

Inhibition of the Electrode by Adsorption of the Perchlorate and the Opening Ring Products on the Surface in the Oxidation of Furans

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Abstract: The oxidation of furan, 2-methylfuran and 2,5-dimethylfuran on the rotating disk platinum electrode, in acetonitrile was investigated using cyclic voltammetry method. The results have shown, in presence of stirring, that the electrochemical behaviour of the 2-methylfuran is similar to furan, but it is different to 2,5-dimethylfuran. IR spectrum of the anodic deposit from the 2-methylfuran or furan show the presence of tetra-n-butylammonium perchlorate and the opening ring product in the film, which is strongly adsorbed on the electrode. The supporting electrolyte probably interferes in the formation of well-organized organic film. Also, others contaminants, such as oxygen and water which are inevitably present in solution affect the mechanism of oxidation and contribute to the structural film.

Key words: Furans, organic conducting polymer, opening ring product, Rotating disk electrode, cyclic voltamperometry

INTRODUCTION

The organic conducting polymers with an extended π -electron system have attracted the interest of scientists because of the possibility of transforming them into conducting materials by chemical or electrochemical doping. Electrochemical polymerization is one of the most widely used methods for preparing conducting polymers due to its advantages. A large number of application have been proposed for these materials (rechargeable batteries, sensors, devices) (Goward *et al.*, 1998; Sargent *et al.*, 1999; Horowitz *et al.*, 1993). Among conducting polymers of the 5 membered heterocyclic monomers, polypyrrole and polythiophene are the most widely studied. These conducting polymers are synthesized by electro-oxidation of relative monomer. However, polyconjugated polyfuran polymers have been one of the less studied due to synthesis difficulties and to prepare it in good quality (Demirbog̃a and Õnal, 1999; Li-Fajari *et al.*, 1998; Nessark *et al.*, 1990). Although, theoretical research has been performed on polypyrrole, polythiophene and polyfuran, this later has been the object of much less experimental research. Polyfurans produced by acid-catalysed have been dedicated to them, but they are not polyconjugated as they contain variously hydrogenated furans units (Zotti *et al.*, 1990; John *et al.*, 1991).

We have interested in this study to the comparison of the electrochemical behaviour, of the furan, the 2-methylfuran and the 2,5-dimethylfuran, in acetonitrile containing tetra-n-butylammonium perchlorate as supporting electrolyte, on platinum electrode, using cyclic voltamperometry. Among polyconjugated polymers, polyfuran has been particularly neglected, although the furans are raw materials easily accessible from biomass which able to open a large research field mainly in the view point of organic electrosynthesis (Fig. 1).

The anodic oxidation of furans leads to the formation of a deposit on the electrode surface and to the dissolved products in solution. The nature of the formed film, its electrochemical and spectroscopic properties are not still properly known and a few research works have been carried out on this subject. The problem is to know if the formed film is a polymer obtained by electrochemical coupling of the furan ring or a product resulting from ring opening. This supposes that the water or the acetonitrile addition on the ring, which after radical cation formation by anodic oxidation, leads to product strongly adsorbed on the electrode. The present research involves, a rigorous study of the voltammetric behaviour, in order to correlate it with the surface chemistry. IR spectroscopy and Scanning Electron Microscopy (SEM) were also used in order to characterize the surface chemistry of the electrode and to explain the origin of inhibition of the

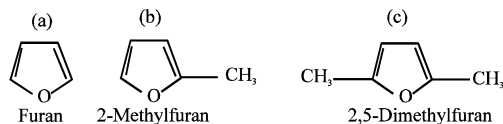


Fig. 1: Chemical structure of furan, 2-Methylfuran and 2,5-Dimethylfuran

electrode by the formed film. The effect of contaminants such as water, oxygen and of supporting electrolyte, on the electrochemical properties and on the morphology of the surface chemistry of the film were also taken into consideration.

EXPERIMENTAL

Cyclic voltamperometry was performed in Tacussel cell containing the furan compound (10^{-2} mol L⁻¹) dissolved in acetonitrile containing Tetra-n-Butylammonium Perchlorate (TBAP) (10^{-1} mol L⁻¹). A Saturated Calomel Electrode (SCE) was used as reference; the working electrode was a rotating platinum disk with a surface of 3.14 mm² and the auxiliary electrode was a 2 mm platinum wire. The solution had been deoxygenated by a continuous flow of argon for 30 mn. Study was carried out at room temperature. Before each electrolysis, the working electrode was treated by submerging it in a heated solution of sulphuric acid and then in nitric acid. It was rinsed with distilled water, acetone and then dried.

The experimental set-up consists of a Taccussel type PRT40-1X potentiostat, a Tacussel type GSATP arbitrary signal generator, a Sefram type TGM X-Y (Chart recorder), an MVN millivoltmeter and a MAR-U microamperometer (Tacussel).

Acetonitrile (Merck product) was dehydrated on linde 4 A molecular sieves and purified by two successive distillations over anhydrous sodium sulphate. Tetra-n-butylammonium perchlorate (Fluka product) was dried under a vacuum at 100°C. Furan, 2-Methylfuran and 2,5-Dimethylfuran (Merck products) were purified by 2 consecutive distillations. The obtained film on the electrode, after electrolysis was washed with acetonitrile, dried and was finally analysed by IR-spectroscopy and scanning electron microscopy.

RESULTS AND DISCUSSION

As reported in our previous study Nessark *et al.* (1990), the cyclic voltamperograms show an anodic peak at 1.85 V for furan, at 1.64 V for the 2-methylfuran and at 1.45 V for the 2,5-dimethylfuran. The study showed that the anodic peak of 2-methylfuran decreases during

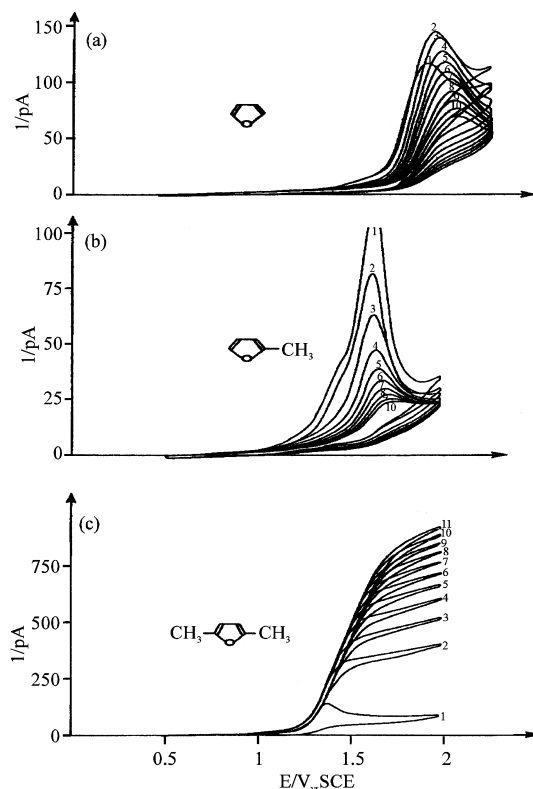


Fig. 2: Cyclic voltammograms of (a) furan, (b) 2-methylfuran and (c) 2,5-dimethylfuran on a Pt rotating disc electrode in acetonitrile containing 0.1M Nbu₄ClO₄: (1) 0; (2) 500; (3) 1500, (4) 2000, (5) 2500; (6) 3000; (7) 3500; (8) 4000; (9) 4500; (10) 5000 rpm; at a scan rate of 100 mV s⁻¹

cycling and it stabilizes at a small value when the electrode surface is coated by an insulating film. We observed also, for the three furan compounds a cathodic peak at -0.10 V, which was attributed to the reduction of proton. This indicates that the oxidation of furans gives protons. Thus, in order to have others informations on the electrochemical furans, we had studied its behaviour on rotating disk electrode. The variation of the current with respect of stirring rate (ω) of the Rotating Disk Electrode (RDE) realized at a scan rate of 100 mV/s shows in the case of furan and 2-Methylfuran an oxidation peak (Fig. 2). The current of this peak decreases and its potential shifts towards positive values, when ω varied between 500 and 5000 rpm. But, we remarked in this study, that these peaks are not observed when the study was carry out at very weak values of scan rate ($v = 10$ mV s⁻¹) in case of these compounds; the current increases, evenly, after 2 V for first and at 1.60 V for the second compound, without stabilized. However, in the case of the 2,5-methylfuran, we observed a voltamperometric wave

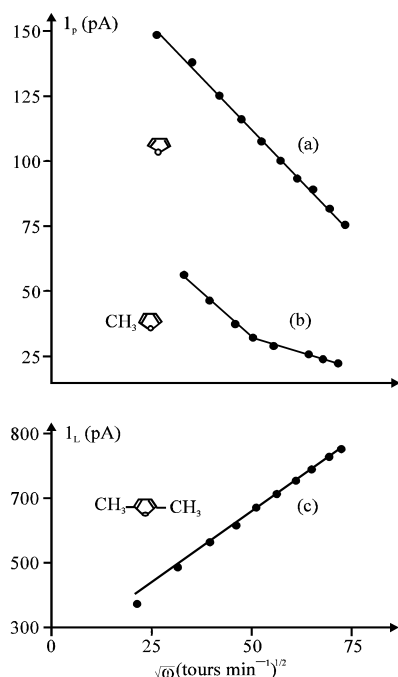


Fig. 3: Variation of the current peak with $\omega^{1/2}$ in the case of: (a) the furan, (b) the 2-methylfuran and (c) the 2,5-dimethylfuran, on a Pt rotating disc electrode, at a scan rate of 100 mV s^{-1}

which increases with ω . It was noticed that whatever the value of scan rate (v), no peak is observed for this third compound, either at high or weak stirring rate (ω).

The Fig. 3 shows the variation of the current peak with $\omega^{1/2}$. In the case of the furan and the 2-methylfuran, the straight lines obtained, had negative slopes. A change slope explaining an innovation of the global kinetic reaction caused by a modification of the structural formed film, was observed in the case of the 2-methylfuran at $\omega = 2500 \text{ rpm}$. Its straight line $I_p = f(\omega^{1/2})$ was parallel with that the furan at weak values of ω . This justifies again that the kinetic of this 2 compounds is the same. However, in the case of 2,5-dimethylfuran, the current taken at 1.80 V increases linearly with $\omega^{1/2}$. The equation of Levich is checked. This shows that the reaction was limited by a mass transfer (Bard and Faulkner, 1980).

The analysis of electrochemical behaviour of furans compared to thiophene and pyrrole was envisaged. The furan is different of the others 5 membered heterocyclic as pyrrole and thiophene, by the heteroatom nature. In the case of pyrrole and thiophene the anodic oxidation leads to the polymeric film that whose view favourably, which coated on the electrode. The electrochemical analysis of its corresponding films, in the solution which contain only support electrolyte shows that the obtained deposit was

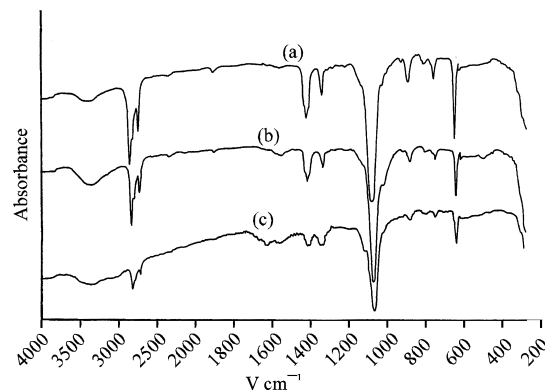


Fig. 4: IR spectrum in KBr of: (a) NBu_4ClO_4 , (b) deposit obtained during electrolysis of the furan at constant potential 1.85 V , (c) of the 2-methylfuran at 1.65 V

electroactive Genies *et al.* (1983) and Heinze (1990). During the cycling, the voltamperograms relative to pyrrole or thiophene solution show an increasing of the oxidation current peak, indicating that an electroactive polymeric film is being deposit on the electrode. However, this phenomenon was not observed in the case of furans. The cyclic votamperograms of these latters show an oxidation peak, characteristic of the irreversible mechanism. It is less wide than those observed in the case of the others 5 membered heterocyclic monomers. By comparison to the behaviour of thiophene and pyrrole, the current peak intensity remains stable, or decrease during cycling and stabilizes after many cycles at a very weak current in some case of furans. The obtained film has greyish colour. It is less thick and it is not sometime view or observed favourably. Its presence on the electrode is only underlined after analysis by IR spectroscopic or by scanning electronic spectroscopy of the electrode surface. The IR spectroscopic analysis of the deposit, compared with supporting electrolyte shows that the film contains the supporting sol (TBAP). Also, it is known that the polythiophene and the polypyrrole show always an oxidation peak. However, the analysis of films obtained during the electrolysis of furan or 2-methylfuran, in the solution which contains only the supporting electrolyte does not show any oxidation peak. The anodic deposit is non electroactive, this suggests, that the oxidation of the furans leads to the formation of the insulating polymeric film, which accumulates irreversibly on the electrode.

The IR spectrum of polymer (Fig. 4), shows bands due to an aliphatic CH stretch (2900 cm^{-1}), an aromatic CH stretch (3100 cm^{-1}), which is weakly observed, a little modification in the CH deformation region at 795 and

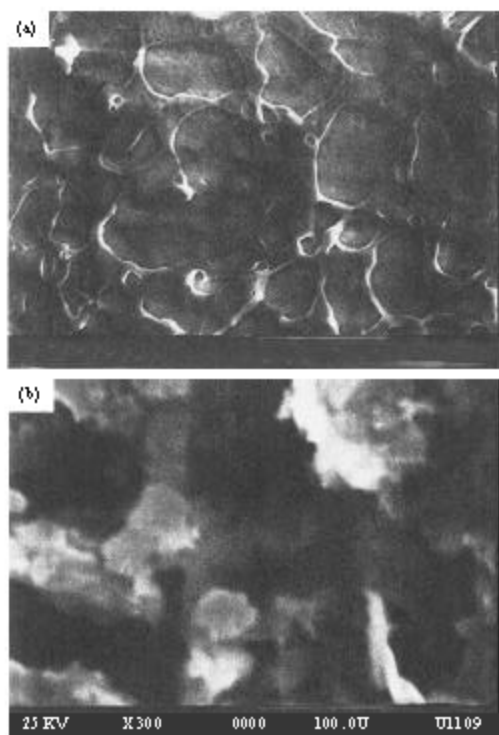


Fig. 5: Scanning Electron Microscopy (SEM) of the anodic deposit formed at the electrolysis, (a) potentiostatic ($e = 1.65 \text{ V}$), (b) intentiostatic ($I = 100 \text{ mA}$) of the 2-methylfuran

740 cm^{-1} , where we usually observe the bands corresponding to the deformation of aromatic and olefinic hydrogen atoms, respectively. In addition, a band at 1710 cm^{-1} due to the carbonyl groups indicates an extensive ring opening (Carrillo *et al.*, 1994; John *et al.*, 1991). In comparison with the spectrum of supporting electrolyte (Fig. 4a), we observe, in addition, that the IR spectrum of the film exhibits characteristics carboxylic acid or carbonyl vibrational bands (O-H Stretching at 3400 cm^{-1} , C = O stretching at 1710 cm^{-1} , C = C stretching at 1640 cm^{-1}) and O-H bending at 1380 cm^{-1} , clearly observed in the case of the deposit resulting of the oxidation of 2-methylfuran (Fig. 4c). According with that reported in aqueous solution for furan, where adsorbed acid carboxylic is detected on the electrode surface. This is showed by a strong carboxylate stretching band at 1603 cm^{-1} . The result suggest that furan undergoes hydrolysis with ring opening product to form adsorbed pendant butanoic acid, which forms an adsorbed layer having carboxylate bonding to the surface.

The Fig. 5a shows a SEM micrograph of the deposit film obtained on platinum surface from 0.1 M TBAP + 0.01 M 2-methylfuran solution, at constant potential

electrolysis (1.65 V/ECS), after prolonged anodic process (7 h). The deposit micrograph shows a droplet/matrix morphology, characteristic of a normal rheological behaviour. Therefore, it is probably that some transition morphology was formed between this co-continuous and dispersed morphology. The formation of co-continuous morphology, at constant potential must be attributed to stable interconnected structures that had formed during the oxidation. The presence of physical crosslinks in polymer means that the film had rheological properties. Also, a strong interfacial tension of the product on platinum is noticed. The Fig. 5b shows a typical SEM micrograph of the film deposited on platinum surface from 0.1M TBAP + 0.01 M 2-methylfuran solution, at constant current ($I = 100 \text{ mA}$), during 10 mn of electrolysis. This morphology of the film demonstrates that the platinum electrode becomes covered by a deposit with dendrites or holes.

Thus, on the basis of the surface chemistry of these systems, the SEM and the IR studies indicate the presence of the film rich in support electrolyte and the presence of the opening ring product which is strongly adsorbed on the electrode. The perchlorate anion probably interferes in the formation of well-organized organic film. Also, others additive contaminants, such as O_2 , H_2O which are inevitably present in solution affect the mechanism of oxidation and contribute to the structural film. As, what reported by the other studies Yosef and Aurbach (1990) and Aurbach and Goffer (1991), the cyclic voltammetry behaviour and the micrographs of the morphology of the film is also markedly affected by the initial state of electrode.

In order to obtain more information on the origin of this electrochemical behaviour and on the mechanism of furans in particular and on the 5 membered heterocyclic in general, we have investigated the furan and 2 of its derivatives 2-methylfuran and 2,5-dimethylfuran. So, if we exclude the possibility of polymerization belong β -position Pons and Scott (1984), the first product (furan) which has the 2 free positions must lead, according to the mechanism of eletropolymerization Heirze (1991), to the polyfuran, the 2nd (2-methylfuran) with one free position to the dimer form and the third product (2,5 dimethylfuran) with the 2 positions α and α' occupied by the methyl groups does not polymerise. However, we remarked that even in absence of any traces of oxygen and in the very hygroscopic conditions, to avoid any nucleophilic attack by the OH^- which can provide to the dissociation of the traces water or by the oxygen, that the 2,5-dimethylfuran is the most easy oxidized. Its potential oxidation is the less than those of the 2 other compounds. The yield of the electrolysis of this latter is the best of the 3 compounds

studied. Furthermore, in the case, of the furan and the 2-methylfuran the electrode becomes inactive after few minutes because of the insulating deposit film rich in perchlorate. If we consider that the mechanism involves the reversible 1-electron oxidation of the substrate, followed by an irreversible chemical reaction of the initially electrogenerated cation radical (A^+), as the rate-determining step. It is probably, that this species is unstable in the medium and decomposes to more stable products, by a reaction with the very small amount of water present in the acetonitrile. No polymer was formed as final product of 2,5-dimethylfuran since no deposit was observed on the platinum electrode through out the cyclic voltamperometry experiments.

The analysis of the anodic deposit obtained by oxidation of furan and 2-methylfuran by IR spectrum shows the presence of tetra-n-butylammonium perchlorate. On the other hand, we have never observed an anodic deposit during the electrolysis of the 2,5-dimethylfuran at constant potential. The anodic reaction of this latter leads only, to soluble products. Thus, in the case of furan and 2-methylfuran, it is possible, that the stirring and the scan rate favours the inhibition of the electrochemical reaction by increasing the adsorption rate of the perchlorate which facilitated by the adsorption of opening ring products on the surface and which therefore leads to a diminution of the current peak. Also, at the high values of the potential; 1.65 V for the 2-methylfuran and 1.85 V for the furan, other impurities could participate to the global process taking place at the electrode. In particular the dissolved oxygen and traces of water always present in the solution could intervene in the mechanism and contribute to the formation of non conducting film.

CONCLUSION

From these results, it emerge, that the poisoning of the electrode in the case of furan and the 2-methylfuran is probably caused by the adsorption of the insulating film which contains aldehydic or acidic group. The presence of these groups shows that ring opening products are formed during the electrolysis of these compounds. The formation of these products are justified by the presence of O-H and C = O bands in the film adsorbed on the electrode, as well as, in the products dissolved in the solution. The fact, that any deposit is not observed in the case of the 2,5-methylfurann constitutes a support that the mechanism of this compound leads to the product which is not adsorbed due to the steric discomfort of the methyl group and leads consequently to products resulting from the ring opening which dissolved in the solution.

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