



Veratrole anodic oxidation in presence of perchlorate

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Resumen

El veratrol (1,2-dimetoxibenceno) fue electro-oxidado sobre platino en medios electrolíticos de acetonitrilo/perclorato de tetrabutyl amonio y acetonitrilo/perclorato de litio. Se obtuvo un depósito, el cual fue caracterizado por técnicas espectroscópicas, microscópicas y espectroelectroquímicas. Se identificaron especies hexametoxi-trifenilénicas asociadas con los aniones perclorato. Los experimentos espectroelectroquímicos y microscópicos mostraron que la oxidación de aniones perclorato, a potenciales sobre los 2.3V, a radicales perclorato, produce la disolución del depósito. Si el potencial es barrido de regreso, el depósito se regenera y el proceso puede ser ciclado. Esta propiedad es interesante en el campo de los sensores, electrónica, dispositivos ópticos y química analítica. **Palabras claves:** electrooxidación, electrodeposición, electropolimerización, poliveratrol, interruptor orgánico

Abstract

Veratrole (1,2-dimethoxybenzene) was electrooxidized on platinum in acetonitrile/ tetrabutylammonium perchlorate and acetonitrile / lithium perchlorate. A deposit was obtained, which was characterized by spectroscopic, microscopic and spectroelectro-chemical techniques. Hexamethoxytriphenylene radical cation species, associated to perchlorate counterions, were identified. Spectroelectrochemical experiments showed that the oxidation of perchlorate anions to perchlorate radicals produced dissolution of the deposit. When the potential was swept backward, the solid was regenerated and this process could be cycled. This property is of interest in fields such as sensors (electrical potential sensors), electronics (electrical contacts), optical devices (screens) and analytical chemistry (selective quantification). **Keywords:** electrooxidation, electrodeposition, electropolymerization, polyveratrole, organic switch.

Introduction

Many aromatic organic compounds produced conducting polymers on electrodes. Benzene is a common fundamental unit in monomers such as phenylene¹, aromatic heterocycles² and π -conjugated systems such as azulene and naphthalene³. Some authors⁴ proposed that a radical cation is formed when methoxy-benzene (veratrole) is electrochemically oxidized and that methoxy groups have stabilizing effect. Bechgaar and Parker⁵ reported that the anodic oxidation of veratrole in dichloromethane/trifluoroacetic acid generated hexamethoxy triphenylene radical cation (HMTP)^{•+}. The three voltammetric peaks were associated to monocation, dication and trication radicals of hexamethoxy-triphenylene. Márquez and coworkers⁶ showed that a green conducting material was deposited on a platinum electrode, when 1,2- dimethoxybenzene was oxidized in acetonitrile/tetrabutylammonium tetrafluoroborate (TBuNTBF₄). That deposit, which is an association of (HMTP)^{•+} and TFB anions, was called

Polyveratrole (PV). The reaction mechanism and solid structure were determined by spectroscopic, spectrometric, thermal and elemental analysis⁶⁻⁸. Relation of chrono-amperometric transients with nucleation and growing processes have been treated in literature^{9,10}. As it is known, the nature of the supporting electrolyte influences the electro polymerization process. In this case, we are considering the effect of using perchlorate salts in the electrolytic medium.

Experimental

High purity chemicals (Sigma and Aldrich) were used without treatment. Experiments were performed using a 263 PAR Potentiostat/Galvanostat. A classical three electrodes one compartment cell was used for cyclic voltammetry, chronoamperometry and electrolysis experiments. A platinum disk (0.34cm²) working electrode, a platinum foil (1cm²) counter electrode and a

silver/silver nitrate (0.01M) in 0.1M perchlorate reference electrode, were used.

In situ UV-Visible Spectroelectrochemical experiments were carried out with a 1461 EG & OMA III spectrometer equipped with a silicon cooled diode array optical system, coupled to a 173 PAR Potentiostat / Galvanostat and a 175 PAR Universal Programmer. This experimental setup allowed us to record a spectrum from 300 to 900 nm every 30 ms. Mass spectra were taken with a 5939A Hewlett Packard Spectrometer and FTIR spectra with a 2000 Perkin-Elmer spectrometer.

Results

Cyclic voltammetry:

A cyclic voltammogram of Veratrole in $\text{CH}_3\text{CN}/\text{TBuNCIO}_4$ (fig.1.a) shows two oxidation peaks at 1.8 V and 2.1 V which, according to previous results⁷, are assigned to

monocation and dication radicals of hexamethoxy triphenylene. A red intermediate species that diffuses from the electrode surface to the bulk solution is observed at the first voltammetric peak. At higher potentials a green material is deposited on the working electrode. An estimation of reaction order was performed from voltammetric experiments; an order of one was obtained for monomer and a half for the participating electrolyte.

Repetitive voltammetry showed an initial suddenly increase of the second oxidation peak current, followed by a discrete increase of the peak current along consecutive cycles, meaning that formation of the dication is faster on the same deposit compared to bare platinum and is diffusion controlled. Figure 1.b shows the existence of an adsorption-desorption prepeak, corresponding to the presence of electroactive reaction products.

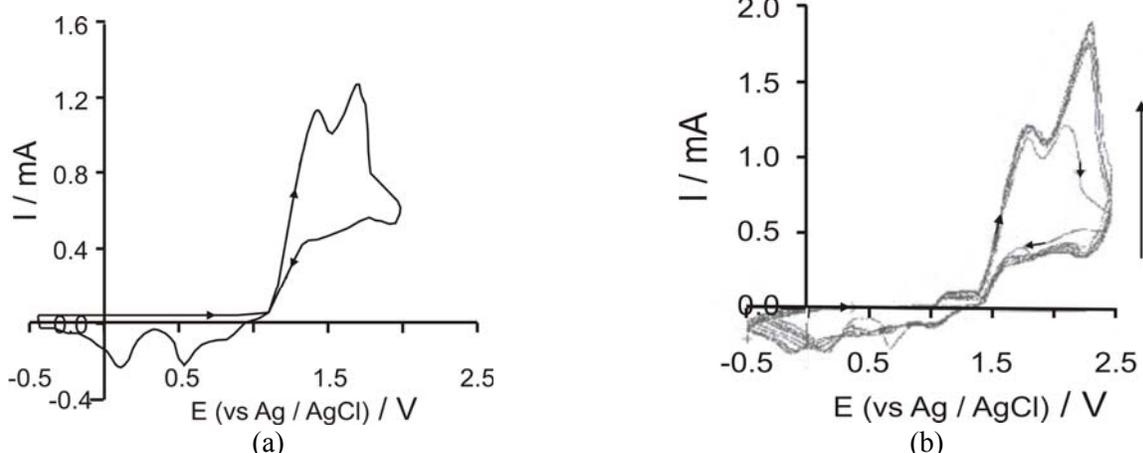


Fig. 1- Cyclic voltammetry of 0.1 M veratrole in acetonitrile and 0.1 M tetrabutyl-ammonium perchlorate. $\nu = 100 \text{ mV s}^{-1}$. (a) first sweep.(b) repetitive sweeps

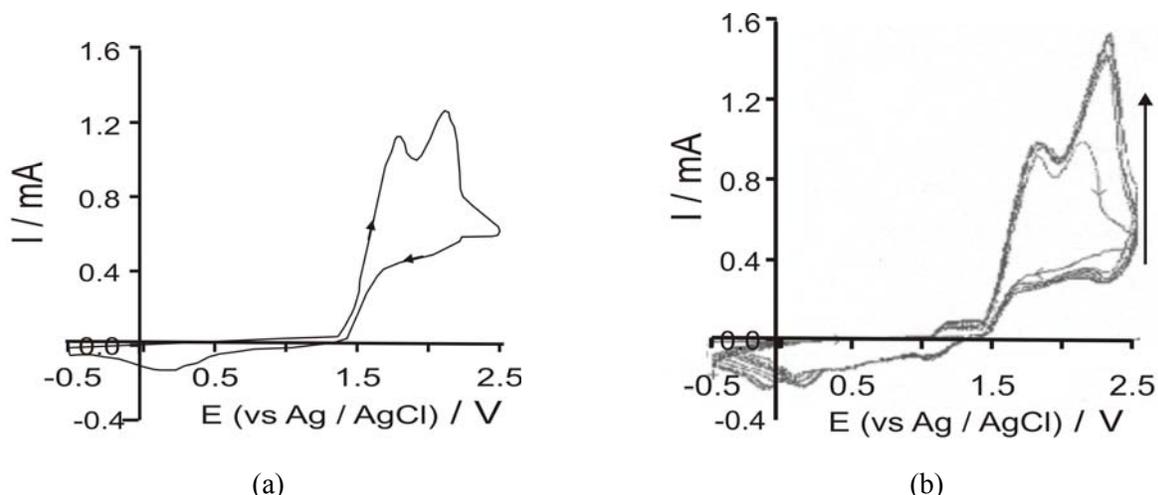
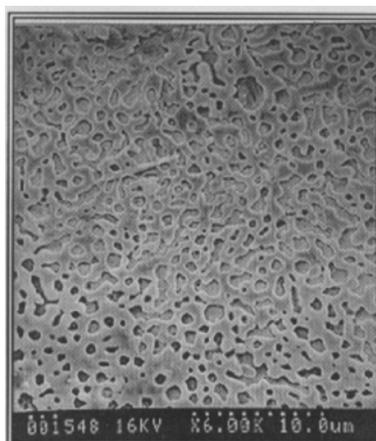


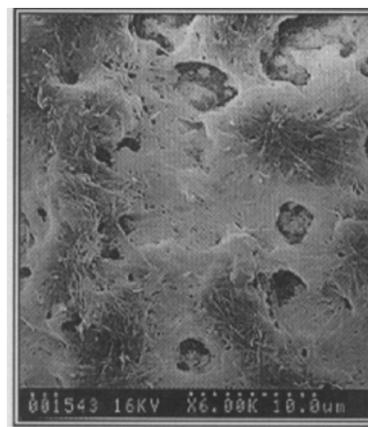
Fig 2.- Cyclic voltammetry of 0.1 M veratrole in 0.1 M lithium perchlorate. $\nu = 100 \text{ mV s}^{-1}$. (a) first sweep.(b) repetitive sweeps.

It is also observed that redissolution of the deposit occurs over 2.3V, due to oxidation of the perchlorate anion to the radical species, with the collapse of deposited structure. The deposited material can be reestablished by switching the potential back-wards. A similar behavior is observed when the supporting electrolyte is lithium perchlorate (fig.2).

The dissolution/re-deposition process was followed by Scanning Electronic Microscopy, SEM (fig.3). Only the external (fibrillar) layer is undergoing this process, while the inner layer remains on the electrode surface.



(a)



(b)

Fig. 3.- Micrographies of polyveratrole synthesized in tetrabutylammonium perchlorate. (a) oxidation at 2.3 V. (b) reduction at 2.0 V

Chronoamperometry

Figure 4 shows current transients taken at short times (<50 ms). Analysis of those transients confirms an instantaneous nucleation followed by a bidimensional growth type of mechanism, following equation 1.

$$I \propto k_g^n t^{n-1} \quad (1)$$

where $n = 2$ and k_g is expressed in $\text{mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$

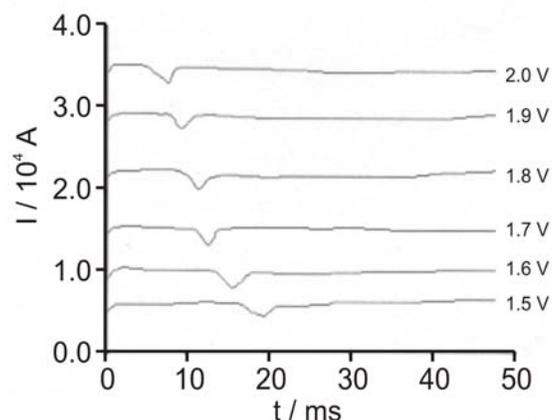


Fig. 4.- Chronoamperogram of 0.05 M Veratrole in 0.1 M tetrabutyl-ammonium perchlorate at short times, at different potentials

The charge under curves, previous to the nucleation process, has been found to be independent of the applied potential and corresponds to double layer charge. A critical number of nuclei were formed prior to the growth step and then a deposit with few layers instead of a single one. The current transients taken at long times (>20 s) show the presence of an increasing periodical sequence of events (fig.5) and formation of fibrils could be monitored by Scanning Electronic Microscopy (fig.6). The overlapping curve of the transient fits a progressive 3D type of mechanism while the maxima of waves can be assigned to a discrete progressive formation of nuclei, obeying equation 2.

$$I_m = k t_m \quad (2)$$

where t_m is the time at the maximum of the wave.

($k_{ex} = 1.07 \text{ mA} \cdot \text{s}^{-1}$)

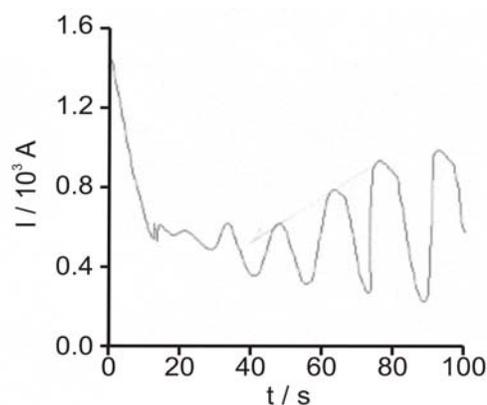


Fig. 5.- Chronoamperogram of 0.05 M veratrole, in 0.1 M tetrabutyl-ammonium perchlorate at long times ($E = 1.8 \text{ V}$)

The charge involved in each event increases with time since formation of new fibrils is accompanied by growth of those fibrils previously formed. The way in which the deposit is

produced is highly dependant upon the chemistry of formation of the trimer and it explains the transient response¹¹.

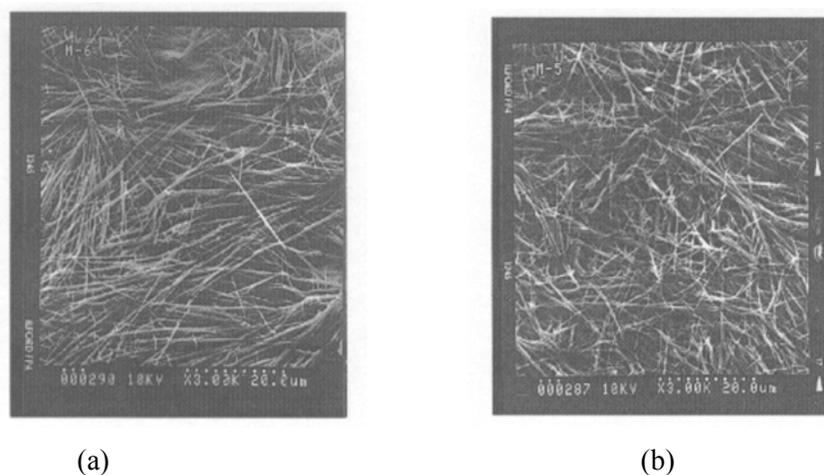


Fig 6.- Micrographs of polyveratrole after 1000 s of electrolysis at 1.8 V Synthesized in: (a) 0.1 M lithium perchlorate. (b) tetrabutylammonium perchlorate.

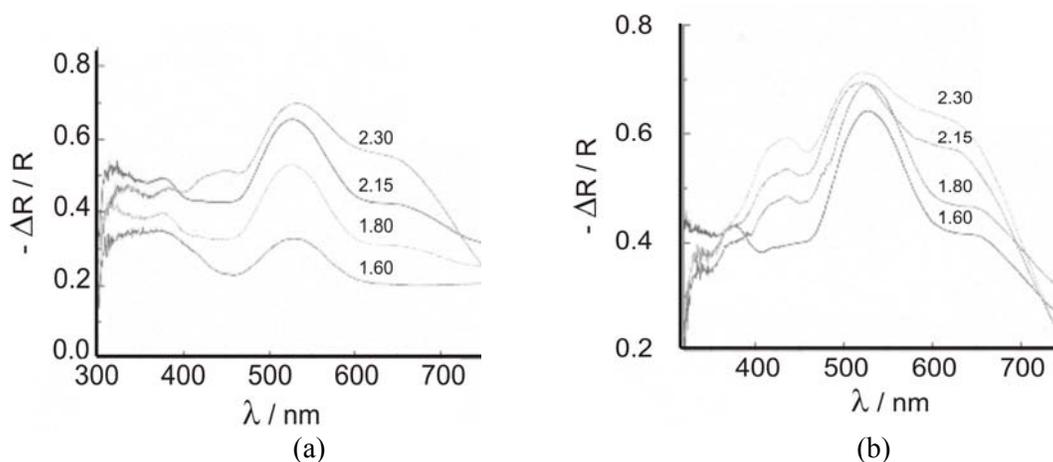


Fig. 7.- UV-Visible spectra taken during the electrooxidation of veratrole at different potentials in: (a) tetrabutyl-ammonium perchlorate. (b) lithium perchlorate.

Spectroelectrochemistry

UV-Vis. spectra were taken along the cyclic voltammogram (fig.7). At 1.6 V the absorption band corresponding to veratrole cation radical (530nm) is observed; at the potential were 640 nm and 420 nm signals are observed, a deposit is formed on the electrode surface. These bands disappear at potentials beyond 2.3 V (in per-chlorate medium) as fibrils collapse and they are restored when the potential is sweep back. UV-Vis Spectra showed the same absorption bands as those found during the electrosynthesis of Poly-veratrole in the presence of tetrabutyl-ammonium tetrafluoroborate and the bands observed are in agreement with those calculated by Hoijitink⁽⁴⁾ for hexamethoxytriphenylene species.

Additional ex-situ analysis confirmed the structure suggested for the deposit. Mass spectrum fragmentation fits well with the proposed fragmentation pattern⁸. FTIR spectrum showed signals corresponding to aromatic and methoxy bonds ($\nu(\text{CH})_{\text{ar}}$: 2962 cm^{-1} ; $\nu(\text{CH}_3)_{\text{asym}}$: 2935 cm^{-1} ; $\nu(\text{CO})$: 1274 cm^{-1} ; $\beta(=\text{CH})_{\text{ar}}$: 1165 cm^{-1} ; $\nu(=\text{CH})_{\text{ar}}$: 842 – 836 cm^{-1} ; $\delta(\text{ring})$: 663-630 cm^{-1} ; $\delta(\text{ring})$: 560 – 480 cm^{-1} . The signal at 1100 cm^{-1} corresponds to the ClO_4^- counterion, which stabilizes the HMTF cation.

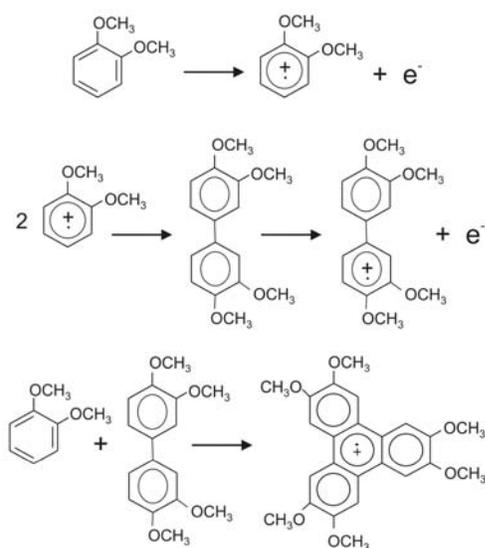
Conclusions

Electrolysis of veratrole on platinum in perchlorate solution, performed at potentials over the first

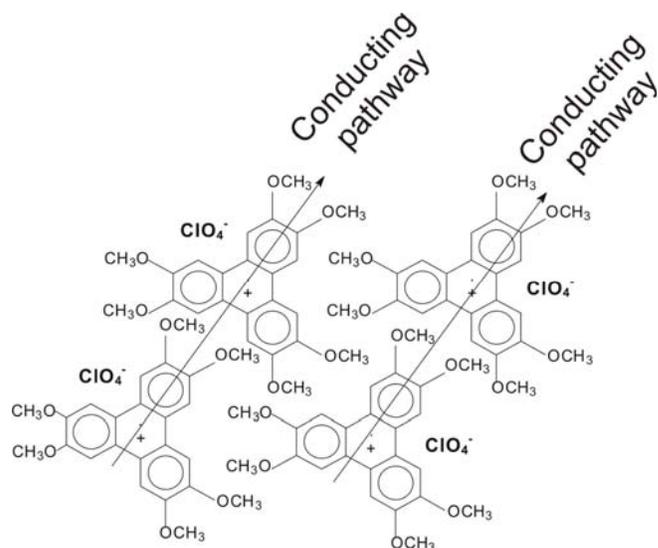
voltammetric wave, produces a trimer that associates with the perchlorate counter ion, forming a deposit on the electrode surface. An EC type of mechanism is initially followed and a cation radical is formed, followed by a deprotonation step. The reaction order was found to be one with respect to the veratrole concentration. Two layers are formed on the electrode surface, the first one by interaction of trimers with electrode surface, being thin and smooth, while the second one has fibrillar morphology, formed by association

of trimers with perchlorate counterions. As the potential is increased up to 2.3 V the perchlorate free radical is formed, it is a non charged species, causing the collapse and dissolution of the fibrillar layer. In the reverse sweep, the solid is formed again and the process proceeds as a loop. This property is of interest for switching, alarms, analysis, devices, etc. Scheme I and figure 8 illustrate the phenomenon.

The general reaction scheme, the organic structure and the device.



Scheme I



Structure proposed for polyveratrole electrothesized in ClO_4^-

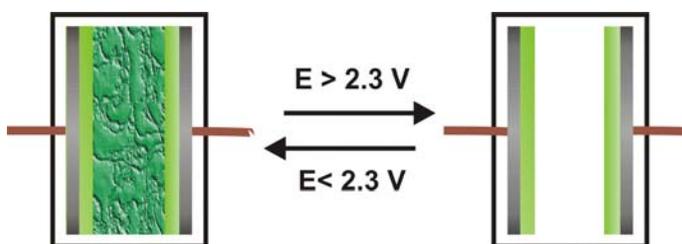


Figure 8.- Diagram showing the electric switch of polyveratrole at different potentials

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