

STUDY OF THE ELECTROPOLIMERIZATION OF O-TOLUIDINE AND THE EFFECT OF THE TEMPERATURE ON THE RESISTANCE OF THE POLYMER,

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INTRODUCTION

Organic polymeric deposits like polythiophene (1), polypyrrole (2) and polyaniline (3) won a privileged position in the research field. They are deposited onto and electrode surface by using various methods: radiofrequency plasma (4), electropolymerization (5) etc.

The electropolymerization of some monomers is particularly attractive since the polymeric deposit exhibit some very interesting properties, they are generally homogeneous, strongly adherent to the electrode, and chemically stable.

Different strategies have been used for obtaining highly ordered polymers one of that is the polymerization at low temperature (6). The conductivity of the polymers could be increased by doping with various donors or acceptors, Chiang et al. (7) reported that the electrical conductivity of $(\text{CH})_x$ doped with halogen could be systematically increased by more than 8 orders of magnitude. Electrochemical oxidation/reduction of these materials can lead to large changes in their conductivity.

EXPERIMENTAL

The o-toluidine was distilled under vacuum. The electrolyte was prepared by using distilled water and reagent grade sulfuric acid and perchloric acid. Polymer films were synthesized at various temperatures in the range 8°C to 60°C. Electrochemical experiments were done in a conventional cell with three electrodes. Polymerization was carried out by cycling the potential between -0.5 and +0.6 V vs MSE at scan rate of $50 \text{ mV}\cdot\text{s}^{-1}$. In situ resistance measurements were performed by the procedure of Contractor et al. (8). The scanning electron microscopy was used for evaluating the morphology of the films.

RESULTS AND DISCUSSION

The film was directly prepared on the working electrode (Au) by continuous potential cycling between -0.5 and +0.6 V/MSE. in a solution containing 0.65 M in o-toluidine, 1.5 M HClO₄ and 1.5 M H₂SO₄ (Fig.1). The cyclic voltammograms recorded at different temperatures show the same comportment. For the first positive scan, there is a little oxidation until the potential is greater than +0.2 V. Beyond this potential high anodic current - flow due to the oxidation of o-toluidine.

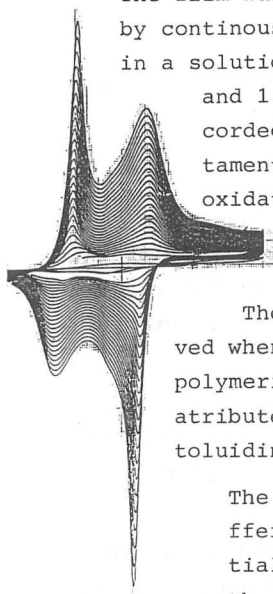


Fig.1. Cyclic voltammogram of poly-o-toluidine at 25°C.

The exponential dependence with the time is observed when the temperature is increased, for the rate of polymerization formation. The exponential growth may be attributed to the same mechanism of the oxidation of o-toluidine at all temperatures.

The redox behaviour of the polymer obtained at different temperatures has been studied. The potentials for the redox couples are -0.2V and 0.1V and these potentials are not shifted with the formation temperatures of the polymer.

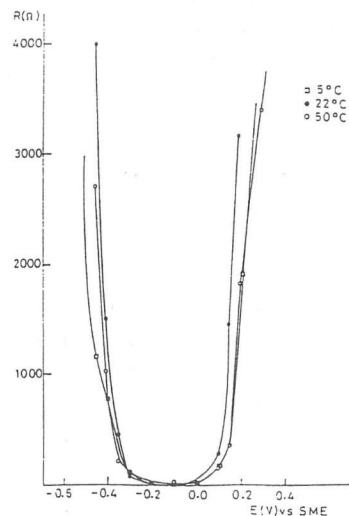


Fig.2. Resistance of poly-o-toluidine as a function of applied electrochemical potential.

The polymer formed at different temperatures shows the same variation of the resistance with the electrochemical potentials (Fig.2). The resistance measurements were carried at 25°C in 0.5M H₂SO₄. The poly-o-toluidine is insulating at sufficiently negative (-0.4 V) or positive +0.15 V electrochemical potentials, but becomes conducting in the intermediate range potentials. The polymer has the ability to drive redox reactivon whose redox equilibrium potentials are into the range where the polymer is conductor.

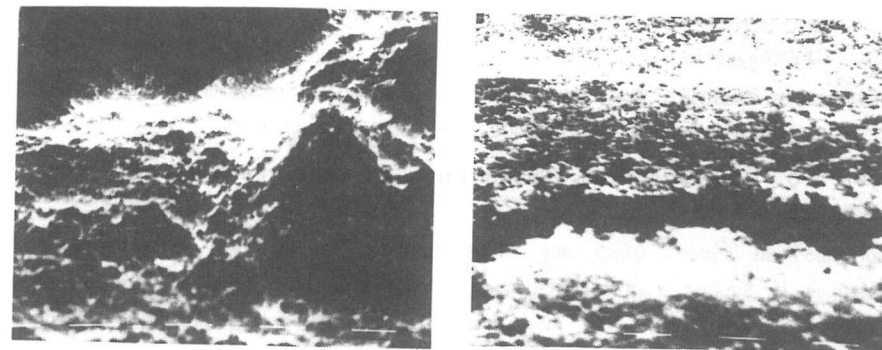


Fig. 3. Electron micrographs of films a) 35°C (1250x), b) 60°C (1250x).

The microstructure of poly-o-toluidine films change with the temperature of synthesis. The polymer formed at 8°C was found to be highly compact, when the temperature is increased to 25°C the film exhibits little aglutinations, for 35°C (fig.3a) the film is less homogeneous and for 60°C the adherence of the film is very poor, fissures and cracks are observed (fig. 3b).

REFERENCES

- (1) G. Tourillon and F. Garnier; J. Electrochem. Soc., 130(1983)2042.
- (2) K.K. Kanazawa, A.F. Diaz, R.H. Geirs, M.D. Gill, J.F. Kwak, J.A. Logan, J.F. Rabolt and G.B. Street; J. Chem. Soc. Chem. Commun., (1979)854.
- (3) T. Ohsaka, Y. Ohnuki, N. Oyama, G. Katagin and K. Kamisako; J. Electroanal. Chem., 161(1984)399.
- (4) R. Nowak, F.A. Shultz, M. Umana, H. Abruña and R.W. Murray; J. Electroanal. Chem., 94(1979)219.
- (5) A. Volkov, G. Tourillon, P.C. Lacaze and J.E. Dubois; J. Electroanal. Chem. 115(1980)279.

- (6) M. Ogasawara, K. Kunahasti and K. Iwata.; Mol. Cryst. Liq. Cryst., 118(1985)159.
- (7) C.K. Chiang, Y.W. Park and A.J. Heeger; J.Chem. Phys., 69(1978)1.
- (8) A.Q. Contractor, M. Gholamian.; J. Electroanal. Chem. 252(1988)291.

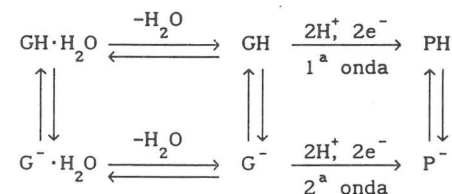
REDUCCION DEL ACIDO GLIOXILICO SOBRE ELECTRODO DE MERCURIO

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INTRODUCCION.

Hay varios trabajos en la bibliografía que tratan sobre la reducción electroquímica del ácido glioxílico sobre mercurio (1-5), y aunque el esquema global de reducción está perfectamente determinado:



quedan aún por resolver algunas cuestiones sobre su comportamiento electroquímico.

En el presente trabajo se lleva a cabo un estudio sobre el proceso de reducción de este compuesto, en base al uso de la polarografía DC y DP, la voltametría cíclica, el registro de las curvas C-E y la obtención de parámetros cinéticos a potenciales correspondientes al pie de las ondas.

RESULTADOS.

El ácido glioxílico se reduce sobre el E.C.M. dando lugar a una o dos ondas en polarografía DC, según el pH del medio. La primera onda es visible hasta pH=7, en tanto que la segunda comienza a partir de pH=5.

La corriente límite varía con el pH del medio. Las variaciones correspondientes a ambas ondas se muestran en las figuras 1 y 2.

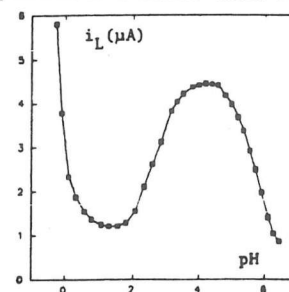


fig. 1

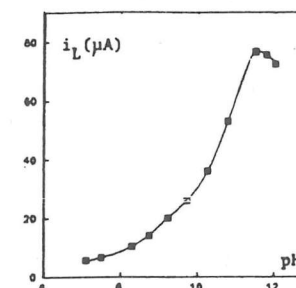


fig. 2