



Experimental and theoretical studies on carbon surface modification by reduction of *in situ* generated diazonium salt

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ABSTRACT

The electrochemically induced functionalization of glassy carbon electrode by aryl groups was achieved by reduction of *in situ* generated diazonium cations in aqueous media. Surface modification experiments were performed by cyclic voltammetry (CV) scanning from +0.5 to −1.1 V. The barrier properties of the grafted layers were evaluated by cyclic voltammetry in the presence of $\text{Fe}(\text{CN})_6^{3-/4-}$ electroactive redox probe. The modified electrodes showed very slow electron transfer compared to that unmodified surface. Once the monolayer is switched ON, it supports rapid electron exchange with the redox system but not with dopamine, which requires adsorption to the electrode surfaces. *Ab initio* density functional theory calculations allow determining HOMO–LUMO gap distance.

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1. Introduction

A very great endeavor has been expended to develop the surface modification methods for many years. Electrochemically assisted covalent modification of surfaces is a reliable recent development in modified electrode researches [1]. In this method, the substituted aryl groups by reduction of the corresponding diazonium salt are an attractive way to modify carbon-based surfaces [2–5]. Pinson and coworkers introduced this in the early 1990s [6]. Scheme 1 describes the two-step process of this reaction as (1) the electrochemical reduction of the diazonium function and the formation of phenyl radical and (2) the chemical grafting of radical at the surface of the electrode with the formation of a covalent bond between a surface atom of the substrate and the phenyl group.

The modification of surfaces with electrochemically active groups may result in potential application in chemical sensing, molecular switching and protection against corrosion [7–9]. Modification of carbon materials is of great interest in several fields of material science and electrochemistry for not analytical purposes [10]. This modification procedure is very attractive because it avoids the use of oxidative conditions which can lead to the detrimental oxidation of the carbon substrate [11,12]. Also it allows the presence of selected functional groups on the aryl rings. The specific substituent on the aryl group can be used to impart useful properties to the modified electrode and to elaborate more complex chemical structures that can have various applications [13]. Ionizable groups can also provide charge selectivity properties that are

useful for sensing applications [14]. However, the substituent could be chosen according to the future chemistry aims such as enzyme immobilizing [15], attachment of electroactive groups [16], and combinatorial chemistry [17]. On the other hand, a major disadvantage of the modification approach based on aryl diazonium salt is that the synthesis of the salt is required. Indeed, the synthesis and isolation of the diazonium salt are not always straightforward. The synthesis is commonly carried out in acidic media from the corresponding amine by using NaNO_2 as a reactant [18]. It might be interesting to have a modification procedure that will avoid this synthesis by using the amine as a precursor.

In this work, we report the modification of glassy carbon electrode by electrochemical reduction of a diazonium salt synthesized *in situ* in the aqueous deposition solution without the isolation of the diazonium salt. More specifically, the electrochemical modification was performed with *N,N*-dimethyl-1,4-phenylenediamine. The modified electrodes were also characterized by cyclic voltammetry and electrochemical impedance spectroscopy in the presence of electroactive species. In addition, the current work also investigates conductance switching in an electrochemical context.

2. Experimental

2.1. Reagents

Sodium nitrite, potassium hexacyanoferrate (III), hexaaminonickel chloride (III), potassium chloride, hydrochloric acid, *N,N*-dimethyl-1,4-phenylenediamine. The chemicals were used as received from MERCK. Solutions were prepared fresh daily and degassed with ultra pure (99.99%) nitrogen gas for 10 min before use.

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2.2. Electrode preparation and modification

Working electrode was glassy carbon (GC). The reference electrode was Ag/AgCl (saturated KCl), and the platinum wire was employed as the counter electrode. The glassy carbon electrode surface was cleaned by polishing with Buehler 0.05 μm alumina slurry. After polishing, the electrode was washed with pure water. The carbon electrode surface modification using *in situ* generated diazonium cations was performed in two steps: first, 400 μL 0.1 M NaNO_2 was added to the electrolytic solution (20 mL) containing 5 mM *N,N*-dimethyl-1, 4-phenylenediamine (DMPD) and 0.5 M HCl under stirring at room temperature. Second, the mixture was left to react for about 5 min prior to the electrochemical modification. Electrochemical modification of the glassy carbon electrode was carried using cyclic voltammetry during 25–30 cycles at the potential between +0.5 and -1.1 V vs. Ag/AgCl. After modification, the electrode was rinsed abundantly with Nanopure water and sonicated in Nanopure water for 30 s. The solutions containing the various electroactive probes were hexammineruthenium and ferricyanide/ferrocyanide (1 mM; 0.1 M KCl). All solutions were deaerated with extra dry nitrogen during 15 min.

2.3. Instrumentation and procedure

Electrochemical measurements were performed in a one-compartment cell with a three electrode configuration. Cyclic voltammetry (CV) was carried out using a Potentiostat/Galvanostat EG&G Model 263 A; USA with a PC and electrochemical set ups well equipped with M270 software. Electrochemical impedance spectroscopy (EIS) was performed with a Frequency Response Detector EG&G Model 1025; USA. An ac voltage of 5 mV in amplitude with a frequency range from 50 mHz to 65 kHz was superimposed on the dc potential and applied to the studied electrodes. Experimental data of the electrochemical impedance plot were analyzed by Boukamp software.

2.4. Computational methods

Molecular orbitals and geometries were calculated with density functional theory (DFT) B3LYP using the GAUSSIAN 98 programs package with a 6–31G** basis set [19]. For anion radicals the unrestricted, open-shell method was used, and the HOMO–LUMO gap was taken as the difference between the half-occupied orbital and the highest filled orbital. Also the anion radical's ground state wave functions were checked for stability.

3. Results and discussion

Electrode modification by chemisorption of aryl radicals was accomplished by the redaction of diazonium salts [20–23]. The presence of a grafted layer at the electrode surface can be demonstrated by cyclic voltammetry in the presence of soluble electroactive probes. The choice of the redox couple strongly influences the observed blocking effect. The corresponding CV exhibits a well-defined reduction peak assigned to the formation of the aryl radical, which then attaches to the surface. The second and third cycles of a set of consecutive CVs (Figure 1) exhibit a slight shift of the

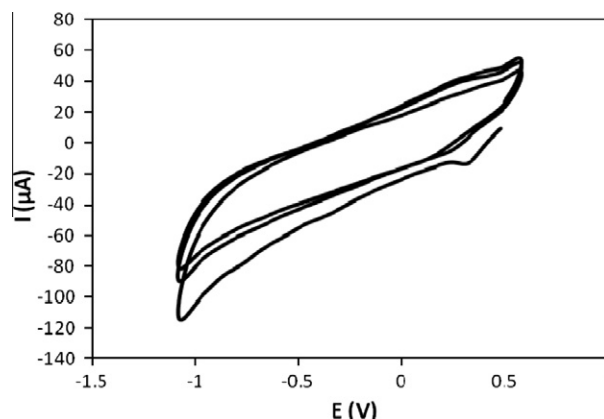


Figure 1. Cyclic voltammograms at a scan rate of 100 mV/s for a glassy carbon electrode in a solution containing 2 mM *N,N*-dimethyl-1,4-phenylenediamine and 2 mM NaNO_2 in aqueous 0.5 M HCl.

cathodic peak to more negative potentials and lower currents, consistent with the passivation of the glassy carbon electrode owing to the formation of a grafted layer.

The blocking effect of the grafted layer depends on the charge and the hydrophobicity of the redox probe, the nature of the solvent and electrolyte. The blocking behavior of the resulting modified glassy carbon electrodes was investigated by electrochemical measurements in the presence of $\text{Fe}(\text{CN})_6^{3-/4-}$ as an electroactive redox probe. Figure 2 shows CVs before and after the modified GC electrode by the electrochemical reduction of *in situ* generated diazonium cations.

The attachment of a *N,N*-dimethyl-1,4-phenylenediamine film on GC surfaces was also proven by the irreversible wave observed in the cyclic voltammogram of the modified electrode in a dopamine solution. As dopamine (DA) oxidation provides a useful test for pinholes [24], DA requires an adsorption site for rapid oxidation and becomes electro-inactive on electrode surfaces modified by *N,N*-dimethyl-1,4-phenylenediamine monolayer completely. Therefore, DA response is an indication of the presence of bare electrode area or might occur from pinhole formation. Figure 3 shows voltammograms of 1 mM DA in 0.1 M H_2SO_4 for GC electrode, unmodified, initial *N,N*-dimethyl-1,4-phenylenediamine -

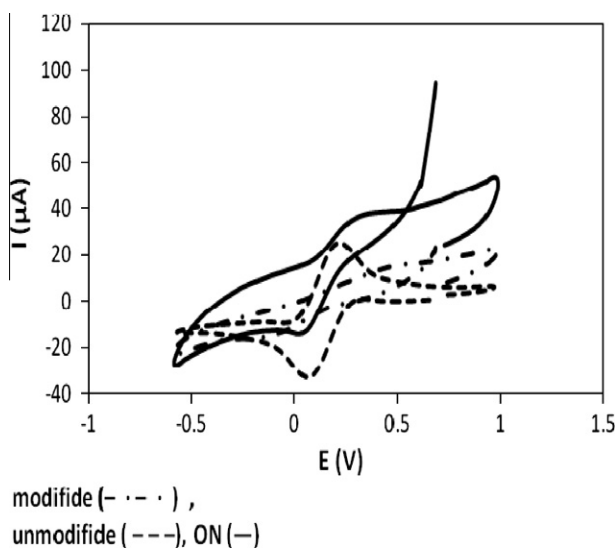
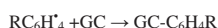
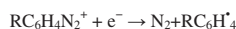


Figure 2. Cyclic voltammetry results of 1 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ in 0.1 M KCl, unmodified (—), modified (---), and modified GC electrode after switching ON (— · —), 100 mV/s scan rate.



Scheme 1. Mechanism of diazonium salt electrografting on carbon surfaces.

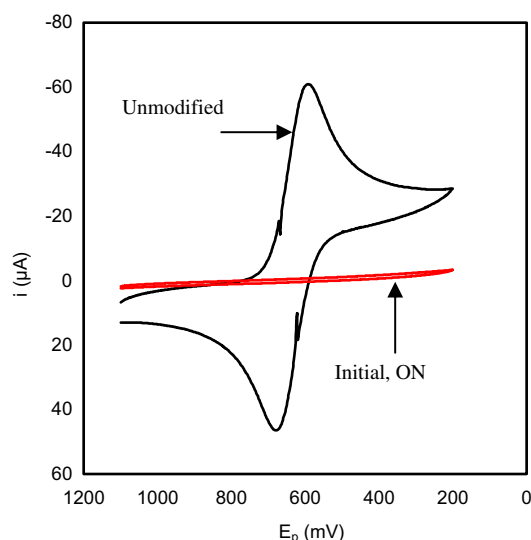


Figure 3. Cyclic voltammogram of 1 mM Dopamine + 1 mM H₂SO₄, 100 mV/s scan rate. Responses on GC, unmodified, initial *N,N*-dimethyl-1,4-phenylenediamine-modified, ON.

modified, and 4-*N,N*-dimethyl-1,4-phenylenediamine-modified after placing it in acetonitrile containing 0.1 M TBABF₄ and scanned from 0.4 to −1.1 V vs. Ag/AgCl for 25 cycles at a scan rate of 100 mV/s.

The last process will be referred to as turning the electrode to the conducting state (ON). Figure 3 shows that no observable DA response is visible for GC modified with *N,N*-dimethyl-1,4-phenylenediamine radical and there is no DA signal on GC-*N,N*-dimethyl-1,4-phenylenediamine electrode after scanning the modified electrode to −1.1 for 25 cycles. The cyclic voltammogram of DA indicated that scanning GC-*N,N*-dimethyl-1,4-phenylenediamine in blank electrolyte at a potential of less than −1.1 V damaged the surface of the modified GC electrode. The phenomenon of conducting state of modified electrode in an electrochemical cell was examined by Fe(CN)₆^{3−/4−} redox system (see Figure 1). Also, the summary of kinetic data for modified electrode and ON electrode was reported in Table 1.

The primary hypothesis noted above stated that negative potential excursion caused a change in the monolayer that promoted faster electron transfer. The initial *N,N*-dimethyl-1,4-phenylenediamine monolayer significantly decelerates the electron – transfer (ET) rate for Fe(CN)₆^{3−/4−}. When a *N,N*-dimethyl-1,4-phenylenediamine monolayer is turned to conducting state, Δ*E*_p changed from zero to 74 mV, which corresponds to an ET rate increase from zero to 1.057 × 10^{2−} cm/s. There are several possibilities for the mechanism of rate enhancement associated with negative potential excursions, and they will be considered in turn. First the monolayer might be reductively desorbed to create pinholes or bare electrode areas, which exhibit faster kinetics than the intact monolayer.

However such pinholes should be electroactive toward dopamine, and should not yield the flat response of Figure 3. The lack of dopamine response rules out significant regions of uncovered GC surface. Second, a possible explanation for the apparent change

in ET kinetics is the contribution of monolayer resistance to the uncompensated resistance. The monolayer acts as a resistor in series with the cell, and a significant decrease upon conducting state would results in a decrease in Δ*E*_p. However, the weak dependence of Δ*E*_p on redox system concentrations confirms a significant contribution of monolayer resistance to ohmic potential error. Kinetic effects that may be responsible for the observed change in ET rate involve electron tunneling through the monolayer.

To gain further support about the above mentioned points we calculated the surface coverage using the data obtained by EIS measurements. Figure 4 shows the Nyquist plots of the bare and modified GC electrode.

The Nyquist plot of the modified electrode exhibited a depressed and small semicircle. Using an appropriate equivalent circuit (did not show here), the value of charge-transfer resistance (*R*_{CT}) was found to be 81 and 1.5 × 10⁴ Ω for the bare and modified GC electrode, respectively. These numerical values highlight a significant change in the structural properties of the GC surface after modification. The increase in the charge-transfer resistance could be related to the electrode coverage according to the following equation [29]:

$$(1 - \theta) = R_{CT}^0 / R_{CT} \quad (1)$$

Where θ , is the apparent electrode coverage, R_{CT}^0 and R_{CT} represent the charge-transfer resistance of the bare and modified electrodes. Using Eq. (1), the value of surface coverage was found to be 99.5%. Obviously, the blocking effects are due to the surface coverage, thickness, the structure of the used diazonium salt (terminal group), applied potential in electrochemical method, modification time, the salts concentrations, dipole moment of the aryl radical and etc. Since we did not get a full coverage (less than 100%), the possibility for (sub) monolayer formation is higher than multilayer formation. But, it dose not means that the produced films were monolayer, certainly. Discussion about the multilayer or monolayer formation is reasonable if the layer thickness could be measured. Detailed descriptions about the controlling factors on the evolution of monolayer or multilayer were reported by Pinson et al. [30]. The electron transfer kinetics of Fe(CN)₆^{3−/4−} could be influenced by different experimental conditions used for the modification process. The reactivity of the bare electrode that might be changed by the heterogeneous rate constants will has significant effect on the barrier properties. When K^0 of the bare electrode is higher (see Table 1), it means that the film being more permeable. This verifies that the change of electrode materials will has important role on the barrier properties.

While the aim of the present research was not a mechanistic characterization of glassy carbon surface by an *in situ* generated diazonium salt, it should be emphasized that grafting of the respected diazonium salt on GC surface might be performed owing to the formation of a C–C bond via the generation of radical or cationic intermediates. Therefore, the formation of aryl cation intermediate by thermal decomposition of the diazonium salt must be considered as an alternative route for GC surface modification. Evidences for aryl cation formation during the thermolysis of diazonium salts in solution and in solid state have been proved previously [31,32]. A detailed study about the importance of the above mentioned grafting pathways and the influencing factors

Table 1
Some kinetic parameters for the modified electrode.

	Δ <i>E</i> (unmodified) (mV)	Δ <i>E</i> (modified) (mV)	Δ <i>E</i> (ON) (mV)	<i>K</i> ⁰ (unmodified) (cm/s)	<i>K</i> ⁰ (modified) (cm/s)	<i>K</i> ⁰ (ON) (cm/s)
Fe(CN) ₆ ^{3−/4−}	74	Non-determinable	76	2.01 × 10 ^{−2}	Non- determinable	1.05 × 10 ^{−2}

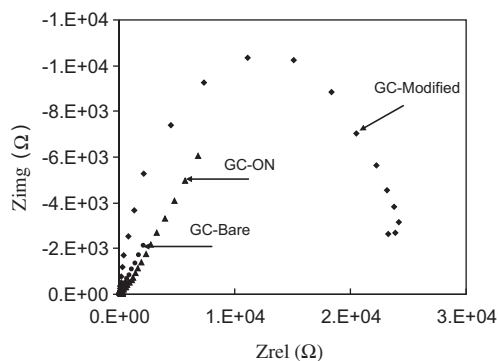


Figure 4. Nyquist representations of the electrochemical impedance spectroscopy data in ferricyanide/ferrocyanide (1 mM; 0.1 M KCl) for the bare and modified glassy carbon electrodes.

on their contribution was addressed by Compton et al. [33,34]. However, it seems that the contribution of the grafting by aryl cation route should not be significant since the diazonium salt was produced by an *in situ* generated procedure and the experiments were carried out at room temperature.

The tunneling may be modified by a change in monolayer structure that accompanies conducting state. Electron tunneling through structurally similar phenylethynyl monolayers has been studied using the Au/thiol self-assembled monolayer system, for which the ET rate decreases exponentially with monolayer thickness [25]. The rate of tunneling decreases exponentially with the thickness of the barrier and is given in its simplest form by the Simmons relation, Eq. (1) [26], where J = current density, A/cm², q = electron charge, V = applied voltage, h = Planck's constant, m = electron mass, Φ = barrier height and d = barrier thickness.

$$J = \frac{q^2 V}{h^2 d} (2m\Phi)^{1/2} \exp \left[\frac{-4\pi d}{h} (2m\Phi)^{1/2} \right] \quad (2)$$

Eq. (1) shows only the linear term for a rectangular tunneling barrier, but it does exhibit the exponential dependence on d . This equation is often simplified to a useful form for comparison to experimental data, Eq. (2), where B is a constant and β has units of inverse angstroms or inverse nanometers. By comparison to Eq. (1), we note that β is proportional to the square root of the barrier height.

$$J = Be^{-\beta d} \quad (3)$$

The observed tunneling rates in molecular junction often depend exponentially on the junction thickness. Reported exponential β factors of 0.4–0.6 (Å⁰)^{−1} for electron tunneling in such monolayer lead to a predicted decrease in tunneling rate by factors 70–700 for this range of β values, compared to an unmodified electrode. The calculated HOMO–LUMO gap and the tunneling parameter which corresponds to the distance of the carbon surface to the van der

waals radius of terminal atom (Bromine) are shown in Table 2. Tunneling factor for $\beta = 0.4$ (Å⁰)^{−1} are listed in Table 2 to serve as an indication of the magnitude of the effect.

The electronic structure and thickness of the monolayer should both affect the tunneling rate and the dependence of electron transport on molecular structure is currently an active area of research [27]. It was proposed that the electron injection into the monolayer from the GC substrate results in a reduced HOMO–LUMO gap and a higher electronic conductance. The product of electron injection can be considered as an anion radical, depending on the nature of the monolayer–GC bond a significant decrease in HOMO–LUMO gap was observed due to the electron injection. The Simmons model has often been used to estimate the effect of tunneling barrier height and thickness on the electron tunneling rate and predicts that the rate is exponential in the product of the thickness and the square of the barrier height [28]. Both the Simmons model and theoretical calculations results, are approximations of the real phenomena and structures, but these estimates do indicate that the changes in the electronic structure of the monolayer upon electron injection can result in large changes in the rate of electron tunneling. In Table 2, the length of molecule and anion radical are not so different. However, it seems that the rate of tunneling determined mostly by HOMO–LUMO gap. The effect is attributed to an apparently irreversible structural change in monolayer, which increases the rate of electron tunneling. The transition to the 'ON' state is associated with electron injection into the monolayer similar to that observed in previous spectroscopic investigations and causes a significant decrease in the calculated HOMO–LUMO gap for the monolayer molecule. Once the monolayer is switched ON, it supports rapid electron exchange with outer-sphere redox systems. Information of computational study for diamine and its radical was reported in Table 2.

4. Conclusion

This study reports the electrochemical modification of glassy carbon surfaces by *in situ* generated of a diazonium cation in aqueous media. This direct modification of GC surface in a one step strategy by electrochemical reduction of corresponding diazonium cation is an advantage. Computational study revealed that the phenyl radical is active for connection surface. Modified electrode exhibited slower electron transfer, but after a negative potential, electron transfer kinetics becomes faster. The oxidation of 1 mM Dopamine hydrochloride in 0.1 M H₂SO₄ has been used to test for pinholes presence. They should be present in the initial modified electrodes or after switching ON. The effect is assigned to an apparently irreversible structural change in the *N,N*-dimethyl-1,4-phenylenediamine monolayer which increases the rate of electron tunneling. The transition to the conducting state is associated with electron injection into the monolayer and causes a significant decrease in the calculated HOMO–LUMO gap for the monolayer molecule. Once the monolayer is switched to conducting state, it

Table 2
Calculated parameters for the monolayer deposit.

Substance	HOMO–LUMO ^a (E/eV)	Length ^b (Å ⁰)	Simmons ratio ^c	Tunneling factor ^d for $\beta = 0.4$
<i>N,N</i> -dimethyl-1,4-phenylenediamine	0.17141	1.4034	---	0.0785
Phenyl radical	0.09478	1.3862	1.4069	0.0694

^a From GAUSSIAN 98, B₃LYP with 6–31G** basis set.

^b From carbon surface to van der Waals radius of terminal atom, using GAUSSIAN geometry.

^c Predicted ratio of tunneling rates calculated from a linear Simmons equation. Cited number is the ratio of the tunneling rate for the radical molecule to that for the parent molecule and is controlled mainly by the different in HOMO–LUMO gap.

^d $\exp(-\beta d)$, where d is the molecule length. Units of β are (Å⁰)^{−1}.

supports rapid electron exchange with redox system, but not with dopamine, which requires adsorption to the electrode surface. A conductive surface modified electrode may have useful properties for electroanalytical applications and possibly in electrocatalysis.

References

- [1] A.J. Downard, *Electroanalysis* 12 (2000) 1085.
- [2] B. Ortiz, C. Saby, G.Y. Champange, D. Belanger, *J. Electroanal. Chem.* 455 (1998) 75.
- [3] S. Ranganathan, I. Steidel, F. Anariba, R.L. McCreery, *Nano Lett.* 1 (2001) 491.
- [4] M. D'Amours, D. Belanger, *J. Phys. Chem.* 107 (2003) 4811.
- [5] F. Anariba, S.H. DuVall, R.L. McCreery, *Anal. Chem.* 75 (2003) 3837.
- [6] M. Delamar, R. Hitmi, J. Pinson, J.M. Saveant, *J. Am. Chem. Soc.* 114 (1992) 5883.
- [7] J. Lyskawa et al., *J. Am. Chem. Soc.* 126 (2004) 12194.
- [8] V.M. Fernandez, A.L. De Lacey, *J. Am. Chem. Soc.* 127 (2005) 16008.
- [9] C. Combella, M. Delamar, F. Kanoufi, J. Pinson, F. Podvorica, *Chem. Mater.* 17 (2005) 3968.
- [10] B.D. Bath, H.B. Martin, R.M. Wightman, M.R. Anderson, *Langmuir* 17 (2001) 7032.
- [11] E. Fitzer, K.H. Geigl, W. Heitner, R. Weiss, *Carbon* 18 (1987) 389.
- [12] W.P. Hoffman, W.C. Curley, T.W. Owens, H.T. Phan, *J. Mater. Sci.* 26 (1991) 4545.
- [13] J. Pinson, F. Podvorica, *Chem. Soc. Rev.* 34 (2005) 429.
- [14] A.J. Downard, A.D. Roddick, A.M. Bond, *Anal. Chim. Acta* 317 (1995) 303.
- [15] C. Bourdillon, M. Delamar, C. Demaille, R. Hitmi, J. Moiroux, J. Pinson, *J. Electroanal. Chem.* 336 (1992) 113.
- [16] O. Ghodbane, G. Chamoulaud, D. Belanger, *Electrochem. Commun.* 6 (2004) 254.
- [17] E. Coulon, J. Pinson, J.D. Bourzat, A. Commerçon, J.P. Pulicani, *J. Org. Chem.* 67 (2002) 8513.
- [18] M.F.W. Dunker, E.B. Stakey, G.L. Jenkins, *J. Am. Chem. Soc.* 58 (1936) 2308.
- [19] A.J. Downard, M.J. Prince, *Langmuir* 17 (2001) 5581.
- [20] P. Allongue, M. Delamar, B. Desbat, O. Fagebaume, R. Hitmi, J. Pinson, J.M. Saveant, *J. Am. Chem. Soc.* 119 (1997) 201.
- [21] N. Kornblum, D.C. Iffland, *J. Am. Chem. Soc.* 71 (1949) 2137.
- [22] S. Baranton, D. Belanger, *J. Phys. Chem. B* 109 (2005) 24401.
- [23] B.P. Corgier, A. Laurent, P. Perriat, L.J. Blum, C.A. Marquette, *Angew. Chem. Int. Ed.* 46 (2007) 4108.
- [24] S. Duvall, R.L. McCreery, *J. Am. Chem. Soc.* 122 (2000) 6759.
- [25] S. Creager et al., *J. Am. Chem. Soc.* 124 (1999) 1059.
- [26] D.R. Lamb, *Electrical Conduction Mechanisms in Thin Insulating Films*, Methuen and Co., London, 1968.
- [27] D. Segal, A. Nitzan, W. Davis, M.R. Wasielewski, M.A. Ratner, *J. Phys. Chem. B* 104 (2000) 3817.
- [28] J.G. Simmons, *Conduction in Thin Films*, Mills and Boon Ltd., London, 1997.
- [29] E. Sabatani, *J. Phys. Chem.* 91 (1987) 6663.
- [30] J. Pinson, F. Podvorica, *Chem. Soc. Rev.* 34 (2005) 429.
- [31] C. Gardner Swain, J.E. Sheats, K.G. Harbison, *J. Am. Chem. Soc.* 97 (4) (1975) 783.
- [32] E.P. Kovalchuk, O.V. Reshetnyak, Z.Y. Kozlovskaya, J.B. zejowski, R.Y. Gladyshevskiy, M.D. Obushak, *Thermochim. Acta* 444 (2006) 1.
- [33] P. Abiman, G.G. Wildgoose, R.G. Compton, *J. Phys. Org. Chem.* 21 (21) (2008) 433.
- [34] P. Abiman, G.G. Wildgoose, R.G. Compton, *Int. J. Electrochem. Sci.* 3 (2008) 104.