

1,2-Dichloroethane 내 백금 전극에서의 dicarboximide 레이저 염료에 대한 convolutive 순환 전압-전류법 연구

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(접수 2010. 6. 16; 수정 2010. 8. 16; 게재확정 2010. 11. 8)

Convolutive Cyclic Voltammetry Investigation of Dicarboximide Laser Dye at a Platinum Electrode in 1,2-Dichloroethane

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(Received June 16, 2010; Revised August 16, 2010; Accepted November 8, 2010)

요 약. N,N-bis(2,5-di-tert-butylphenyl)-3,4,9,10 perylenebis(dicarboximide) 레이저 염료에 대한 전기화학적 연구가 0.1 M tetrabutyl ammonium perchlorate(TBAP)/1,2 dichloroethane(CH₂Cl-CH₂Cl) 용액내에서 백금 전극을 이용하여 순환 전압-전류법 및 디지털 시뮬레이션 기술과 결합된 convolution-deconvolution 전압-전류법으로 수행되었다. 연구에 사용된 염료는 두 개의 전자를 순차적으로 소모하며 radical anion과 dianion으로(EE 메커니즘) 환원되었다. 전위를 positive scan으로 전환하면, 이 화합물은 두 개의 전자를 잃고 산화된 뒤 빠른 응집 과정(EC₁EC₂ 메커니즘)을 거치게 된다. 이 화합물의 전극 반응 경로, 화학 및 전기화학적 파라미터는 순환 전압-전류법과 convolutive 전압-전류법을 이용하여 측정되었다. 이렇게 구한 전기화학적 파라미터는 디지털 시뮬레이션 방법을 통하여 검증되었다.

주제어: 태양 전지, 전류-전압법, convolutive 전류-전압법, 디지털 시뮬레이션, 전기화학적 파라미터

ABSTRACT. The electrochemical investigation of N,N-bis (2,5-di-tert-butylphenyl)-3,4,9,10 perylenebis (dicarboximide) laser dye have been carried out using cyclic voltammetry and convolution - deconvolution voltammetry combined with digital simulation technique at a platinum electrode in 0.1 mol/L tetrabutyl ammonium perchlorate (TBAP) in solvent 1,2 dichloroethane (CH₂Cl-CH₂Cl). The investigated dye was reduced via consumption of two sequential electrons to form radical anion and dianion (EE mechanism). In switching the potential to positive scan, the compound was oxidized by loss of two electrons, which were followed by a fast aggregation process (EC₁EC₂ mechanism). The electrode reaction pathway and the chemical and electrochemical parameters of the investigated compound were determined using cyclic voltammetry and convolutive voltammetry. The extracted electrochemical parameters were verified and confirmed via digital simulation method.

Keywords: Solar cells, cyclic voltammetry, convolutive voltammetry, digital simulation, electrochemical parameters

INTRODUCTION

The bis(2,5-di-tert-butylphenyl) imide(DBPI) of 3,4,9,10-perylenetetracarboxylic dianhydride is a member of a class of vat dyes that intrinsically are strongly colored and have high fluorescence quantum yield.^{1,2} These properties make dyes such as DBPI potentially useful as photo sensitizers in energy and electron transfer reaction^{3,4} and in site-selective spectroscopy experiments with biological systems.^{5,6} Applications of perylene diimides as laser dyes and in p-n

heterojunction solar cells have already been demonstrated by Bird and co-workers.⁷

In order to evaluate the potential usefulness of dyes such as DBPI as photosensitizer, it is necessary to determine their photophysical properties and redox potentials. The bulky tert - butyl groups on DBPI dye make this dye relatively soluble in a number of organic solvents.⁸ DBPI dye was first prepared and studied by Rudemacher *et al.*⁹ and its large scale synthesis was more described by Langhals.¹⁰ The commercial product was probably a mixture

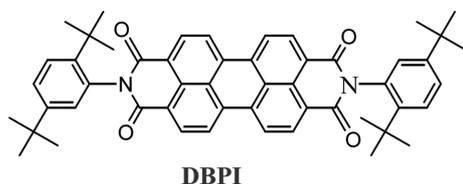
of cis and trans a tropic isomers, whose spectral properties are very similar.¹⁰ In addition to fluorescence properties of DBPI in solid state, kinetic and energetic properties of the singlet and triplet excited states have been examined.¹¹⁻¹⁶

Up till now no report on the electrochemistry of DBPI via cyclic voltammetry and convolution-deconvolution transforms at a Pt electrode in 1,2 dichloroethane solvent / 0.1 M TBAP. So, in the present manuscript we investigated the electrochemical behaviour of DBPI dye using cyclic voltammetry and convolution-deconvolution transforms. The chemical and electrochemical parameters were determined experimentally and verified theoretically via digital simulation method.

EXPERIMENTAL

Materials

N,N-bis(2,5-di-tert-butylphenyl) - 3,4,9,10 perylenebis (dicarboximide) laser dye (DBPI) and tetrabutylammonium perchlorate (TBAP) were of polarographic grade and used as supplied from Aldrich. Fresh solutions of DBPI (5×10^{-3} M) were prepared in fresh electrolyte solution (0.1 M TBAP/ $\text{ClCH}_2\text{CH}_2\text{Cl}$). All working solutions were thoroughly degassed with oxygen free nitrogen and a nitrogen atmosphere was maintained above the solution throughout the experiments. The investigated compound have the general formula:



Instrumentation

Cyclic voltammetry measurements were made using a conventional three electrode cell configuration linked to an EG & G model 170 PAR apparatus. The platinum electrode surface was 7.8×10^{-3} cm² as a working electrode, silver-silver chloride as a reference electrode, coiled platinum wire as a counter electrode and 0.1 mol/L tetrabutyl ammonium perchlorate (TBAP) as background electrolyte. Cyclic voltammograms were recorded after background subtraction and *iR* compensation to minimize double-layer charging current and solution resistance. The working electrode was polished on a polisher Ecomet grinder. Cyclic voltammetric data were obtained at scan rates ranging from 0.02 to 5 V/s in non aqueous media at 22 ± 2 °C. Digital simulation of the data for cyclic voltammetric experiments was carried out on a PC computer using EG & G condessim

package. Convolution- deconvolution voltammetry was performed using EG & G condecon software package.

RESULTS AND DISCUSSION

Electroreduction Process

Cyclic voltammetric behaviour: Cyclic voltammetry of the reductive process of 6×10^{-4} M of the laser dye compound DBPI was measured in solvent, 1,2-dichloroethane at scan rates ranging from 0.02-5 V/s. It was found that the peak current increases with increasing the scan rate, while the cathodic and anodic peak potentials of the reduction process were independent on scan rates values. From cyclic voltammetric investigation, it was found that, the cathodic reduction process of the investigated laser dye proceeds as fast charge transfer at all sweep rates. This behaviour demonstrates that the first charge transfer produces a radical anion which gains another electron to form a dianion in a reversible process. *Fig. 1* gives an example of the cyclic voltammogram at sweep rate of 0.1 V/s of the DBPI dye. As shown in *Fig. 1*, the first reductive peak (A) was coupled with the oxidative peak (D) in the reverse scan, while the second reductive peak (B) was coupled with the oxidative peak (C) in the backward sweep. The ratio of the backward peak to the forward peak ($i_{p,b}/i_{p,f}$) is equal to one for the two peaks, confirming the rapidity of the charge transfer rates. *Fig. 2* displays the cyclic voltammograms of sensitized solar cells DBPI compound at various scan rates. Inspection of *Fig. 2* revealed that, the reduction peak current, after elimination of the background current, is proportional to $v^{1/2}$, and the peak separation between the forward and backward peak potentials, ΔE_p (60 mV), is independent on the scan rate indicates the rapidity of charge transfer. Also, the measured values of peak width of

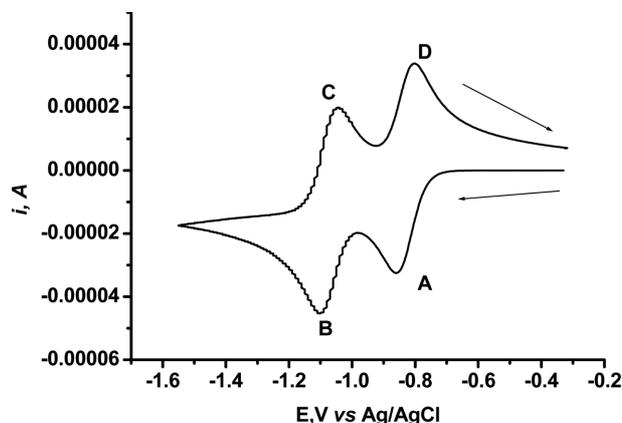


Fig. 1. Reductive cyclic voltammogram of 6×10^{-4} M of DBPI in $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}/0.1$ M TBAP at scan rate of 0.1 V/s.

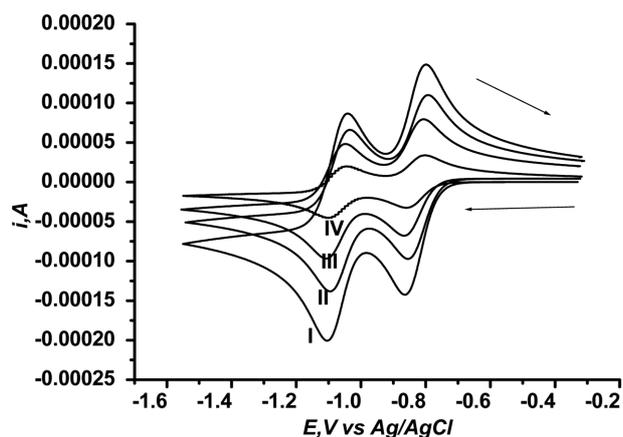


Fig. 2. Reductive cyclic voltammograms of 6×10^{-4} M of DBPI in $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$ / 0.1M TBAP at (I) scan rate of 2V/s, (II) scan rate of 1 V/s, (III) scan rate of 0.5 V/s, (IV) scan rate of 0.2 V/s.

the two waves, $E_p-E_{p/2}=56.5/n \text{ mV} \pm 2 \text{ mV}$, demonstrate that the reversibility behaviour of the investigated system, where E_p , $E_{p/2}$ and n are the peak potential, the potential at the half- peak height and the number of electrons consumed in electrode reaction respectively.

The redox potential (E^0) was determined from the mean position of the forward and backward peak potentials (Table 1). It was found that E^0_2 of the couple DBPI/DBPI⁻ shifts to more negative potential than E^0_1 . This behaviour demonstrates that the second reduction process needs high energy than the first one due to increasing the potential energy barrier of the second electron transfer. The standard heterogeneous rate constant (k_s) was determined from the generated cyclic voltammograms.¹⁷ From the plot of i_p vs. \sqrt{v} , the diffusion coefficient (D) of the electroactive species was determined.^{17,18} The calculated values of D were cited in Table 1. The results given in Fig. 3 employ the experimental and theoretical values of the electrochemical parameters of the DBPI dye, which demonstrate excellent agreement between the captured and the simulated data. The effect of the scan rate (v) on peak current (i_p) of the first peak for DBPI at a platinum electrode is shown in Fig. 4. Though the i_p - v relation is curved, the i_p - $v^{1/2}$ relation is lin-

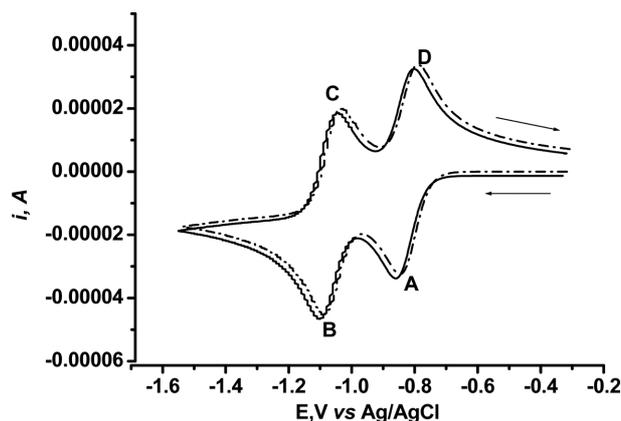


Fig. 3. Matching between reductive experimental voltammogram of DBPI dye (—) and simulated voltammogram (.....) at a sweep rate of 0.1 V/s.

ear, indicating that the current is diffusion-controlled.¹⁸

Convolutive transforms

In cases of straight forward electron transfer or subsequent chemical reaction, the I_1 convolution which is defined as:¹⁹⁻²³

$$I_1 = (1/\sqrt{\pi}) \int_0^t \frac{i(u)}{\sqrt{(t-u)}} du \quad (1)$$

allows to determine the diffusion coefficient of the bulk species from Eq. (2):¹⁹

$$I_{lim} = nFAC\sqrt{D} \quad (2)$$

where I_{lim} is the limiting value achieved for I_1 when the potential is driven to a sufficiently extreme value past the wave; the other terms have their usual significance. The values of the diffusion coefficients (D) corresponding to the reduction steps calculated via Eq. (2) were listed in Table 1. The I_1 convolution of the reductive voltammogram of DBPI at a scan rate of 0.2 V/s is indicated in Fig. 5. The I_1 convolution of the backward sweep is completely overlay on the forward one and return to zero, confirming the simple electron transfer and the rapidity of the charge transfer between electrode and electroactive dye DBPI, i.e

Table 1. Electrochemical parameters of the cathodic reduction processes of laser dye compound DBPI

$-E^{01}$ V	$-E^{02}$ V	$k_{s1} \times 10^3 \text{ ms}^{-1}$	$k_{s2} \times 10^3 \text{ ms}^{-1}$	$D_1 \times 10^9 \text{ m}^2 \text{ s}^{-1}$	$D_2 \times 10^9 \text{ m}^2 \text{ s}^{-1}$	α
0.830 ^a	1.075	2.70	3.20	4.10	4.76	---
0.832 ^b	1.075	2.80	3.40	4.91	4.85	0.5
---	---	---	---	4.66	4.50	---
0.835 ^d	1.075	---	---	4.23	4.54	---
---	---	---	---	4.16	4.62	---

^aExperimental values. ^bSimulated values. ^cValues of D calculated via Eq. (2). ^dValues of E^{01} & E^{02} calculated from Eq. (7) and values of D calculated from Eq. (6). ^eValues calculated from Cottrell plot.

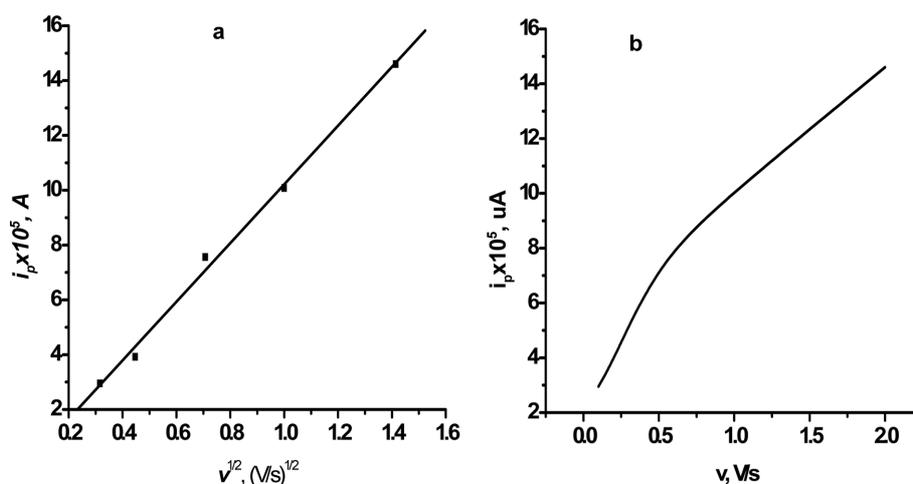


Fig. 4. Effect of scan rate (v) on the cathodic peak current (a) $i_p - v^{1/2}$ relations, (b) $i_p - v$ relations.

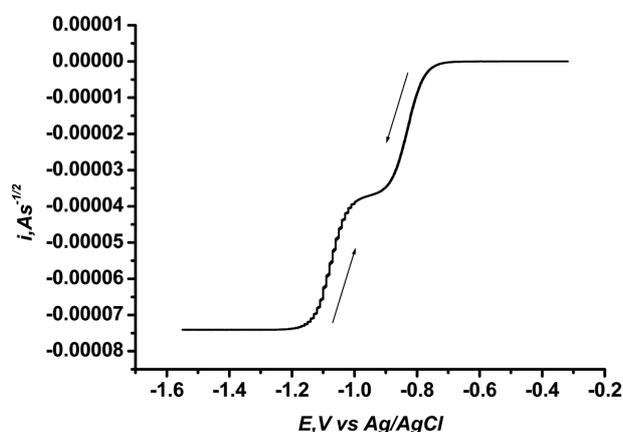


Fig. 5. Convolution voltammery (I_1) of the reductive process of DBPI dye at sweep rate of 0.2 V/s.

fast EE mechanism.

The presentation of i vs t of the voltammogram at sweep rate of 0.1 V/s is shown in Fig. 6a. The plot produces discontinuity Δi_c at $t = 12.5$ s due the reversibility of the scan.

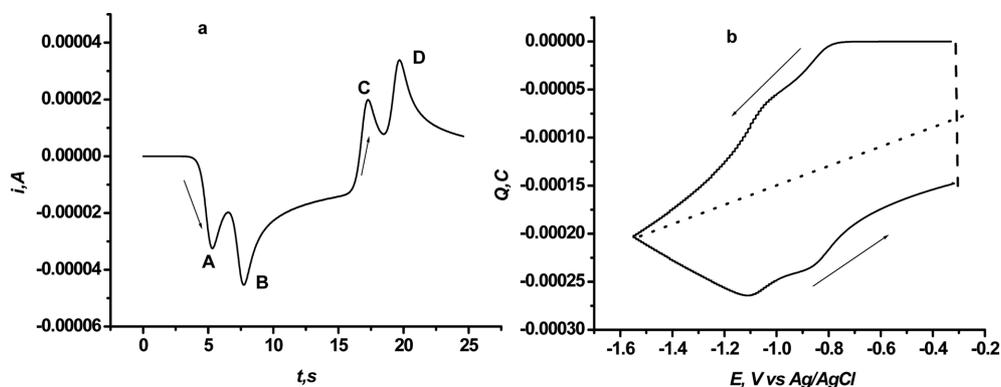


Fig. 6. (a) plot of i versus t corresponding to a reductive cyclic voltammogram at sweep rate of 0.1 V/s. The point $t = 12.5$ s is the time at which the potential scan is switched to the reverse direction, (b) plot of Q versus E .

By selecting the data points a Cottrell plot are obtained as current versus the reciprocal square root of time. The slope of Cottrell plot yields a diffusion coefficient $D = 4.16 \times 10^{-9} \text{ m}^2/\text{s}$. Inspection of Fig. 6a revealed that, the height of the forward and backward peaks are the same, i.e the height of peak A equals the height of peak D and the height of peak B equals the height of peak C confirming the rapidity of the simple charge transfer processes of DBPI dye. The results shown in Fig. 6b represents the plot of charge versus potential which indicates that the cathodic charges in the forward scan is equal to the anodic charges in the backward scan confirming the reversibility of the charges transfer.²⁴

Deconvolution transforms

The deconvolution transforms of the current (dI_1/dt) as a function of E of reversible process is defined as:²⁵

$$ep = (dI_1/dt) = nFAC\sqrt{D} a\zeta / (1+\zeta)^2 \quad (3)$$

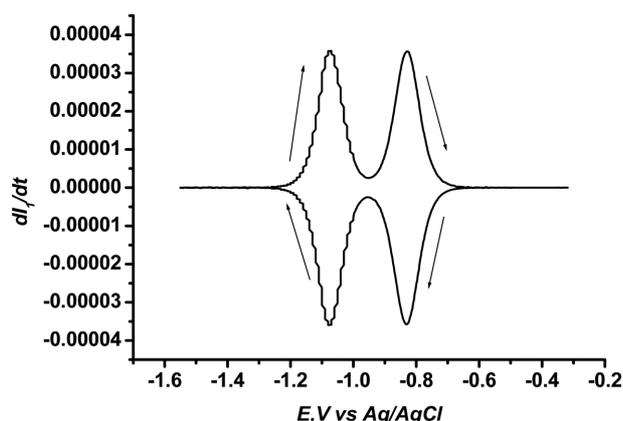


Fig. 7. Deconvolution voltammery (dI/dt) of the reductive cyclic voltammogram of DBPI at a sweep rate of 0.1 V/s.

where $a = mvF/RT$ (4)

and $\zeta = \exp [(nF/RT)E - E^0]$ (5)

and the representation of this equation at $v = 0.1$ V/s are indicated in Fig. 7. The width of deconvoluted peak (w_p) in the case of fast charge transfer is equal to $3.53 RT/nF = 90.5/n$ mV for fast charge transfer. It was found that $w_p = 90 \pm 2$ mV, indicating and confirming the rapidity of both charge transfer.

The symmetry and alignment of the forward and reverse sweep, further confirming the rapidity of EE nature of the reduction process of DBPI dye. The standard reduction potentials were determined from the deconvoluted peak potentials of the two peaks (Table 1). The values of E_1^0 & E_2^0 determined from deconvolution voltammery via Figure 7 compare well with the values calculated from cyclic voltammery (Table 1).

As indicated in Fig. 7 the height of the two peaks are equal confirming the equality of the number of electrons consumed in both steps. From the above discussion it was found that, the I_1 vs E and (dI_1/dt) vs E curves were easier to interpret than i vs E curve.

Also, the values of the diffusion coefficient were calculated from deduced convoluted current (I_{limd}) via the following relationship:^{17,19}

$$I_{limd} = \frac{i_{prev}}{2.788\sqrt{nv}} \quad (6)$$

where I_{limd} is the deduced limiting convoluted current, which is defined as the limiting convoluted current. The values of diffusion coefficient calculated from I_{limd} agree well with the values calculated from cyclic voltammery and convolutive voltammery of the experimental voltammograms (Table 1).

Also, the number of electrons consumed in electrode reaction can be calculated from the following equation:¹⁶

$$n = 0.103 ep / v I_{limd} \quad (7)$$

which found to be equal to 2 for the overall reduction process.

It was found that, as the degree of interaction increase, ΔE^0 and K_c also increase. The separation of the peak potentials for systems with two redox centers are in terms of the comproportionation equilibrium constant of the intermediate (*i.e.* the product of the first electron transfer reaction) is given by the following equation:²⁶

$$Kc = \exp \left[\frac{(E_1^0 - E_2^0)F}{RT} \right] \quad (8)$$

which gives 3.6×10^9 for Kc value, indicating extensive delocalization of charges between the centers of DBPI dye ($Kc > 10^6$).²⁶

Electro-oxidation of DBPI dye

Cyclic voltammetric behaviour: Electro-oxidation of the investigated dye sensitized solar cells compound DBPI exhibited two oxidative peaks. The first oxidative peak (A) is coupled with one reductive peak (D) at all sweep rates (0.02 - 5 V/s), while the second oxidative peak (B) is coupled with one reductive peak (C) which appears at sweep rate ≥ 0.2 V/s. An example response of the oxidative cyclic voltammograms of DBPI dye at sweep rates of 0.1, 0.2 and 0.5 V/s is illustrated in Fig. 8. As indicated the ratios of the first oxidative peak i_{pC}/i_{pA} are less than 1.0 at all sweep rates, while for the second one the coupled reductive peak C appears only at sweep rate ≥ 0.2 V/s with ratios of i_{pC}/i_{pA} less than one, indicating that the EC_1EC_2 mechanism for

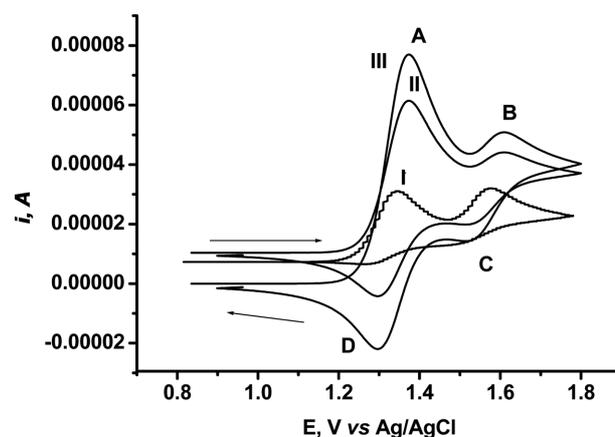


Fig. 8. Oxidative cyclic voltammograms of DBPI in CH_2Cl-CH_2Cl (I) at scan rate of 0.1 V/s, (II) at scan rate of 0.2 V/s and (III) at scan rate of 0.5 V/s.

Table 2. Electrochemical parameters of the oxidation process of laser dye compound DBPI

$E^{\circ 1}$ V	$E^{\circ 2}$ V	$k_{s1} \times 10^4 \text{ ms}^{-1}$	$k_{s2} \times 10^4 \text{ ms}^{-1}$	$D_1 \times 10^9 \text{ m}^2 \text{ s}^{-1}$	$D_2 \times 10^9 \text{ m}^2 \text{ s}^{-1}$	α
1.335 ^a	1.570	6.83	7.65	3.45	3.76	0.49
1.337 ^b	1.575	6.92	7.55	3.60	3.85	0.48
---- ^c	----	----	----	3.45	3.50	----
1.336 ^d	1.576	----	----	3.60	3.54	----
---- ^e	----	----	----	3.70	3.62	----

^a)Experimental values. ^b)Simulated values. ^c)Values of D calculated via Eq. (2). ^d)Values of D calculated from Eq. (9). ^e)Values calculated from Cottrel plot.

the oxidative processes. The appearance of second coupled peak (C) at higher sweep rate confirms the presence of a fast chemical process after the second charge transfer. Also the shift of peak potential to more positive values with increasing the sweep rate reflects the moderate rate of electron transfer.

The formal potentials ($E^{\circ 1}$ & $E^{\circ 2}$) of DBPI dye were calculated from the average peak position and were listed in Table 2.

The standard heterogeneous rates constant (k^1 s & k^2 s) were determined from the working curve¹⁷ and from digital simulation by matching between the experimental and the theoretical voltammograms. Also, the diffusion coefficients (D_1 & D_2) were determined from digital simulation (Table 2).

Convolution-deconvolution transforms: In the case of moderate fast electron transfer, the diffusion coefficients (D_1 & D_2) of the dye sensitized solar cells DBPI were determined from the following equation:^{17,19}

$$I_{\text{limd}} = i_p / 3.099(\alpha n_a \nu)^{1/2} \quad (9)$$

The calculated values of the diffusion coefficients (D_1 & D_2) were listed in Table 2. Fig. 9 exhibits the I_1 convolution and deconvolution transforms of the oxidative pro-

cesses at 0.2 V/s indicating the quasi-reversibility of charge transfer processes and confirm the presence of chemical processes following the two charge transfer¹⁹ i.e EC_1EC_2 mechanism. The values of formal potentials ($E^{\circ 1}$ & $E^{\circ 2}$) were determined from the average peak position of the deconvoluted voltammograms (Table 2).

The true homogeneous chemical rate constant (k_c) of the chemical process following the first and second charge transfer were determined from digital simulation and found $1.85 \pm 0.05 \text{ s}^{-1}$ and $3.45 \pm 0.05 \text{ s}^{-1}$ respectively.

Fig. 10 shows an example response of the comparison between the oxidative experimental and the theoretical voltammograms of DBPI dye at sweep rate of 0.1 V/s, which indicates good agreement between the two curves confirming the accuracy of the electrochemical parameters obtained from experimental cyclic voltammograms.

The presentation of i vs t of the oxidative anodic voltammogram at sweep rate of 0.1 V/s is shown in Fig. 11. The plot produces discontinuity Δi_c at $t=9.9 \text{ s}$ due to the reversibility of the scan. Inspection of Fig. 11 revealed that, the inequality of the height of the forward and backward peaks, i.e the height of peak A is unequal to the height of peak D and the height of peak B is unequal to the height of peak C confirming that both charges transfer are fol-

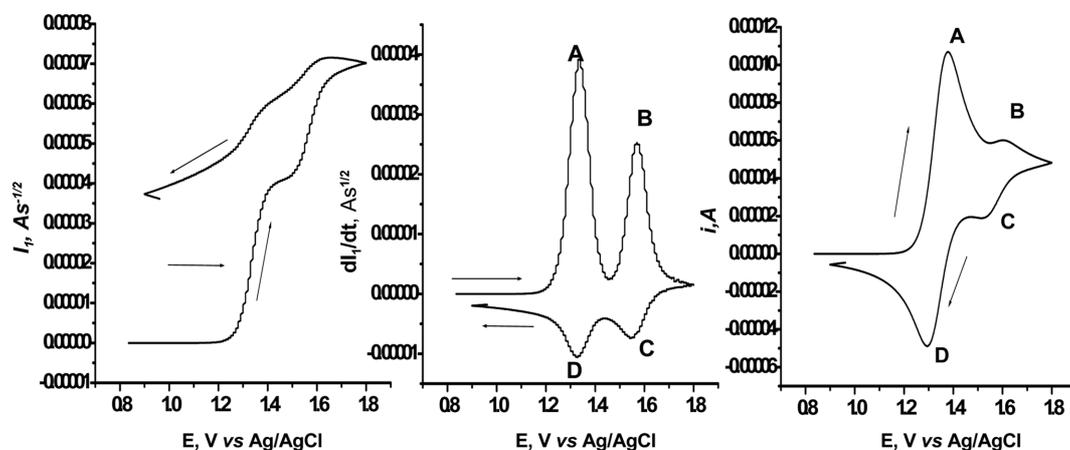


Fig. 9. (a) I_1 convolution transforms, (b) (dI_1/dt) deconvolution transforms, (c) cyclic voltammogram of oxidation process of DBPI dye at sweep rate of 1.0 V/s.

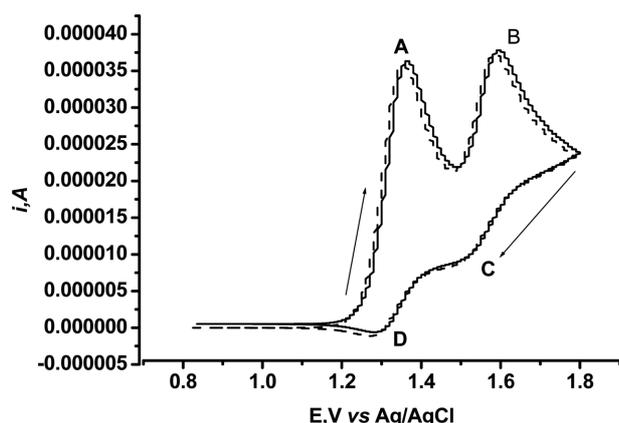


Fig. 10. Matching between oxidative experimental voltammogram of DBPI dye (—) and simulated voltammogram (.....) at a sweep rate of 0.1 V/s.

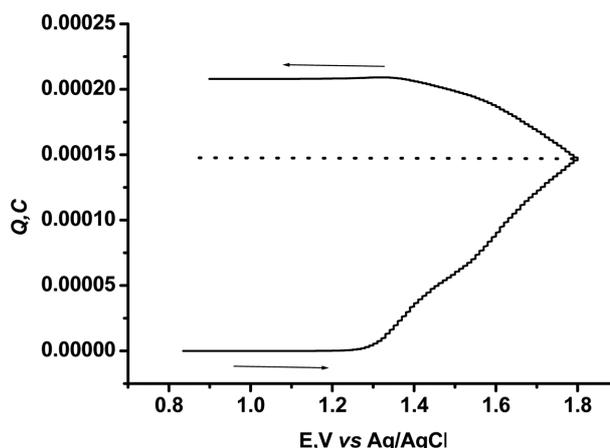


Fig. 12. plot of Q versus E corresponding to oxidative cyclic voltammogram at sweep rate of 0.1 V/s.

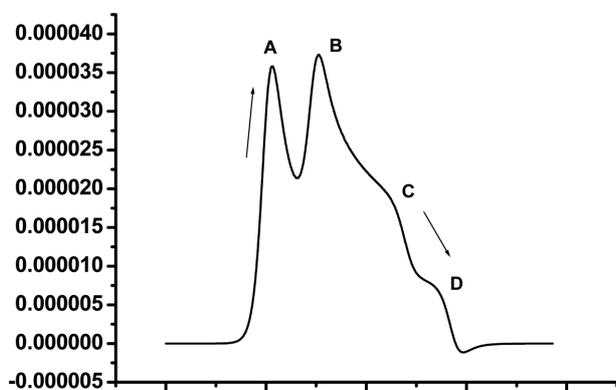


Fig. 11. plot of i versus t corresponding to oxidative cyclic voltammogram at sweep rate of 0.1 V/s. The point $t=9.9$ s is the time at which the potential scan is switched to the reverse direction.

lowed by a chemical processes which may be attributed to the aggregation of the mono cation $DBPI^+$ with the initial dye molecule $DBPI$ due to the columbic attraction force represented in the simple form as $DBPI^+ \dots DBPI$ i.e. $(DBPI)_2^+$ of the first chemical process and the aggregation of dication $DBPI^{++}$ with the initial dye $DBPI$ as $DBPI^{++} \dots DBPI$ i.e. $(DBPI)_2^{++}$ of the second step. Also, the extended π -systems of $DBPI$ forms cause an high aggregation tendency forming dimeric and oligomeric species. By selecting the data points a Cottrell plot is obtained as current versus the reciprocal square root of time. The slopes of Cottrell plots yield a diffusion coefficients D_1 & D_2 cited in Table 2.

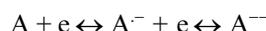
The plot of the charge (Q) versus the potential (E) is shown in Fig. 12 which reflects that the forward anodic charge is more than the backward cathodic charge confirming that the presence of a chemical processes after the

charges transfer.²⁴

From the value of E^0 , the K_c value was calculated using Eq. 8 and found to be 1.715×10^9 indicating extensive delocalization of charges between the centers of $DBPI$ dye ($K_c > 10^6$);²⁶

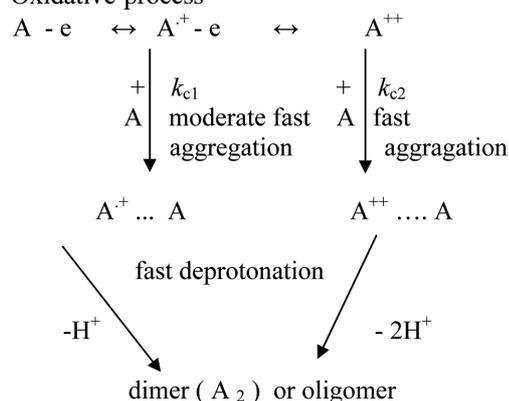
From the above electrochemical studies the electrode behavior of $DBPI$ dye can be proposed to proceed as follows:

Reductive process



i.e. EE mechanism

Oxidative process



i.e. EC_1EC_2 mechanism

CONCLUSION

The electrochemical behavior of dye sensitized solar cells ($DBPI$) was investigated in 0.1 M $TBAP/CH_2Cl-CH_2Cl$ at a platinum electrode. The reductive process proceeds as EE mechanism; the first charge transfer produces

a radical anion that gains another electron to form a dianion. Electro-oxidation of DBPI dye gave two anodic oxidation peaks, the second one behaves as unidirectional irreversible peak at sweep rate < 0.2 V/s. The experimental kinetic parameters were determined experimentally and verified via a digital simulation method by comparing the generated theoretical voltammograms with the experimental voltammograms. The electrode reaction proceeds as EC_1EC_2 . The chemical processes may be attributed to the aggregation between the initial neutral molecules and the monocation and dication species.

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