (4)$$

Therefore the convolution convert the cyclic voltammogram (i–E) shape to a S shape I(t) –E curve which exhibits a steady-state plot and in some cases is more adjustable for data analysis [11-14]. In addition the sluggish of heterogeneous kinetics or R_u do not affect the magnitude of the $I_{\lim}$ plateau of a steady-state cyclic voltammogram.

The evaluation of the convolution integral $I_1(t)$ was carried out via the following algorithms[15 -26]:

$$I(t) = I(k\Delta t) = \frac{1}{\sqrt{\pi}} \sum_{j=1}^{j=k} \frac{\Gamma(k-j+1/2)}{(k-j)} \cdot \Delta t^{1/2} i(j\Delta t) \qquad (5)$$

At equally spaced time intervals of Δt the current is symbolized by $I(j\Delta t)$ and $\Gamma(x)$ is the Gamma function of x.

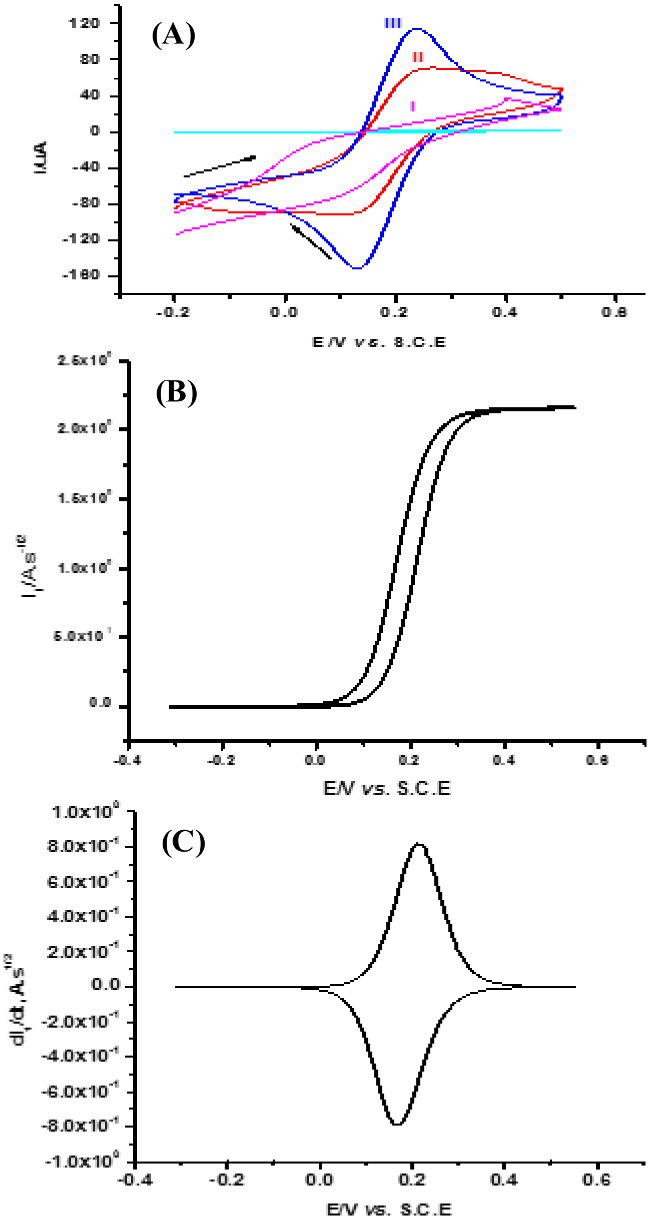

Figure 1. (A). Cyclic voltammograms at 50 mV s^{-1} in 5.0 mM Fe(CN)$_6^{4-}$ and 0.1 M KCl for (i) modified CNTs with –$C_6H_4CH_2NHBoc$ linker at 60 °C overnight. (ii) as in (i) at 25 °C, (iii) bare CNTs, 1(B) Convoluted voltammetry of curve (iii), (C) Deconvolution voltammetry of (iii) at 50 mV s^{-1} in 5.0 mM Fe(CN)$_6^{4-}$ and 0.1 M KCl in case of bare CNTs.

3.1. Applications of Convolution Voltammetry

3.1.1. Electro-oxidation of $K_4Fe(CN)_6^{4-}$ in 0.1 M KCl at modified CNTs

The converting of cyclic voltammetry data to convolution is benefit in the investigation of the adsorption at the modified electrodes because the processes of adsorption and diffusion controlled redox reactions occur at the same potential or near the same potential [27]. An S-shaped curve is obtained by Semi-integration of current, $I(t)$, of the peaked shape i–E curve CV. The forward and backward direction of $I(t)$ curves reach limiting values and completely overlay in case of fast electron transfer reaction. On the other hand, sweeping the potential in both forward and reverse direction produce $I(t)$ curves reach a limiting value, but do not overlay. This demonstrate the presence of quasi-reversible elec-

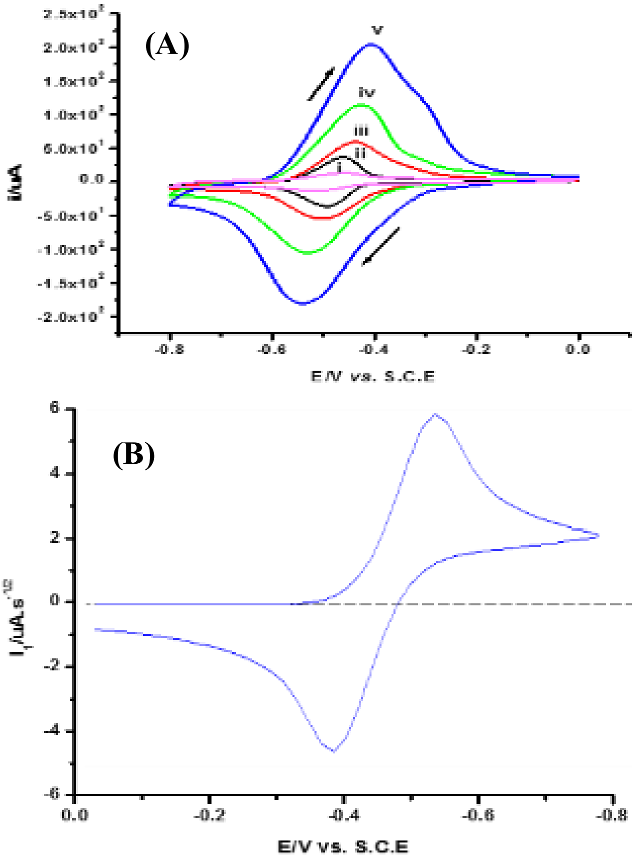

Figure 2. (A) i – E plots at 50 mV s^{-1} for AQ modified CNTs through linker $–C_6H_4CH_2NH–$, deposits of 2, 5, 6, 10 & 20 µL dispersion in 0.1 M of PBS (pH = 7), (B) $I_1 – E$ of curve (iii)

trode reaction, due to the shift of the reductive and oxidative peak potentials from their reversible values [28]. The appearance of a peak on top of the S-shaped *I*(*t*) curve [29-31] indicate the presence of adsorption of electroactive species at the electrode surface, hence, the redox species which exhibits adsorption at an electrode can be distinguish even when their redox potential is near or at the redox potential of diffusing species. Fig. 1A shows the cyclic voltammograms of $C_6H_4CH_2NH$-Boc linker modified CNTs $Fe(CN)_6^{4-}$while the plots of the I(t) convolution of the current versus potential are shown in Fig. 1B . The resultant curves in Fig. 1B are typical of semi- integral plot and the semi-differential curve for quasi-reversible systems under semi-infinite diffusion conditions is shown in Fig. 1C [32].

Table 1. Values of adsorption parameters at 50 mV s^{-1} in 0.1M of PBS at pH = 7 for modified CNTs with AQ through $–C_6H_4CH_2NH–$ linker at various amount of , deposits dispersion.

CNTs loading /µl	$i_{p/uA}$	Γ,mol.cm^{-2}	ΔE_p, mV
2	15	1.8e-5	32
4	25	8.3e-5	41
5	50	1.66e-4	63
10	100	3.3e-4	104
20	190	6.3e-4	136

The peak separation in Fig.1A was found to be 90 mV indicate and confirm the moderate fast of electron transfer rate. It was noted that the height of the peak is decreased slightly and the peak become broad. When the CNTs modification performed at 60 °C (curve i) the peaks are completely vanished and the voltammogram exhibits steady shape more like blocked electrode response.

Fig. 2A shows the i – E plot at 50 mV s^{-1} in 0.1 M solution of phosphate buffer (PBS) at neutral pH, for various amounts of the CNTs modified AQ. The data show that at 2.0 µl capacity, the redox peaks potential of AQ at a formal potential of 480 mV(±10 mV) and with a peak separation of 70 mV (±5 mV). It was observed that when the amount of AQ modified CNTs loaded on the GC electrode increases, the peak current of i-E plot increased linearly. Moreover, as the amount of modified CNTs increases the redox peak separation (ΔE) increases (Table 1) [10 -12].

Also, the increasing of peak separation more than 15 mV demonstratesthe deviation of the rate of electron transfer from Nernstian behavior [31]. The obtained results are shown in table 1.

For adsorption process the equation (6) can be used for the diffusion coefficient calculation assuming adsorption process follow Langmuir-type with a non-compact monolayer film of the adsorbed molecules on the exterior of the electrode (Table 2) [33].

$$i_p = 1.06 \times 10^6 n^2 ACvD^{1/2} t_p^{1/2} \qquad (6)$$

where t_p is the time of adsorption between the starting of the drop life to E_p position . The other parameters have their normal definitions.

Laviron equation was used for estimation the transfer coefficient (α) and apparent rate constant (k_{app}) for surface immobilized anthraquinone [14] by presentation the separation of peaks location (ΔE_p) against the logarithmic of scan rate. The apparent transfer coefficient could be determined using the peak half-width ,W ,$^{1/2}$ according to the following relationship [14]:

$$\alpha n = 2.44RT/W^{1/2}F = 62.5/W^{1/2} \qquad (7)$$

The average peak half-widths for more than 10 measurements were 65.6± 0.04 mV. From this value, an αn value of 0.952 was determined. If the value of α was assumed to be 0.48, then a value

Table 2. kinetic parameters obtained from Cyclic voltammograms, convolutive voltammetry and digital simulation at 50 mV s^{-1} in 5.0 mM $Fe(CN)_6^{4-}$ and 0.1 M KCl bare CNTs with AQ through $–C_6H_4CH_2NH–$ linker.

Species	D, $cm^2.s^{-1}$	k_s, cm.s^{-1}	α	E^0 V
$Fe(CN)_4^{-2}$	$4.71x10^{-6a1}$ $4.16x10^{-6b}$ $4.54x10^{-6c}$	$6x10^{-3a}$	0.48	0.182^a 0.187^b 0.185^c
AQ–linker, deposits of 20 µL dispersion	$2x10^{-6\,a1}$ $2.1x10^{-6c}$	$3.2x10^{-3d}$ $3.5x10^{-3e}$	0.50^d	-0.471^d -0.478^{a1} -0.472^b -0.475^c

a1: Cyclic voltammetry, a: Eq. (7), b: Convolution, c: Deconvolution, d: simulation, e: Eq. (10)

for n of 2 was obtained.Within the rising portion of the CV, the current values, I, at each potential, (E) were used to calculate the apparent electron transfer rate constant using the following equation:

$$k_{app}(E) = I(E) / nFAC \tag{8}$$

where A is the geometric area of electrode surface and C is the bulk concentration of substrate. The apparent standard rate constant of electron transfer rate constant value ($k^0_{CV},^{mono} = 6x10^{-3}$ cm.s^{-1}) for $Fe(CN)_6^{4-}$ was obtained from extrapolation of the Tafel linear variation of log $k_{app}(E)$ with the electrode potential, E, to the standard oxidation potential (E/E^0).The anodic and cathodic branches symmetry shown in Fig. 2A was confirmed from the values of electron transfer coefficient (α) which found to be nearly equals 0.5.

To estimate αn and *k*s values, Laviron's equation [31] was used:

$$E_p = E^{0'} + (RT/\alpha nF)\,[\ln (RTk_s/\alpha nF) - \ln \upsilon] \tag{9}$$

with α is the symmetry coefficient of charge transfer, the symbol *k*s is the standard rate constant of the surface reaction, υ is the sweep speed, *n* is the number of electrons transferred and E^0 is the standard potential. *k*s and α*n* values was determind from the intercept and slope of the linear plot of E_p *vs.* ln υ. The obtained values of α*n and ks were found* 1.08±0.04 and *k*s =3.425 s^{-1}respectively. For a totally irreversible electrode reaction, α was assumed as 0.5, the value of n was calculated to be 2.14 which explain that two electrons was consumed in the electrode reaction.

The electron transfer rate constant (*k*s) of electrode reaction at modified electrode was calculated according to the equation (10) below, taking a charge transfer coefficient α of 0.5, and a scan rate of 50 mV s^{-1}. The determined value of k_s was listed in table 2.

$$\begin{aligned} Log\ ks = {} & \alpha\log (1-\alpha) + (1-\alpha)\log\alpha - \\ & \log (RT/nF\upsilon) - [\alpha(1-\alpha)nF\Delta E_p/2.2RT] \end{aligned} \tag{10}$$

As shown in Fig.1B. the backward scan return to the initial current value, confirming the presence of moderate fast charge transfer rate, i.e.the pathway of the electrode proceeds as simple electron transfer.

From $I_1 - E$ curves the half-wave potential ($E_{1/2}$) was calculated according to the following equation

$$E_{1/2} = E_{i=0} - (RT/F) \ln [(I_{lim} - I_{i=0}) / I_{i=0}] \tag{11}$$

Where $E_{i=0}$ and $I_{i=0}$ are the potential and the current of convolution in case of passing the current i(t) through zero on the backward scan.

It was noted that, the i - E curve for a system approaching the behavior of thin layer [27] (i.e., where the condition of semi-infinite behavior is not satisfied) as indicated in Fig. 2A. The convoluted current does not exhibit the behavior of limiting value, and the resulting I vs E curve has the behavior of a diffusion-controlled cyclic voltammogramas shown Fig. 2B.

3.2. Deconvolution voltammetry

Deconvolution voltammetry is performed as semi-differentiation of the current (d I_1 /dt) with respect to the applied potential of reversible process is defined as [28 - 31]:

$$(dI_1/dt) = nFAC\sqrt{D}a\zeta / (1+\zeta)^2 \tag{12}$$

The symbols *a* and ζ is defined respectively as:

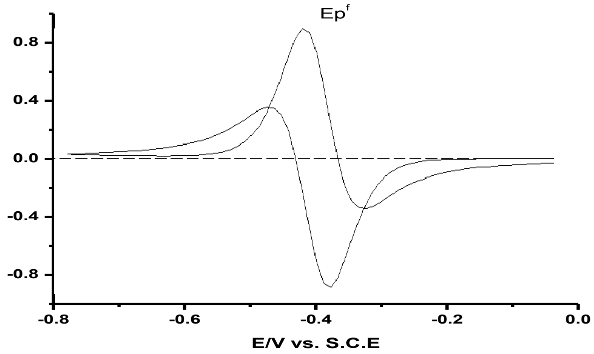

Figure 3. Deconvolution voltammogramat 50 mV s^{-1} in 5.0 mM$Fe(CN)_6^{4-}$ and 0.1 M KCl, at modified CNTs with AQ through $-C_6H_4CH_2NH-$ linker, deposits of 10 µL dispersion.

$$a = nvF/RT \tag{13}$$

$$\zeta = exp\ [nF/RT\ (E - E^0)] \tag{14}$$

The deconvolution voltammetry at *v* = 0.05 V.*s*$^{-1}$is represented and summarized in Fig.3. It was found that the width of deconvoluted peak (*w*p/2= 80) ± 2 mV), elucidating and supporting the moderate nature of electron transfer of the electrode reaction at CNTs which is slower than in case of absence AQ- linker.

The displacement of the maximum and minimum peaks of deconvolution gives strong evidence on the quasi-reversibility of electron transfer of the oxidative processes. The standard redox potentials were determined from the average value of maximum and minimum points of deconvoluted peak potentials (Table 2).The values of E^0 calculated from (dI_1/dt) *vs.*Fig. 3 compare well with the values calculated from cyclic voltammetry and I_1 convolution (Table 2).

The height of deconvolution peak was used for calculation the diffusion coefficient (*D*) via Eq.(15)[15 -17].

$$e_P = \frac{\alpha n^2 F^2 v C^{bulk} D^{1/2}}{3.367RT} \tag{15}$$

The symbol e_p is the height of the forward de-convolution peak (in ampere) and the remaining parameters have their known meaning. The determined values of the diffusion coefficient using Eq. (15) are cited in Table 2. Also from equation (16) the number of electrons involved in mechanistic pathway was calculated.

$$\begin{gathered} \mathrm{n} = \frac{e_P 3.367RT}{\alpha F v I_{\mathrm{lim},}} \\ n = \frac{0.086 e_P}{I_{\mathrm{lim}} \alpha v} \end{gathered} \tag{16}$$

The number of electrons, n, involved in the electrode reaction was calculated via Eq. (16), and found to be 2.11. As shown the above equation provides a successful, and simple method for determination of the number of electrons consumed in the electrode reaction without knowing the electrode surface area. From the above results it was noted that, the I_1*vsE* and *(dI_1/dt) vs E* curves were easier to elucidate, and confirm the nature of electrode reaction.

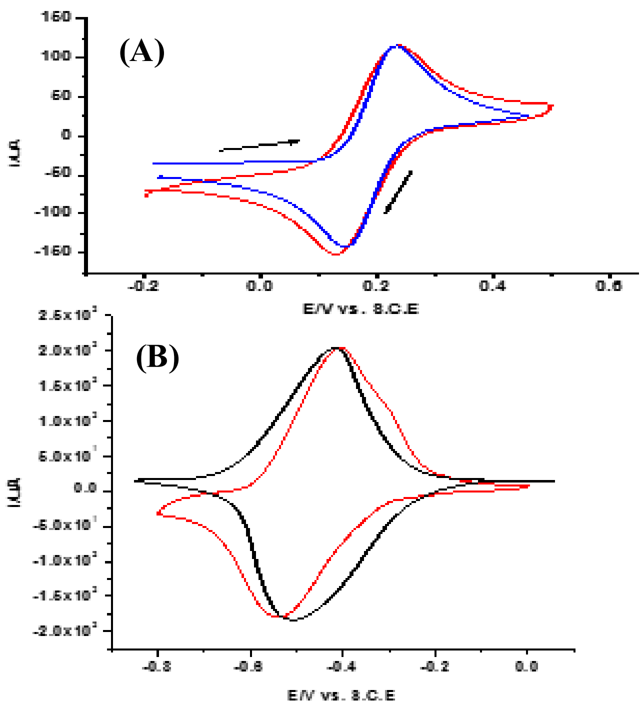

Figure 4. (A) Simulated (blue & black) and experimental (red) cyclic voltammograms of $Fe(CN)_6$ at CNTs, (B) for modified CNT with AQ through $–C_6H_4CH_2NH–$ linker, deposits of 20 μL dispersion.

3.3. Digital simulation

The electrochemical oxidation of $Fe(CN)_6^{-4}$ in the present study was proposed and approved by diagnostic criteria of cyclic voltammograms. Digital simulation method is considered as important and successful tool for obtaining the kinetic parameters theoretically [28]. According to the obtaining experimental data and assuming semi-infinite one-dimensional diffusion on a planar electrode the simple electron transfer was considered. The experimental parameters used in digital simulation software are the following: initial potential (E_i), reversing potential(E_r), sweep speed (v), half wave potential ($E_{1/2}$) and bulk concentration of species. The mid-point between the forward and backward peak (E_{mid})was used for evaluation the formal potential determined experimentally. The transfer and heterogeneous rate constants for electrode process were estimated by the experimental working curves were used for determination of the heterogeneous rate constants and the transfer coefficient (α) for anodic reaction[29,30].The best fit between experimental and theoretical curves consists of finding the electrochemical parameters which exhibit minimum differences between the digitally simulated and the experimental data[31]. As shown in Figure 4, there is good matching between the theoretical and experimental voltammograms confirming the accuracy of the electrochemical parameters calculated experimentally.

4. CONCLUSION

In the present article, glassy carbon electrode modified by CNTs was used to examine the behavior of $Fe(CN)_6$ at CNTs electrochemically. The electroactive surface coverage (Γ), apparent heterogeneous rate constant (k_{app}) , the transfer coefficient (α), standard rate constant (k_s) and diffusion coefficient (D) were calculated from cyclic voltammetric and convolution deconvolution voltammetry. The consistence between experimentally and theoretically obtained cyclic voltammogramsis used for confirmation the accuracy of the electrochemical parameters determined experimentally.

5. ACKNOWLEDGMENT

The authors would like to extend their sincere appreciation to the Deanship of Scientific Research at King Saud University for funding this Research group No: RG-1437-015.

REFERENCES

[1] M. E. G. Lyons and G. P. Keedey, Int. J. Electrochem. Sci., 3, 819 (2008).
[2] M. E. G. Lyons, Int. J. Electrochem. Sci., 4, 1196 (2009).
[3] M. R. Ganjali, A. Alipour, S. Riahi, B. Larijani and P. Norouzi, Int. J. Electrochem. Sci., 4, 1262 (2009).
[4] P. Norouzi, F. Faridbod, B. Larijani and M. R. Ganjali, Int. J. Electrochem. Sci., 5, 1213 (2010).
[5] H. R. Zare and N. Nasirizadeh, Int. J. Electrochem. Sci., 4, 1691 (2009).
[6] M.A. Ghanem, J.M. Chrétien, J.D. Kilburn, P.N. Bartlett, Journal of Materials Chemistry, 18, 4917 (2008).
[7] M. Chrétien, M.A. Ghanem, P.N. Bartlett, J.D. Kilburn, Chemistry - A European Journal, 14, 2548 (2008).
[8] M.A. Ghanem, J.M. Chrétien, J.D. Kilburn, P.N. Bartlett, Bioelectrochemistry, 76, 115 (2009).
[9] J.M. Chrétien, M.A. Ghanem, P.N. Bartlett, J.D. Kilburn, Chemistry - A European Journal, 15, 11928 (2009).
[10]M.A. Ghanem, I. Kocak, A. Al-Mayouf, M. AlHoshan, P.N. Bartlett, Electrochimica Acta, 68, 74 (2012).
[11]C.E. Banks, T.J. Davies, G.G. Wildgoose, R.G. Compton, Chemical Communications, 829 (2005).
[12]J.D. Watkins, K. Lawrence, J.E. Taylor, T.D. James, S.D. Bull, F. Marken, Electroanalysis, 23, 1320 (2011).
[13]K. Sadowska, K.P. Roberts, R. Wiser, J.F. Biernat, E. Jabłonowska, R. Bilewicz, Carbon, 47, 1501 (2009).
[14]E. Laviron, Journal of Electroanalytical Chemistry, 101, 19 (1979).
[15]Bowden; W. J.; J. Electrochem. Soc., 129, 124 (1982).
[16]E.H. Wong, R.M. Kabbani, Inorg. Chem., 19, 451 (1980).
[17]J. Galvez, Su. M. Park. J. Electroanal. Chem., 235, 71 (1987).
[18]A.J. Bard, L.R. Faulkner, Electrochemical Methods, Fundamentals and Applications, Wiley, New York, 1980.
[19]I.S. El-Hallag, A.M. Hassanien. Collect. Czech. Chem. Commun., 64, 1953 (1999).
[20]I.S. El-Hallag, M.M. Ghoneim, Monatsh, Chem., 130, 525 (1999).
[21]A.R. Seidle, L. Todd. J. Inorg. Chem., 15, 2838 (1976).
[22]R. Hettrich, M. Kaschke, H.Wadepohl, W. Weinmann, M. Stephan, H. Pritzkow, W. Siebert, I. Hyla-Kryspin, R. Gleiter, Chem. Eur. J., 2, 487 (1996).

[23]J. Bould, J.D. Kennedy, M. Thornton-Pett, J. Chem. Soc. Dalton Trans., 563 (1992).

[24]B. Stibr, J.D. Kennedy, E. Drdakova, M. Thornton-Pett, J. Chem. Soc. Dalton. Trans., 2335 (1993).

[25]G. Doetsch, Laplace Transformation, Dover, New York, 1953.

[26]K.B. Oldham, R.A. Osteryoung, J. Electroanal. Chem., 11, 397 (1966).

[27]R. Bowling, R.L. McCreery, Anal. Chem., 60, 605 (1988).

[28]A.J. Bard, L.R. Faulkner, Electrochem. Methods, John Wiley & Sons, New York, 1980, p. 236.

[29]D. Britz, Digital Simulation in Electrochemistry, Springer, Berlin, Germany, 2005.

[30]D. Nematollahi, A. Afkhami, F. Mosaed, and M. Rafiee, “Investigation of the electro-oxidation and oxidation of catechol in the presence of sulfanilic acid,” Research on Chemical Intermediates, vol. 30, no. 3, pp. 299–309, 2004. View at Publisher, View at Google Scholar, View at Scopus

[31]L. Khalafi and M. Rafiee, “Kinetic study of the oxidation and nitration of catechols in the presence of nitrous acid ionization equilibria,” Journal of Hazardous Materials, vol. 174, no. 1-3, pp. 801–806, 2010. View at Publisher, View at Google Scholar, View at Scopus

[32]J. Leddy, A.J. Bard, J. Electrolanal. Chem., 189, 203 (1985).

[33]J.A. Garrido, R.M. Rodriguez, R.M. Bastido, and E. Brillas, J. Electroanal. Chem., 324, 19 (1992).

[34]E. Laviron, J. Electroanal. Chem., 101, 19 (1979).