JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 12, No. 8, August 2010, p. 1805 - 1810

Electrochemical synthesis of azo azulene films

E.-M. UNGUREANU, C. A. AMARANDEI, D. I. CAVAL*, G. O. BUICA, A. C. RAZUS[a], L. BIRZAN[a]
Faculty of Applied Chemistry and Material Sciences, University "Politehnica" of Bucharest, Calea Grivitei 132, 010737, Bucharest, Romania
[a]*Institute of Organic Chemistry "C. D. Nenitzescu" of Romanian Academy, Spl. Independentei 202B, PO Box 15-258, 71141, Bucharest, Romania*

The formation of substituted poly-azo-azulene films was accomplished through electrochemical oxidation by scanning or controlled potential electrolysis. Conductive or isolating films have been obtained on glassy carbon, using acetonitrile as solvent and 0.1 M tetrabutyl ammonium perchlorate as supporting electrolyte, starting from differently substituted azoazulenes. The optimal conditions for the film formation (potential, charge, azoazulene structure) have been established. Their characterization was done by cycling voltammetry and redox probe voltammetry.

(Received December 9, 2009; accepted August 12, 2010)

Keywords: Electrochemical polymerization, Substituted polyazoazulene, Conducting polymer, Films, Electrochemical characterization

1. Introduction

The huge efforts put into the basic research and development of conducting polymers is naturally related to hopes of feasible technical applications. Thus, conducting polymers based on azulene are discussed as active battery electrodes [1], electrochromic displays [2], anticorrosives [3], sensors [4], electrocatalysts [5], or light-emitting materials (OLED). This films formation is explained by the oxidizable aromatic character of azulene, which have an anodic peak at only 0.54 V [6]. Owing to its peculiar polarization, azulene is stabilized during oxidation by its substitution, in position 1, with electron-withdrawing groups (EWGs), especially those possessing a heteroatom with a pair of free electrons linked to azulene [7].

It is known that the electrochemical oxidation of azulene derivatives frequently leads to the deposit of an organic film on the electrode surface. If this film is insulating, the electrochemical current drops off very rapidly, and film growth ceases. If the deposit conducts electricity, however, thick films can be grown.

In the present work we have studied the electrochemical properties of two phenylazoazulene derivatives, 4-metoxy-phenyl-azo-1-azulene (**M**), and 4-nitro-phenyl-azo-1-azulene (**N**), respectively substituted at the phenyl ring with methoxy electron donating group, and with nitro electron withdrawing group. We made a parallel between the two opposite effects on the electrochemistry of the analyzed derivatives. We used phenylazo-1-azulene (**P**) as a model compound.

2. Experimental

Acetonitrile (Rathburn, HPLC grade), tetra-*n*-butylammonium perchlorate (TBAP), and tetra-*n*-butylammonium fluoroborate ($TBABF_4$) from Fluka were used as received for solvents and supporting electrolytes. The investigated compounds were obtained by specific chemical reaction of azulenes with 4-arylamines [8,9]. Structure and physical characteristics were confirmed by elemental and spectral (^{1}H-NMR, ^{13}C-NMR, GC-MS) analyses.

Electrochemical experiments were conducted in conventional three-electrode cells under argon atmosphere at 20°C using a PGSTAT 12 AUTOLAB potentiostat. The working electrode was a glassy carbon disk (3 mm diameter) polished with 200 μm diamond paste. An Ag/10 mM $AgNO_3$ in CH_3CN + 0.1 M TBAP system was used as reference electrode. The counter electrode was a platinum netz in a separate compartment containing CH_3CN + 0.1 M TBAP for the synthesis cell, and a platinum wire for the transfer and redox probe cells. All potentials were referred to the potential of ferrocene/ferricinium (Fc/Fc^+) couple, which was 0.07 V with our experimental conditions.

The films were synthesized in substituted azulene milimolar solutions in CH_3CN + 0.1 M TBAP by cycling the potential or controlled potential electrolysis (CPE). Chronoamperometry was used to calculate the polymerization charge in CPE. The modified electrodes were tested in two different ways: transferred into pure electrolyte (CH_3CN + 0.1 M TBAP) and tested by cyclic voltammetry in the transfer cell, and then in 0.5 mM ferrocene solution in CH_3CN + 0.1 M TBAP in the redox probe cell. CV experiments were usually performed at 0.1 V/s.

The electrochemical polymerization was performed by potentiodynamic (CV) and potentiostatic (CPE) methods in milimolar solutions of substrates in CH_3CN containing 0.1 M TBAP. Once the polymerization reaction has been achieved and after thorough rinsing of the sample with acetonitrile two electrochemical techniques have been used to characterize the formed film:

i) Cycling voltammetry of the modified electrode in CH_3CN containing 0.1 M TBAP in the field of potential characteristic for the activity of the polymeric groups (CV). The reversible voltammogram of the attached polymer is located at the same position. The fact that the cathodic and anodic peaks are located at the same potential (giving rise to the symmetrical shape of the voltammogram) indicates that the species undergoing the redox process do not diffuse to and from the electrode and are therefore bonded to the surface.

ii) Electrochemical response of the redox probe was studied on the GC modified electrodes using ferrocene (0.5 mM) in organic medium (acetonitrile containing 0.1 M TBAP). The influence of the glassy carbon electrode modification conditions on the cyclic voltammetric response of Fc/Fc^+ couple was investigated for different layers obtained by electrochemical polymerization. The slower kinetics and/or blocking effect of the polymer for the redox systems was conveyed by an increase of the separation of the anodic and cathodic peak potentials (ΔEp) and a decrease of the intensity of the anodic/cathodic peak current of the ferrocene cyclic voltammograms.

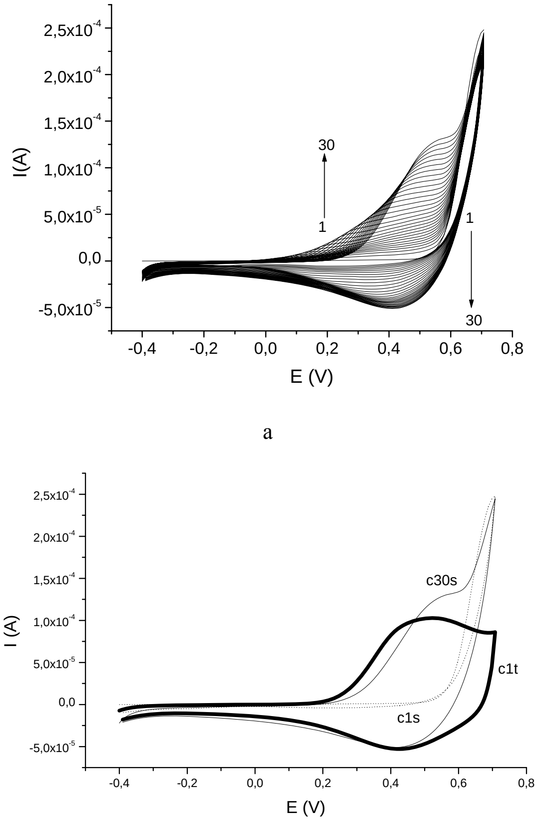
3. Results and discussion

Electrochemical polymerization of the monomers was tried in acetonitrile containing 0.1 M TBAP or $TBABF_4$. Results were obtained only when it was used TBAP as supporting electrolyte. Poly(azulene) films (poly**P**, poly**M**, poly**N**) were synthesized in azulene (**P**, **M**, or **N**) milimolar solutions (5-10 mM) in CH_3CN + 0.1 M TBAP by cycling the potential (CV) or controlled potential electrolysis (CPE). The anodic limit of cycling or the CPE potential were chosen in the potential range characteristic for the corresponding azulene oxidation peak. We used phenylazo-1-azulene (**P**) as a model compound [10].

3.1. Phenyl-azo-1-azulene (P)

The growth of a film of poly**P** by scanning between -0.4 and 0.7 V is shown in Fig. 1. The obtained film presents, in the preparation solution, an anodic peak at 0.567 V and a reduction peak at 0.419 V (Fig.1.A). When the anodic limit is lower (0.6 V), during the formation of thiner films by potential scanning the reduction peak shifts to more cathodic potentials.

In the transfer solution, the modified electrode shows an anodic peak at 0.527 V and a reduction peak at 0.49 V which corresponds to the oxidation of the poly**P** film. The poly**P**/poly$\mathbf{P}^{\cdot+}$ couple has a formal potential of 0.493 V in the synthesis solution and 0.509 V in the transfer solution. Poly**P** films were also synthesized by controlled potential electrolysis (CPE) [10]. The CPE potentials were varied within the potential range characteristic for the azoazulene oxidation (0.6-0.75 V). When the synthesis potential varied between 0.625 and 0.725 V the modified electrodes obtained by EPC with the same synthesis charge (0.5 mC) showed in the transfer solution different shapes of the CV curves (Fig. 2.A). Two anodic peaks and a large cathodic peak can be seen. The anodic peaks are situated at potentials around 0.32 and 0.62 V and the cathodic peak is at about 0.39 V.

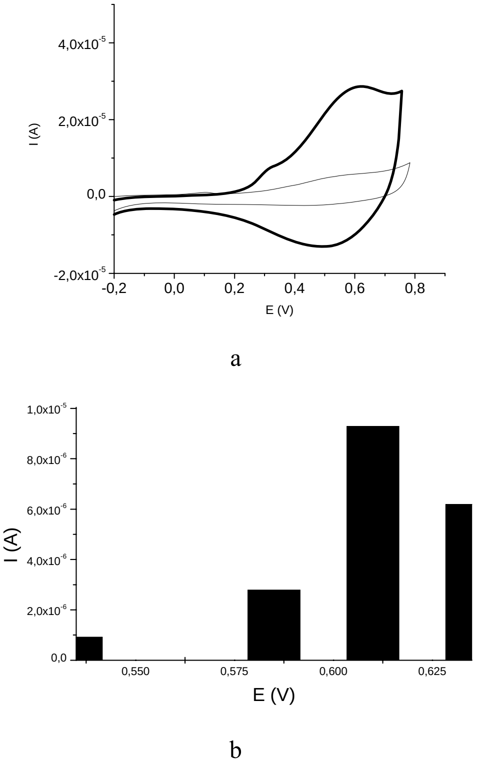


a

b

*Fig. 1a - Succesive CVs at 90 mV/s (cycles 1 - 30) on glassy carbon during the film formation by scanning (anodic limit: 0.7 V) in 10 mM **P**, 0.1 M TBAP, CH_3CN; b – comparison between the CV cycles in synthesis in the 1st and 30th cycles and transfer (cycle 1) in 0.1 M TBAP, CH_3CN.*

The influence of the CPE potential on the CV anodic charge of the poly**P** film in transfer solution (0.1 M TBAP, CH_3CN) shows an optimum potential of 0.61 V for films of 0.5 mC (Fig. 2.B). Films of different thicknesses were obtained at this potential. Fig.3. shows that thicker films did not get higher responses in transfer solution meaning that they become less conductive than the thiner ones. The comparison was made by integrating the anodic current of the film between -0.2 and 0.61 V. This fact is in agreement with the experimental conclusion as we obtained reproductible poly**P** films, especially by scanning and the films are very sensitive to the anodic limit of the scan.



a

b

*Fig. 2a - CV (0.1 V/s) in transfer solution (1st cycle) for poly**P** films formed by CPE at 0.535 V–thin line; 0.585 V– thick line. b) Influence of the CPE potential on the CV anodic charge of the poly**P** film in transfer solution (0.1 M TBAP, CH_3CN); films of 0.5 mC were obtained in 10 mM solution of **P** in 0.1 M TBAP, CH_3CN.*

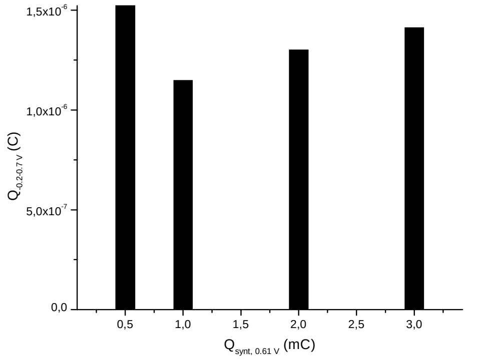


Fig. 3. Influence of the CPE synthesis charge (Q_{synth}) on the anodic charge of the film in transfer solution (0.1 M TBAP, CH_3CN); films were obtained at the optimum potential (0.61 V) in 10 mM solution of M in 0.1 M TBAP, CH_3CN.

The comparison between the CVs (100 mV/s) in 0.5 mM ferrocene, 0.1 M TBAP, CH_3CN of the poly**P** modified electrodes obtained by CPE (3 mC) at different formation potentials shows that the area of the anodic ferrocene signal (between -0.33 and 0.1 V) is the biggest for the potential of 0.61 V. This confirms the optimum potential value of 0.61 V which was obtained also by integration of the anodic branch of the CVs in transfer solution of the film formed by CPE at different potentials (same charge of 0.5 mC).

3.2. p-Methoxy-phenyl-azoazulene (M)

In Fig. 4a are presented succesive CVs during the formation of **polyM.** They show the increase of the film on the electrode surface. Starting with the 5th scan an oxidation peak can be observed at about 0.26 V, corresponding to the oxidation of the polyM film. In the reverse scans, a broad reduction peak can be seen at about 0.36 V. Their currents increase due to the growth of the film on the electrode surface. As the cycling advances, the oxidation peak potential gets more positive values, while the reduction peak potential becomes more negative. When transferred in pure electrolyte (0.1 M TBAP, CH_3CN) the modified electrode obtained after 30 cycles shows a quasi-reversible pair of peaks situated at potential values close to those in the synthesis solution. Fig.4.B gives a comparison between the first cycle in the synthesis solution (c1s), which has no signal for the film, and the 30th cycle in the synthesis solution (C30s) and the 1st cycle in the transfer solution (C1t) which show an obvious redox process of the poly**M** film. When the anodic limit was varied betwen 0.4 and 0.5 V films of different thicknesses (0.026 mC and 0.36 mC) were obtained by scanning.

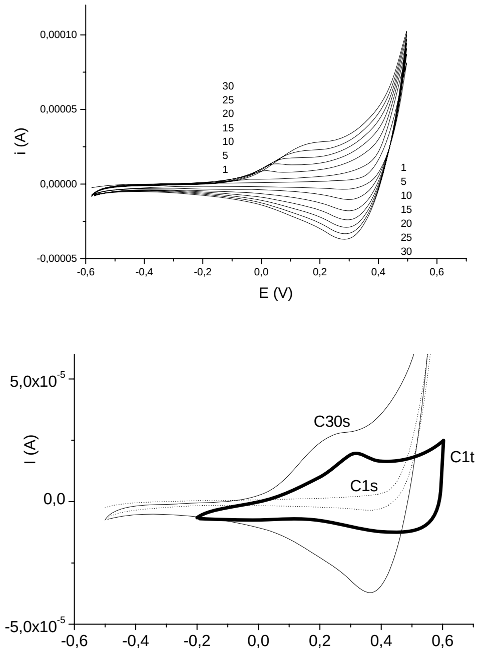


*Fig. 4. a - Succesive CVs at 100 mV/s (cycles 1, 5, 10, 15, 20, 25, 30) on glassy carbon during the film preparation by scanning (anodic limit: 0.5 V) in 10 mM **M**, 0.1 M TBAP, CH_3CN; b – comparison between the CV cycles in synthesis in the 1st and 30th cycles and transfer (cycle 1) in 0.1 M TBAP, CH_3CN.*

Poly**M** films were also synthesized by controlled potential electrolysis (CPE). The anodic limit of cycling or the CPE potential were chosen in the potential range characteristic for the corresponding azulene oxidation peak (0.6-0.9 V). The films were transferred in 0.1 M TBAP, CH_3CN. The influence of the CPE potential on the CV anodic charge of the poly**M** film in transfer solution shows an optimum potential of 0.58 V for films of 0.5 mC. Films of different thicknesses were obtained at this potential. Fig.6. shows that there is an increase of the films as the synthesis charge increases meaning that films are conductive (the comparison was made by integrating the anodic current of the film between -0.2 and 0.7 V).

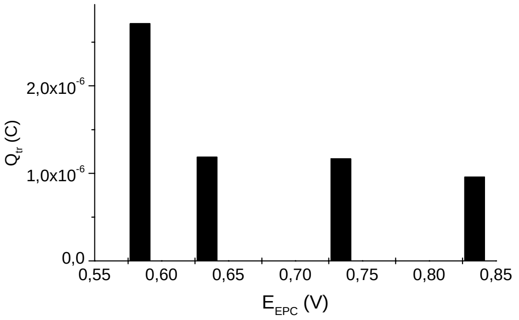


*Fig. 5. Influence of the CPE potential on the CV anodic charge of the poly**M** film in transfer solution (0.1 M TBAP, CH_3CN); films of 0.5 mC were obtained in 10 mM solution of **M** in 0.1 M TBAP, CH_3CN.*

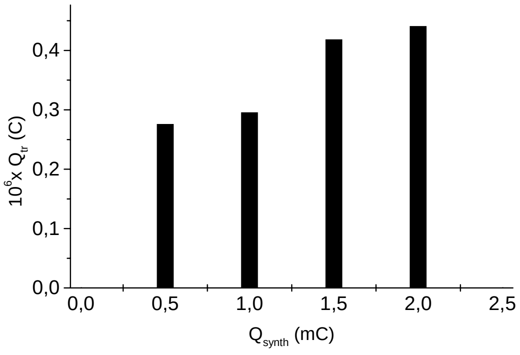
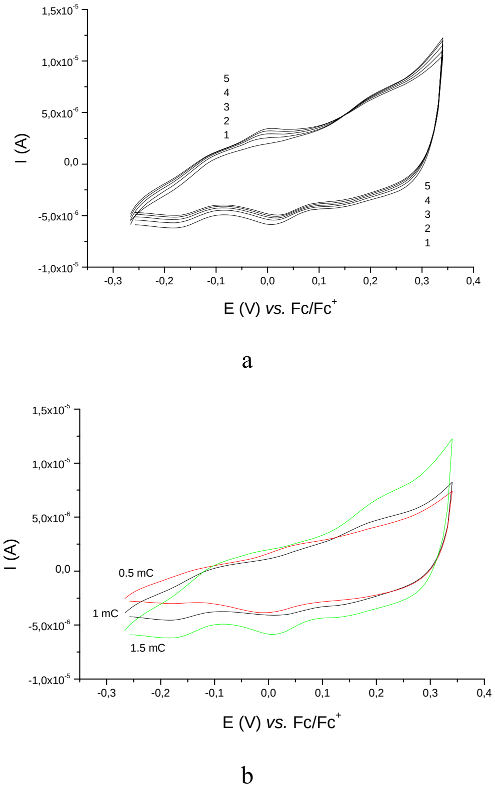


*Fig. 6. Influence of the CPE synthesis charge (Q_{synth}) on the anodic charge of the film in transfer solution (0.1 M TBAP, CH_3CN); films were obtained at the optimum potential (0.58 V) in 10 mM solution of **M** in 0.1 M TBAP, CH_3CN.*

Redox characterization of the films of different thicknesses in transfer solution show the appearance of three types of polymers which have formal redox potentials for the three couples at about -0.15, 0.02 and 0.18 V. Thicker films have all the three couples in the CV signal.



a

b

Fig. 7. A. Succesive CVs at 100 mV/s (cycles 1 -5) of the GC modified electrode by CPE (0.65 V, 1.5 mC) in 0.1 M TBAP, CH_3CN; b.Comparison between cycles 1 for GC modified electrode by CPE (0.65 V) at different charges, in 0.1 M TBAP, CH_3CN;

The films obtained at different charges, at the optimum potential were also characterized by redox probe test (Fig.8., Table 1). It can be seen that they are conductive as the ferrocene signal is increased when the film thickness increases. For thicker films, the poly**M** anodic signal is also visible at -0.054 V.

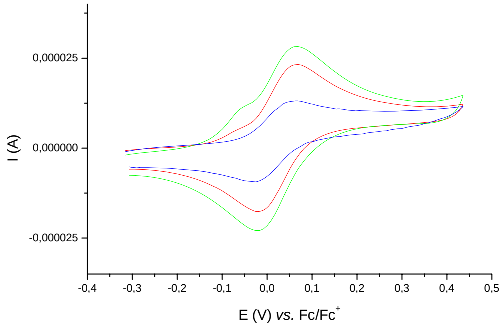


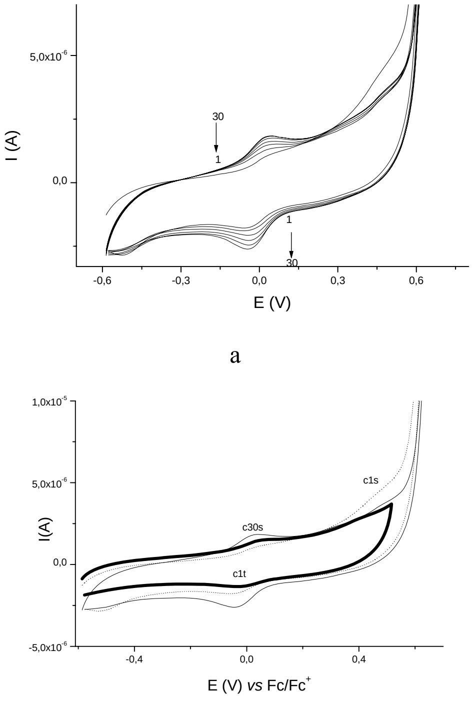
*Fig. 8. Comparison between the CVs (100 mV/s) in 0.5 mM ferrocene, 0.1 M TBAP, CH_3CN of the poly**M** modified electrodes obtained by CPE (0.65 V) at different charges: 0 mC – blue, 1 mC – red, 2 mC – green.*

Table 1. Anodic peak area from the CVs (Fig. 8) in 0.5 mM ferrocene, 0.1 M TBAP, CH_3CN

Formation charge, (mC)	Fc anodic charge x E6 (C)	Remarks
0	5,29	-
1	7,47	-
2	9,19	Other anodic peak at -0.054 V

3.3. p-Nitro-phenyl-azoazulene(N)

In Fig. 9a are presented succesive CVs during the formation of **polyN.** They show the increase of the film on the electrode surface. During subsequent scanning, it can be observed an oxidation peak at 0.044 V. On the reverse scan a cathodic peak can also be obseved at about -0.023 V. This redox couple can be observed at a formal potential of 0.0105 V; both anodic and cathodic peak potentials slightly shift to the left. They can be attributed to the couple poly**N**/poly**N**$^{\cdot+}$. Their currents increase due to the growth of the film on the electrode surface.



a

b

*Fig. 9. a - Succesive CVs at 100 mV/s (cycles 1, 5, 10, 15, 20, 25, 30) on glassy carbon during the film preparation by scanning (anodic limit: 0.64 V) in 10 mM **N**, 0.1 M TBAP, CH_3CN; b – comparison between the CV cycles in synthesis in the 1st and 30th cycles and transfer (cycle 1) in 0.1 M TBAP, CH_3CN.*

When transferred in pure electrolyte (0.1 M TBAP, CH_3CN) the modified electrode obtained after 30 cycles shows a quasi-reversible pair of peaks situated at potential values almost identical with those in the synthesis solution. Fig.9.B gives a comparison between the first cycle in the synthesis solution (c1s), which has no signal for the film, and the 30th cycle in the synthesis solution (C30s) and the 1st cycle in the transfer solution (C1t) which show an obvious redox process of the poly**N** film. When the anodic limit was established at 0.64 V (case presented) only a thin film (of about 0.07 mC) was obtained by scanning.

Poly**N** films were also synthesized by controlled potential electrolysis (CPE). The anodic limit of cycling or the CPE potential were chosen in the potential range characteristic for the corresponding azulene oxidation peak (0.55-0.85 V). The films were transferred in 0.1 M TBAP, CH_3CN. The influence of the CPE potential on the CV anodic charge of the poly**M** film in transfer solution shows an optimum potential of 0.645 V for films of 0.5 mC. Films of different thicknesses were obtained at this potential. Fig.11. shows that there is a constant increase of the films as the synthesis charge increases until a certain charge, meaning that below this certain value (of 2 mC)films are conductive (the comparison was made by integrating the anodic current of the film between -0.2 and 0.4 V). After this value a slight decrease of the films can be observed, meaning that films are getting more and more insulating.

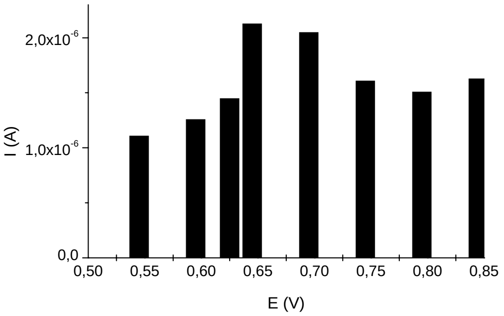


*Fig. 10. The influence of the CPE formation potential on the anodic oxidation peak of the film in transfer solution (0.1 M TBAP, CH_3CN); films of 0.5 mC were obtained in 10 mM solution of **N** in 0.1 M TBAP, CH_3CN.*

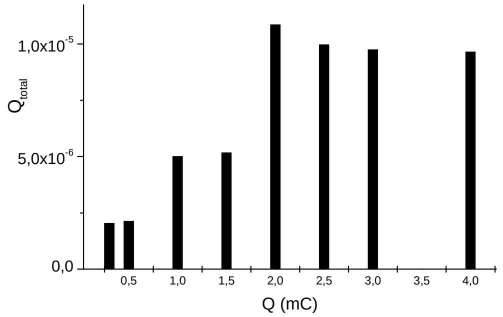


*Fig. 11. The influence of the CPE formation charge on the total current in the film in transfer solution (0.1 M TBAP, CH_3CN); films were obtained at the optimum potential (0.75 V) in 10 mM solution of **N** in 0.1 M TBAP, CH_3CN.*

Redox characterization in transfer solution of the film obtained in optimal conditions (0.645 V, 2 mC), with different anodic limits (0.3, respectively 0.5 V) show the appearance of two different types of polymers which have formal redox potentials for the two couples at about -0.2 and -0.0026 V (Fig.12). When the anodic limit has a higher value , the first anodic peak disappears.

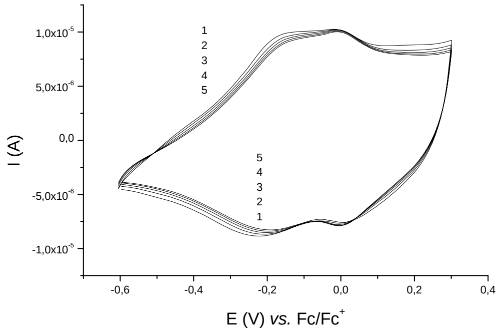


Fig. 12. Succesive CVs at 100 mV/s (cycles 1 -5) of the GC modified electrode by CPE (0.645 V, 2 mC) in 0.1 M TBAP, CH_3CN.

The comparison between the CVs (100 mV/s) in 0.5 mM ferrocene, 0.1 M TBAP, CH_3CN of the poly**N** modified electrodes obtained by CPE (0.5 mC) at different formation charges shows that the area of the anodic ferrocene signal (between -0.33 and 0.4 V) has a maximum for the correspondent charge of 2 mC. This is in perfect agreement with the results obtained by integration of the anodic branch of the CVs in transfer solution of the films of different thicknesses, formed by CPE at the optimum potential of 0.58 V.

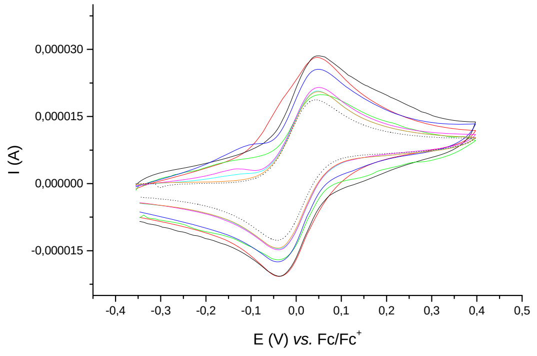


Fig. 13. Comparison between CVs (100 mV/s) for GC modified electrode by CPE (0.645 V) at different charges (mC): 0 – dot, 0.5 – orange, 1– magenta, 1.5 – cyan, 2 – blue, 2.5 – green, 3 – red, 4 – black, in 0.5 mM ferrocene in 0.1 M TBAP, CH_3CN;

4. Conclusions

Poly-azo-azulene films were obtained through electrochemical oxidation by scanning or controlled potential electrolysis starting from starting from differently substituted azoazulenes: 4-metoxy-phenyl-azo-1-azulene (**M**), and 4-nitro-phenyl-azo-1-azulene (**N**), respectively substituted at the phenyl ring with methoxy electron donating group, and with nitro electron withdrawing group. We made a parallel between the two opposite effects on the electrochemistry of the analyzed derivatives. Unsubstituted phenylazo-1-azulene (**P**) was used as pattern compound.

Conductive films have been obtained on glassy carbon from all these compounds. They were characterized by cycling voltammetry and redox probe voltammetry. The results were in agreement. The optimal conditions for the film formation (potential, charge) have been established for each azoazulene being in accordance with their structure.

Acknowledgments

Financial support from CNCSIS 87 and CNMP REMORESE 71-067 is gratefully acknowledged.

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[*] Corresponding author: dan_caval@yahoo.com