

György Inzelt

Cyclic voltammetry of solid diphenylamine crystals immobilized on an electrode surface and in the presence of an aqueous solution

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Abstract Diphenylamine solid crystals have been mechanically attached to platinum or gold electrodes by four different methods and investigated by cyclic voltammetry in the presence of aqueous acidic media. It is demonstrated that the oxidative dimerization and polymerization (observed in non-aqueous solutions or mixed solvent systems) can also be accomplished by using diphenylamine microcrystals in contact with the electrode metal in the presence of aqueous solutions. Formation of a thin polymer layer has been observed even in the areas of the electrode that were not in direct contact with the diphenylamine microparticles. This finding can be explained by surface diffusion of the organic molecules or by oversaturation of the solution close to the diphenylamine microcrystals. A gradual growth of the voltammetric peaks characteristic of the polymer has been observed, while the irreversible wave due to the formation of cation radicals and their dimerization has shown a stationary behaviour. The redox transformation of the oligomeric compound formed at the surface is accompanied by a clear colour change: at pH 0 the colourless reduced form is converted to the bright-blue (violet) oxidized form.

Keywords Diphenylamine · Microcrystals · Dimerization · Polymerization

Introduction

The application of novel, electrochemical techniques for the study of solid materials, including the study of immobilized microparticles on conducting solid surfaces (typically metals or carbons), has opened up new vistas

concerning the analysis of these systems [1]. These methods allow the investigation of compounds which cannot be studied in solution, because of their very low solubility, e.g. in water. In addition, information can be obtained about the processes associated with the redox transformations in the solid materials, e.g. about ion transport, phase transitions, etc. Different techniques have been developed including compact electrodes, mixing with carbon paste, the use of suspension of solid particles, etc., depending on the properties of the materials investigated. The immobilization of microparticles has become one of the most popular methods owing to the ease of the electrode preparation and the surprisingly good reproducibility of the measurements [1, 2]. Furthermore, an advanced theoretical description regarding the thermodynamics and kinetics of redox reactions and the accompanying events is also available [3]. A detailed survey regarding the advantages and disadvantages of these methods has been published [1]. Although even the early studies attested that solid state voltammetry is a powerful tool to study water-insoluble organic compounds, this technique is still less used in this area especially in comparison with the number of similar investigations of inorganic or metalloorganic systems.

Nevertheless, remarkable results have been obtained for solid organic compounds such as tetracyanoquinodimethane (TCNQ) [4, 5], tetrathiafulvalene (TTF) [6], TCNQ-TTF [7], ferrocene [8], azobenzene [9], and different metallophthalocyanines [10, 11]. In this paper the preparation of metal/diphenylamine microcrystal electrodes and the results of voltammetric studies will be presented. The practically water-insoluble diphenylamine has been chosen for several reasons. First, it is a widely used redox indicator; however, the exact mechanism of its redox reactions has not yet been clarified. Diphenylamine is applied as follows: it is dissolved in concentrated sulfuric acid (concentration 0.2–1%) and some drops of this solution are added to the solution of the redox systems to be titrated. It is assumed that diphenylamine is oxidized in two steps. First, *N,N'*-diphenylbenzidine (DPBH₂) is formed by

G. Inzelt
Department of Physical Chemistry,
Eötvös Loránd University, P.O. Box 32,
1518 Budapest 112, Hungary
E-mail: inzeltgy@para.chem.elte.hu

tail-to-tail coupling in an irreversible reaction; then the reversible redox reaction of DPBH_2 to give diphenylquinone diimine (DPBB) may occur in the presence of excess oxidant, resulting in a colour change from colourless to blue or violet. At pH 0 and 20 °C, $E^\circ = 0.76$ V (SHE) [12]. However, depending on the conditions (pH, solvent, etc.), the initially generated cation radical can react very differently and other products may be formed [13]. Second, in the course of the pursuit of new conducting polymers, it was found that the chemical or electrochemical oxidation in non-aqueous media or in mixed solvents resulted in a polymer (or oligomer) with rather good conductivity and electrochromic behaviour [14, 15, 16, 17]. More or less the same dimerization and polymerization mechanism has been assumed, i.e. the formation of cation radicals, dimer then polymer formation via C-C coupling and further reversible redox transition of the product. It has been proved that the redox transition occurs in two steps [15, 16, 17]. However, the reaction schemes proposed differ from each other in the sequence of the protonation/deprotonation steps. It is evident that in this respect the pH dependence would supply information, and such an investigation can be carried out only in aqueous media to obtain reliable results.

Therefore, our aim was the fabrication of electrodes by using diphenylamine microcrystals and the investigation of the electrochemical processes in the presence of acidic aqueous media.

Experimental

Diphenylamine (Merck p.a.), H_2SO_4 , Na_2SO_4 , HClO_4 (all Merck, analytical grade) were used as received. Doubly distilled water was used. The total concentration of the solutions used was 1 mol dm^{-3} (except 5 M HClO_4) and the pH of the electrolyte of the sulfuric acid solutions was adjusted by Na_2SO_4 . The working electrodes used were Pt and Au plates ($A = 1$ cm^2) or a Pt spiral electrode ($A = 2$ cm^2). A sodium saturated calomel electrode (SCE) and a platinum plate served as the reference and auxiliary electrodes, respectively, in a usual three-electrode cell arrangement. The working electrodes were cleaned with fast cycling between -0.25 and 1.3 V (SCE) in 1 M H_2SO_4 solutions. The diphenylamine (DPAH) microcrystals were deposited on the metal substrates in four different ways. The microcrystals were attached to the slightly rough platinum or gold surface ($f_r = 1.2$ – 3.6) by wiping the electrode with a cotton swab or filter paper containing the material. Surprisingly, rather large microcrystals remained attached to the metal surface on immersing the as-prepared electrodes into the aqueous acid solution. Alternatively, the electrode was simply dipped into the layer of the microcrystals that had fallen to the bottom of the electrolyte containing cell (we call this the immersion or dipping technique.) Electrolysis was carried out also in a suspension of diphenylamine. The electrodes were covered by DPAH also by dipping or evaporation techniques, i.e. DPAH was dissolved in tetrahydrofuran (THF) and the electrode was immersed into this solution or some drops of the solution was placed on the electrode surface. The electrodes were used after evaporation of the solvent. By variation of the concentration of the DPAH/THF solution and/or the immersion time, the amount of DPAH deposited can be regulated. Practically identical results have been observed irrespective of the method and electrode material (Pt or Au) applied. When the platinum or gold is immersed into the saturated solution of diphenylamine (solubility in water = 0.03 g/100 cm^3 at 25 °C [18];

however, other books give much smaller values, even $s_v = 0$), practically no oxidation reaction (no considerable current) could be observed even during extensive potential cycling for a rather long period of time. Consequently, the effects observed and described in the present paper are primarily in connection with the metal-microcrystals contacts. The presence of oxygen does not affect the measurements, since no difference was found when the solution was purged with nitrogen or the cyclic voltammetry was carried out without the removal of oxygen.

An Electroflex 450 potentiostat (Szeged, Hungary) connected with an IBM personal computer were used for the control of the measurements and for the acquisition of the data.

Results and discussion

Consecutive cyclic voltammograms of diphenylamine microcrystals attached to a platinum electrode and using a 1 M H_2SO_4 electrolyte solution are shown in Fig. 1. The cyclic voltammograms and their changes during repetitive cycling are quite similar to those for DPAH oxidation in acetonitrile [14, 15, 16, 17] or in acidic water-ethanol mixed solvents [15]. A high oxidation peak appears at ca. $E = 0.73$ V (at 100 m V s^{-1}), which is in connection with the formation of $\text{DPAH}\bullet^+$ cation radicals, the C-C *para*-coupled dimerization of these cation radicals to diphenylbenzidine (DPBH_2) and the further oxidation of DPBH_2 [15, 16, 17]. On the cathodic branch of the voltammograms, two (in highly acidic media, sometimes three) peaks can be observed. The peak (rather a shoulder) at 0.62 V can be assigned to the reduction of the DPAH^{2+} dication and/or the non-dimerized $\text{DPAH}\bullet^+$ cation radicals [15, 16, 17] (a similar conclusion was drawn concerning the redox transformations of *N,N*-dimethylaniline [19]). The progressively developing waves ($E_{\text{pa}} \approx 0.52$ V, $E_{\text{pc}} \approx 0.43$ V) belong to the reversible redox process of the dimer or of the polymer (poly-DPA). The formation of polymer can be assumed because of the permanent growth of these waves [14, 15, 16, 17]. The redox process is accompanied by a colour change from a colourless (reduced) to a bright blue (oxidized) form. It was somewhat surprising that this colour change can be observed not only at the microcrystals but also for a thin film that was formed at the whole platinum surface, even at places where no microcrystals were attached. This can be explained either by lateral diffusion of DPAH and DPBH_2 species and/or by an oversaturation of the solution near the electrode surface (note that if the platinum plate was immersed in a saturated solution of DPAH, no film formation or current have been observed even during long cycling). During cycling with the same sweep rate, an increase of the large peak at ca. 0.73 V can also be seen (Fig. 1); however, it is elusive (in fact this wave is virtually stationary) and the increase is due to the gradual growth of the oxidation wave of the electrochemically active poly-DPA which appears at a less positive potential and overlaps with it.

Since the polymer formed is electronically conducting, the oxidation of diphenylamine microcrystals is certainly a special case concerning the model of the

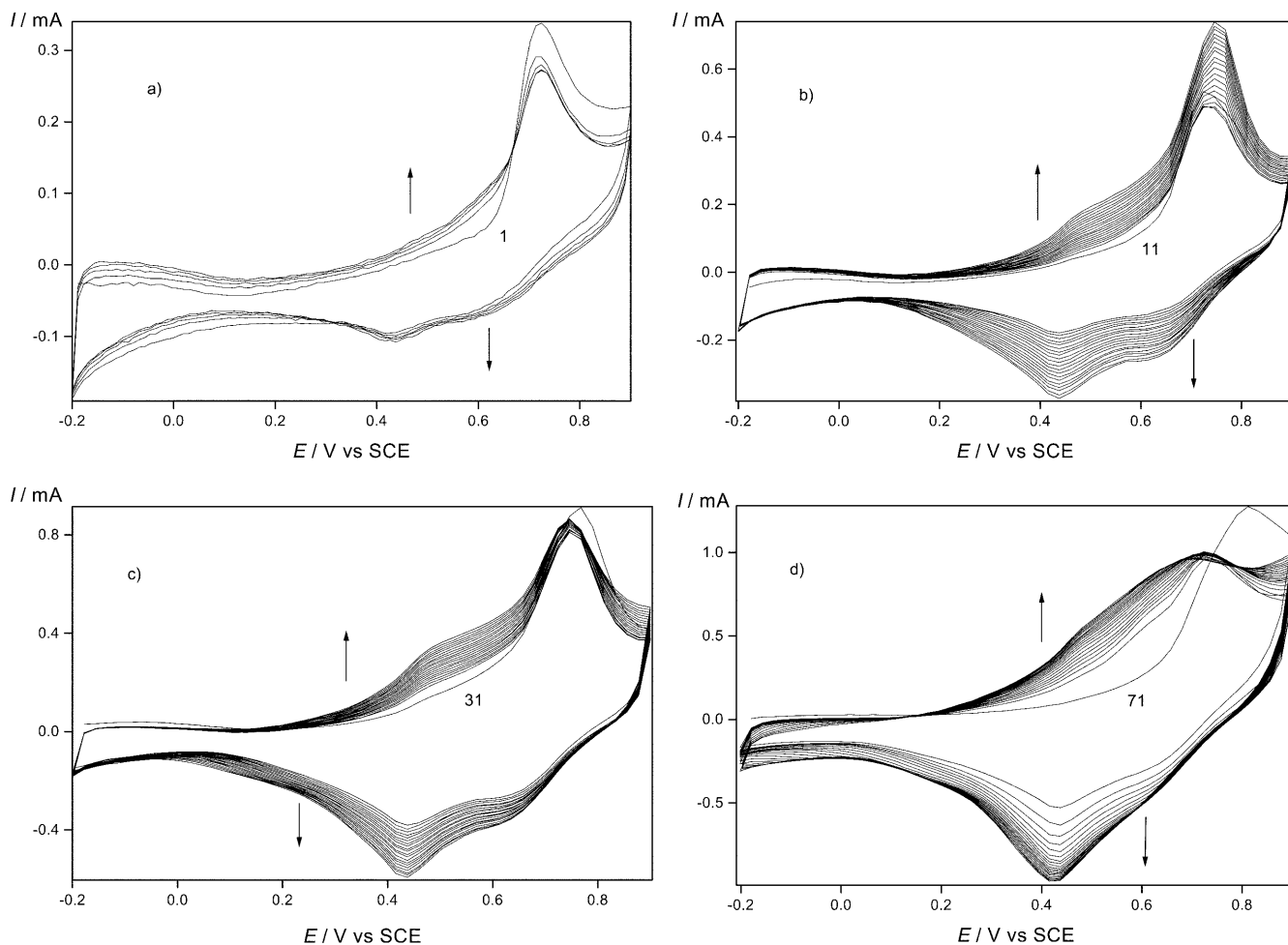


Fig. 1a–d Consecutive cyclic voltammograms obtained for diphenylamine microcrystals attached to a platinum electrode ($A=1\text{ cm}^2$) in the presence of an aqueous solution containing $1\text{ mol dm}^{-3}\text{ H}_2\text{SO}_4$. Scan rate: 100 mV s^{-1} . Cycles: **a** 1 to 5, **b** 11 to 30, **c** 31 to 50 and **d** 71 to 90 (started after 3 min delay at -0.2 V)

charge propagation. According to the theory, when the solid sample attached to the metal is an insulator (or its conductivity is very low) the reaction starts at the three-phase boundary between the electronically conducting support (e.g. metal), the sample and the electrolyte solution. Electrons are exchanged between the metal and the sample and ions between the microcrystal and the solution. The way of propagation of the electrochemical reaction depends on the relative rates of these two charge transport processes. It is likely that in our case the reaction starts at the three-phase boundary, since diphenylamine is an insulator; however, the formation of electronically conducting polymeric wires may provide an opportunity for the enhancement of electron transport within the bulk of the sample. The shape of the voltammograms does not reflect any phase separation or miscibility problem.

After 90 cycles the electrode shown in Fig. 1 was removed from the solution containing diphenylamine and was placed in turn in fresh solutions of sulfuric acid and buffer solutions containing H_2SO_4 and Na_2SO_4

(pH 0–3), respectively, with the total concentration of 1 mol dm^{-3} . The results are shown in Fig. 2 (similar behaviour has been obtained for systems prepared differently). Stable voltammograms were detected, i.e. no dissolution of the material attached to the surface was observed, if the switching potential was kept below 0.9 V . If the positive potential limit of cycling was set to 1.2 V , irreversible changes were observed that eventually led to the destruction of the microcrystals and polymeric film on the electrode. In order to illustrate the stable behaviour of the voltammogram response, two cycles are shown at each pH value. A single, rather wide pair of waves, was observed, which may reflect a high degree of polymerization and the increased delocalization over a longer conjugated backbone. At a low degree of polymerization, two pairs of waves appear which gradually overlap as the chain length of the polymer increases [15]. The electrochemical activity decreases with increasing pH, i.e. the peak currents become smaller and smaller, while the separation of the anodic and cathodic peak potentials increases. This change is not irreversible because the original response develops by replacing the pH 3 electrolyte with a solution of pH 0.

The anodic (E_{pa}) and the cathodic (E_{pc}) peak potentials decrease with the pH: between pH 0 and 1, these changes are -0.01 V and -0.02 V/pH , respectively, while

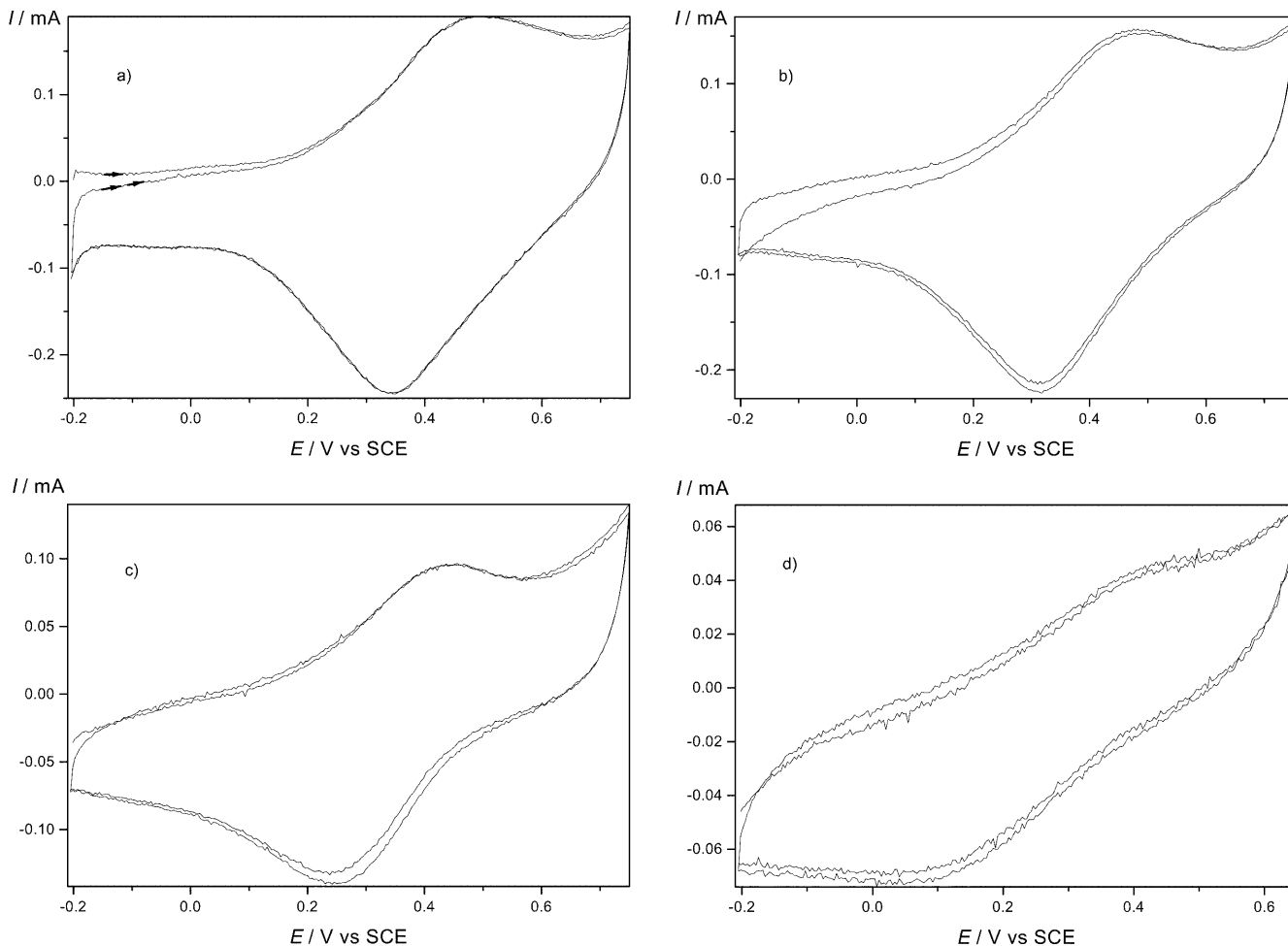


Fig. 2a–d Effect of the solution pH on the cyclic voltammetric curves of partially polymerized diphenylamine microcrystals on a Pt surface. pH: **a** 0, **b** 1, **c** 2.5 and **d** 3. $\text{H}_2\text{SO}_4\text{-Na}_2\text{SO}_4$ solutions with a total concentration of 1 mol dm^{-3} . Two cycles were taken at each pH. Scan rate: 25 mV s^{-1}

at $\text{pH} > 1$, owing to the splitting of the waves the analysis of these values is meaningless. The apparent formal potential ($E^{\circ'} = E_{\text{pa}} + E_{\text{pc}}/2$) changes by $-0.36 \pm 0.04 \text{ V/pH}$, which may indicate that a $2e^-, 1\text{H}^+$ process occurs; however, it is also likely that the oxidation takes place in two separate steps, each involving 0.5 electrons per monomer unit [15] and protons are involved only in one of these steps. Owing to the complexity of the reaction it is difficult to draw a conclusion regarding to the protonation processes; however, it can be stated that protons participate in the overall mechanism. It is also instructive that the picture substantially changes when the electrode prepared in $1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ is placed in $5 \text{ mol dm}^{-3} \text{ HClO}_4$ solution. As can be seen in Fig. 3, two waves develop and the pair of waves that appears at high positive potentials dominates. Figure 4 shows the final response in 5 M HClO_4 . This electrode was prepared by rubbing the platinum surface with DPAH microcrystals. Because in this way rather large microcrystals were attached to the metal surface, substantial currents were detected. Although a slight break-in phe-

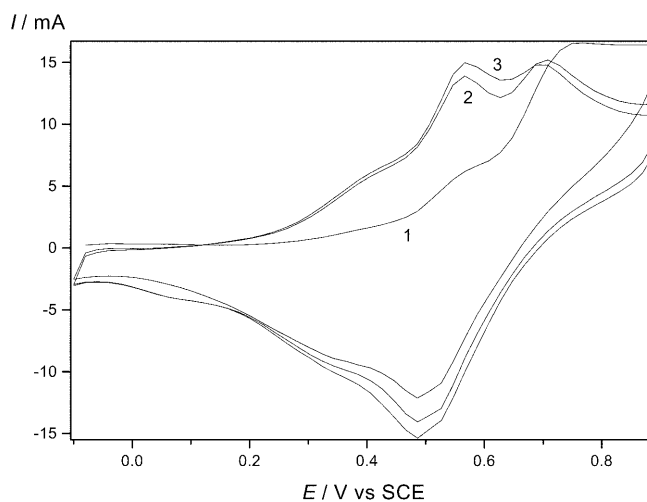


Fig. 3 Cyclic voltammograms obtained for a Pt/DPAH electrode ($A = 2 \text{ cm}^2$) in 5 M HClO_4 solutions. The electrode was prepared in $1 \text{ M H}_2\text{SO}_4$ solutions. The first three cycles after exchanging the electrolytes are shown. Sweep rate: 100 mV s^{-1}

nomenon has been observed, it is evident that the redox reaction proceeds smoothly even in the case of the presence of large crystals. It should also be mentioned that at low pH values the colour change of the crystals is

from colourless to bright blue or violet, while at higher pHs the reduced microcrystals are brownish gray and the oxidized form is greenish blue. According to the results of the spectroscopic studies [15], the violet colour is characteristic of the diphenoquinone diimine dication, the green colour is due to the equimolecular adduct of the colourless, protonated diphenylbenzidine and the oxidized, unprotonated quinone diimine form (diphenylbenzidine blue), while the brown compound is due to the unprotonated diphenylbenzidine. This is in good accord with the colour changes observed at different pH values, and also with the experience that at higher pH values the process is less reversible owing to adduct formation. The formulas of the principal species and the possible reaction schemes are shown in Figs. 5 and 6, respectively.

The peak current linearly varies at low sweep rates ($v < 25 \text{ mVs}^{-1}$), while at higher sweep rates a transition to diffusional behaviour can be observed. The latter

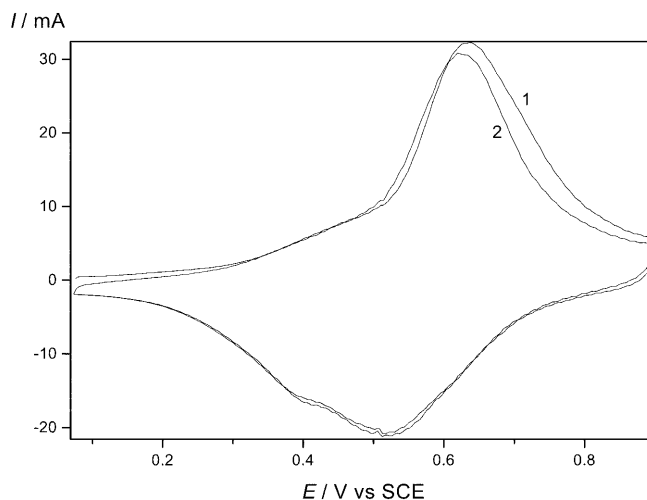
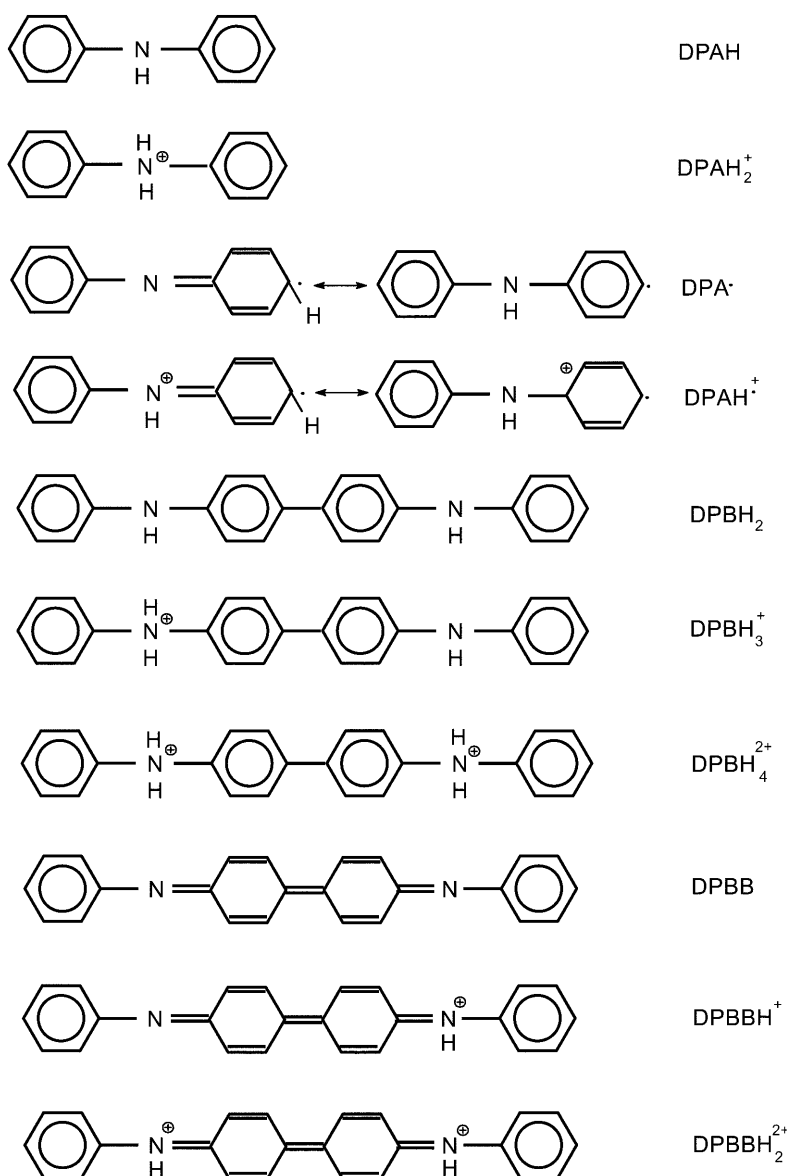


Fig. 4 The stable, final voltammetric response obtained for the electrode shown in Fig. 3 in 5 M HClO_4 . Sweep rate: 100 mV s^{-1}

Fig. 5 The formulas of diphenylamine (DPAH) and diphenylbenzidine (DPBH₂) at different oxidation and protonation states. DPA• and DPAH^{•+} are the primary oxidation products of DPAH; DPBH₃⁺ and DPBH₄²⁺ are the protonated forms of DPBH₂; DPBB (diphenylbenzidine blue), DPBBH⁺ and DPBBH₂²⁺ are the fully oxidized forms of DPBH₂ at different protonation states. DPAH₂⁺ exists at highly acidic media ($\text{p}K_{\text{b}} = 13.15$ for DPAH), while the protonation of DPBH₂ takes place easier since $\text{p}K_{\text{b}1} = 8.92$ and $\text{p}K_{\text{b}2} = 10.39$



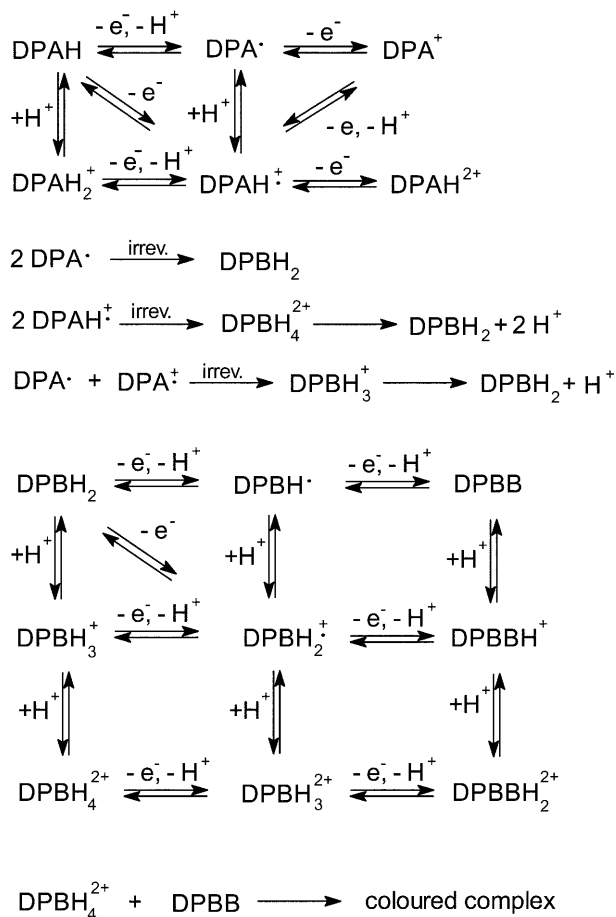


Fig. 6 Scheme of the oxidation of diphenylamine and the redox transformations of diphenylbenzidine. DPBH^\bullet , $\text{DPBH}_2^{\bullet+}$ and $\text{DPBH}_3^{\bullet 2+}$ are the half-oxidized states

effect also manifests itself in increasing peak separation, as can be seen in Fig. 7 where cyclic voltammograms obtained at 100 mV s^{-1} and 10 mV s^{-1} , respectively, are presented.

Conclusions

It has been demonstrated that diphenylamine microcrystals can be attached to platinum or gold surfaces in four different ways and can be investigated in aqueous solutions by electrochemical techniques without the dissolution of the samples. The cyclic voltammogram behaviour can be interpreted by the formation of oligomers and polymers during oxidation in acid media. The redox behaviour of the material formed can be described as reversible transitions between aromatic amine and quinoidal imine forms. The electrochemical response and the colour change indicate that both the reduced and oxidized species are protonated to a certain extent; therefore the electron transport is accompanied with a protonation/deprotonation reaction, depending on the pH of the contacting solution. Once the polymer is formed, its electronic conductivity may

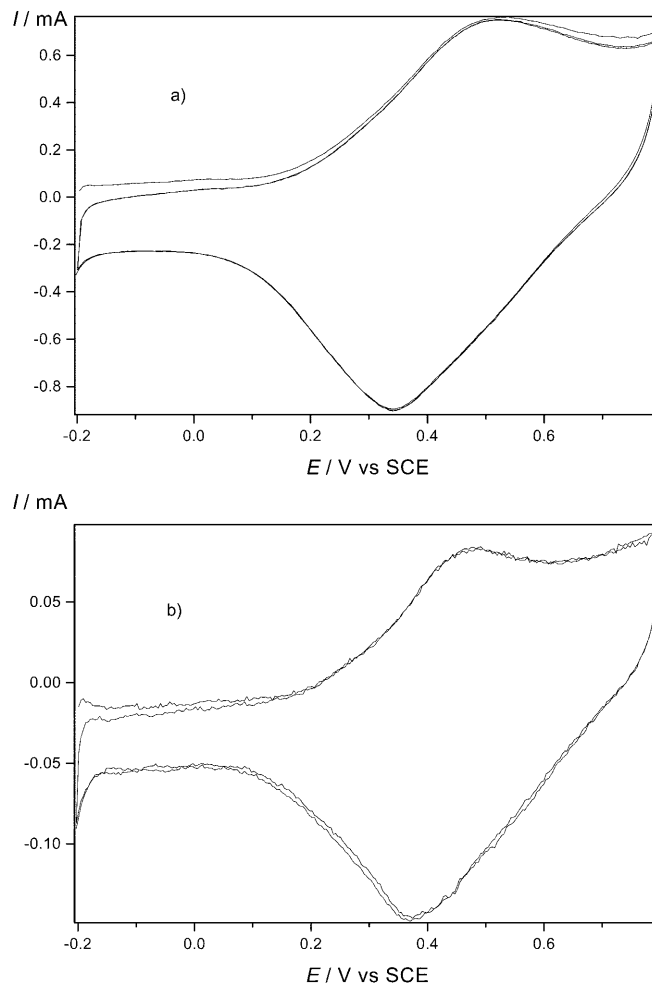


Fig. 7 Illustration of the sweep rate dependence at **a** 100 mV s^{-1} and **b** 10 mV s^{-1} . Solution: $1 \text{ M H}_2\text{SO}_4$. The electrode is the same as described in Fig. 2

enhance the electron transport in the originally insulating surface sample. Further electrochemical radiotracer and quartz crystal microbalance studies are in progress to learn more about the possible ionic exchange processes in the course of the redox transformations.

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References

- Scholz F, Meyer B (1998) Voltammetry of solid microparticles immobilized on electrode surfaces. In: Bard AJ (ed) *Electroanalytical chemistry*, vol 18. Dekker, New York, pp 1–86
- Scholz F, Nitschke L, Henrion G (1989) *Naturwissenschaften* 76:167
- Lovric M, Hermes M, Scholz F (2000) *J Solid State Electrochem* 4:394
- Evans CD, Chambers JQ (1994) *Chem Mater* 6:454
- Bond AM, Fletcher S, Marken F, Shaw SJ (1996) *J Chem Soc Faraday Trans* 92:3925

6. Shaw SJ, Marken F, Bond AM (1996) *Electroanalysis* 8:732
7. Jaeger CD, Bard AJ (1980) *J Am Chem Soc* 101:4840
8. Bond AM, Marken F (1994) *J Electroanal Chem* 372:125
9. Komorsky-Lovric S (1997) *J Solid State Electrochem* 1:94
10. Komorsky-Lovric S (1995) *J Electroanal Chem* 397:211
11. Jiang J, Kucernak A (2000) *J Electroanal Chem* 490:17
12. Dobos D (1975) *Electrochemical data*. Akadémiai Kiadó, Budapest, p 232
13. Reed RC, Wightman RM (1984) Derivatives of ammonia. In: Bard AJ, Lund H (eds) *Encyclopedia of electrochemistry*, vol 15. Dekker, New York, pp 2–168
14. Hayat U, Bartlett PN, Dodd GH, Barker J (1987) *J Electroanal Chem* 220:287
15. Comisso N, Daolio S, Mengoli G, Salmaso R, Zecchin S, Zotti G (1988) *J Electroanal Chem* 255:97
16. Guay J, Dao LH (1989) *J Electroanal Chem* 274:135
17. Yang H, Bard AJ (1991) *J Electroanal Chem* 306:87
18. (1964) *Spravochnik khimika*, vol 2. Khimiya, Moscow, p 659
19. Neubert G, Prater KB (1974) *J Electrochem Soc* 121:745