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The Deposition of Metallic Phases on Polymers with Different Electronic Conductivity and Catalytic Activity*

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The growth of metallic phases and the kinetics of this process are mainly dependent on the electronic conductivity and catalytic activity of the substrate. In this work we used electrodes covered with different polymer films. The conductivity and the number of growth sites of these modified electrodes was changed by the monomer in the polymer chain or by the polarization. We used the metallic conducting polyaniline as deposited material.

From the experimental data current density i and change of mass m as function of time, we got informations about the different steps of electropolymerization as nucleation and growth of a homogeneous film. This investigation shows that the number of growing centers plays an important role and can be varied with the substrate. A modification with semiconducting or insulating polymers, of course, is not useful to accelerate the growth. Further characteristic quantities like the rate of the growth can be calculated and their *in-situ*-transients are depicted. Additionally the electronic behaviour of the used substrate can be characterized.

INTRODUCTION

There is a strong correlation between the electronic behaviour of a substrate and the mechanism of the electropolymerization on it. As shown in Figure 1, the electronic conductivity of the substrate must be metallic-like for the deposition of a homogeneous layer. No deposition is expected in the case of an insulating substrate, whereas the deposition on a semiconducting substrate should be hindered. The results could be complicated by possible deposition and growth in pores. In contrast to the deposition of metals, the substrate must have a »catalytic activity« for polymerisation. This means that a sufficient number of active growth sites is necessary to build up a polymer layer. Therefore we used electrodes modified with polymer films to change the kinetics of the following deposition.

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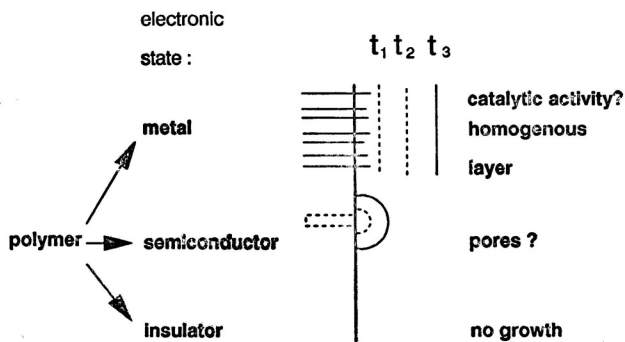


Figure 1. The deposition of metallic conducting phases on a substrate with changeable electronic conductivity

In this paper we want to present new results concerning the electropolymerization on layers with different electronic conductivity and catalytic activity.

The electronic conductivity of the layer is usually modified by the use of different materials as substrates. We changed the conductivity by using a polymer layer, whose properties are determined by the applied potential and by the structure of the polymer chains. So we are able to change the conductivity of the substrate, not by the variation of the substrate, but simply by switching of the potential.

Our recent investigations of the formation kinetics¹ and electronic conductivity² of polyaniline and some methyl derivatives show its applicability for these studies, presented in this paper: on the one hand as substrate, but on the other hand as deposited material. The formed polyaniline is conductive in its oxidized state. The overoxidized form is insulating. Besides the change of the electronic conductivity induced by the applied potential, we also studied the effect of structural changes in the polymer chain of the substrate. The polymer of a methylsubstituted aniline, *i. e.* 2,6-dimethylaniline, offers approximately a semiconducting behaviour.³

We choose the potentiostatic formation of polyaniline to deposit polymer layers with electronic conductivity. The resulting transients are a very powerful tool in the electrochemical investigation of deposition processes. In this paper we present the measurements of the transients of the current density and of the polymer mass by the electrochemical quartz microbalance EQMW, *i. e.* the plots of $\log i / \log t$ and $m_{\text{EQMW}} / \log t$ in the time range between 1 s to 10^3 s.

The current density i changes with the polarization time t . From the dependence of i on t we determined the mechanism of the electropolymerization using equ. (1).⁴

$$i \sim t^n; n = \frac{d \log i}{d \log t} \quad (1)$$

EXPERIMENTAL

All experiments were carried out with gold as substrate (working electrode WE) and counter electrode (CE). The electrode potential E was measured against a mercury/mercury sulfate electrode (RE). All potentials given in this paper refer to the standard hydrogen electrode (SHE). Current densities were measured with a fast-rise potentiostat. The charge was calculated by numeric integration of i over t . The impedance of the electrode was measured by modulating the electrode potential by an AC signal (1 mV, 1 kHz). The changes in mass of polymer were measured simultaneously by an Electrochemical Quartz Micro-Balance EQMB.⁵ A 5 MHz-quartz was covered on both sides by a 300 nm Au film with a total area of 0.4 cm². Figure 2 shows the experimental set-up. The side in contact with the electrolyte is used as a working electrode. The decrease of its frequency f corresponds to a positive mass coating given as »mass density«, referred to the initial frequency at $t = 0$ or $m_{\text{poly}} = 0$. The averaged thickness d is calculated from

$$m = -\Delta f \cdot K \left[\frac{g}{\text{cm}^2} \right]; d = -\frac{\Delta f \cdot K}{\rho} \quad (2)$$

$\rho = 1 \text{ g} \cdot \text{cm}^{-3}$ and the proportional factor $K = 20 \text{ ng} \cdot \text{Hz}^{-1} \cdot \text{cm}^{-2}$, determined by galvanostatic Cu deposition on Au in acid solution.⁶

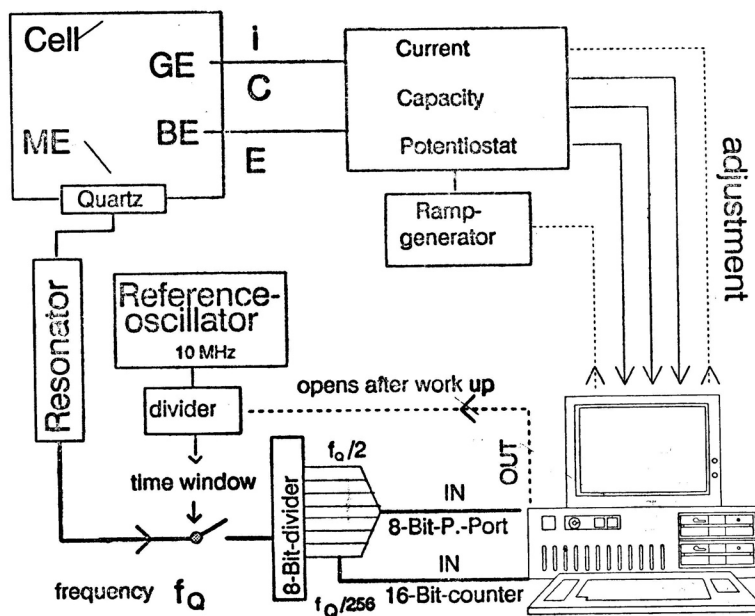
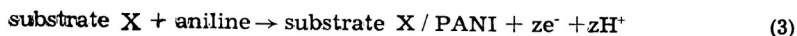


Figure 2. Experimental set up of the electrochemical quartz microbalance.

RESULTS

The polymer layers used as substrates were prepared potentiodynamically between 0.0—1.0 V for aniline, and 0.0—1.2 V for 2,6-dimethylaniline. The thickness of these films was in the range of some 10 nm. The overoxidation of PANI was realized in special experiments at 1.5 V for 2 hours in pure H₂SO₄ under N₂.

The polymerization of aniline on different substrates can be described by the following equation (3):



with $X = \text{Au}$, $\text{Au/PANI}_{\text{dyn}}$, $\text{Au/PANI}_{\text{iox}}$ and Au/P2.6-DMA . The polymerization of 0.1 M aniline on these electrodes was carried out at 1.0 V in 0.5 M H_2SO_4 . The number of exchanged electrons was about 2.2.^{6b}

The formation of polyaniline started on pure Au (conducting but no catalytic activity for polymerization) after an induction period of about 15 s. During this period the current density, Figure 3a, was constant, in $0.1 \text{ mA} \cdot \text{cm}^{-2}$. The increase of the current density up to $10 \text{ mA} \cdot \text{cm}^{-2}$ was correlated with the nucleation and the growth of the nuclei. The exponent $n = 2-3$ can be explained by a progressive nucleation with the following hemispherical growth. The stationary growth occurred after the total coverage of the electrode with the polymer ($t > 500 \text{ s}$).

In the case of the electrode, covered already with polyaniline PANI_{dyn} (metallic conductivity and catalytic activity is expected), the substrate and the deposited polymer are the same. The current density was higher by the factor of more than 10 in the first 100 s. There is no induction period. This experimental result proved the metallic conductivity of the polyaniline film. The large number of active growing centers on the initial formed polymer surface allowed a polymerization without any induction period. After 100 s the current density increased very slowly to $10 \text{ mA} \cdot \text{cm}^{-2}$. This can be understood by a roughening of the polymer surface.

There is a different other result in the case of the overoxidized polyaniline (insulating, catalytic activity unknown). The induction period was extended up to 100 s and the current densities of about $0.01 \text{ mA} \cdot \text{cm}^{-2}$ were low. This result can be interpreted by the insulating character of this PANI modification. The remarkable induction period can be described by the growth of PANI in pores. When the current density increases again, polyaniline grows in hemispheres on the top of the overoxidized PANI substrate. The electronic current flows through the short-circuits in pores filled with common PANI.

The electrochemical investigation of the overoxidation of polymers^{6b} has shown, that the overoxidation was combined with a corrosion and destruction of the polymer. This fact could clarify the progressive nucleation because of an increasing number of pores in the film during the polymerization.

The $\log i/\log t$ — plot of the polymerization of aniline on poly-2,6-dimethylaniline shows an intermediate behaviour. The induction period in comparison to the overoxidized film was 30 s shorter, see Figure 3a. So the poly-2,6-dimethylaniline film had a higher number of growing centers, probably conducting parts (*i. e.* more semiconducting character) as the $\text{PANI}_{\text{ovox}}$.

There was always a stationary current density of about $10 \text{ mA} \cdot \text{cm}^{-2}$ after $t = 1000 \text{ s}$. This can be explained by the fact, that the different substrates were covered with the same polyaniline at these times. The exponent $n = 0$ means a homogeneous film growth. With the existence of an induction period during the deposition, equ. (1) must be modified to

$$i \sim (t - t_0)^n \quad (4)$$

with t_0 = the induction period. The value of t_0 depends on substrate (*i. e.* the electronic conductivity), potential and concentration of the deposited material in the solution.

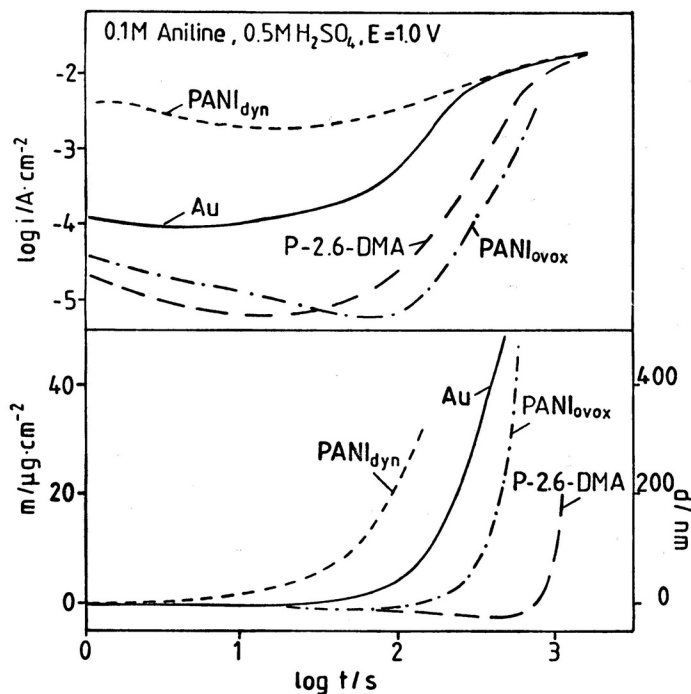


Figure 3. The plots of $\log i / \log t$ and $m / \log t$ for the formation of polyaniline on Au, oxidized and overoxidized polyaniline and oxidized poly-2,6-dimethylaniline; $E = 1.0 \text{ V}$, 0.1 M aniline.

TABLE I

Substrate, induction period t_0 , exponent n during the nucleation and the model of growth of polyaniline on polymer substrates with different electronic conductivity and catalytic activity; $E = 1.0 \text{ V}$, 0.1 M aniline.

substrate	t_0/S	n	model of growth
Au	15	2-3	progressive nucleation, hemispherical growth
Au/ PANI_{dyn}	0	$0 < n < 1$	homogenous polymerization and a roughening surface
Au/ $\text{P-2,6-DMA}_{\text{dyn}}$	80	3	progressive nucleation, hemispherical growth on the top
Au/ $\text{PANI}_{\text{ovox}}$	110	3	progressive nucleation, hemispherical growth on the top

Table I shows a comparison between different substrates and models of growth.

The simultaneous registration of the changes of mass (or thickness) with the electrochemical quartz microbalance, Figure 3b, allows the determination of the real polymerization rate v_{pol} . Such a check is not trivial, since the simultaneous formation of soluble oligomers consumes charge, but does not contribute to reaction (1). Measurements of mass justified the results of the analysis of the current densities in some cases:

- a negligible induction period in the case of PANI_{dyn},
- an induction period of ≈ 10 s on pure Au and
- a long period in the case of PANI_{ovox}.

After these periods of time there was always a strong increase in mass during the nucleation and growth. The investigations with the EQMB showed however a longer induction period on poly-2,6-dimethylaniline than on PANI_{ovox}, in contradiction to the $\log i/\log t$ — plot.

We define a rate of polymerization v_{pol} , equ. (5), to compare the changes of mass with time.

$$v_{\text{pol}} = \frac{dm}{dt} [\mu\text{g} \cdot \text{s}^{-1} \cdot \text{cm}^{-2}] \quad (5)$$

There was an immediate linear increase of v_{pol} with time t in the case of the deposition on pure Au, whereas there was a long period with $v_{\text{pol}} = 0$ in the case of PANI_{ovox} and P2.6-DMA as substrates, Figure 4. The electrode, covered with PANI_{dyn}, showed a polymerization from the beginning, which confirmed the catalytic activity of this PANI modification.

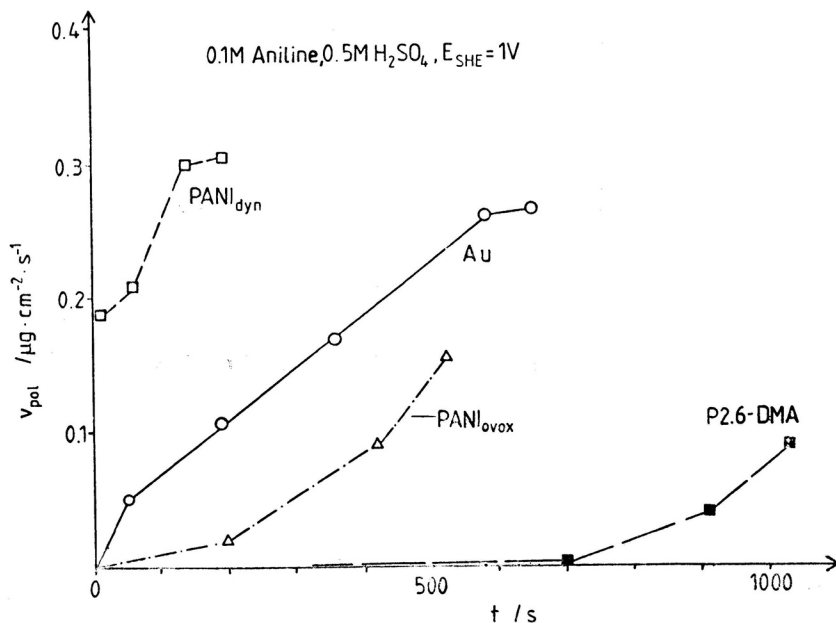


Figure 4. Rate of polymerization, calculated from Figure 3 with eq. 7 as function of the time

MODEL

This article is focussed on two main objectives: the characterization of the electronic conductivity and the number of active growth sites of polymer layers by deposition processes and the optimization of electropolymerization. This aim is important because the polymerization of PANI is hindered by an induction period and the faster potentiostatic polymerization gives films with poorly mechanical behaviour. Therefore we used modified electrodes to accelerate the deposition and to combine the advantages of potentiostatic and potentiodynamic preparation methods.

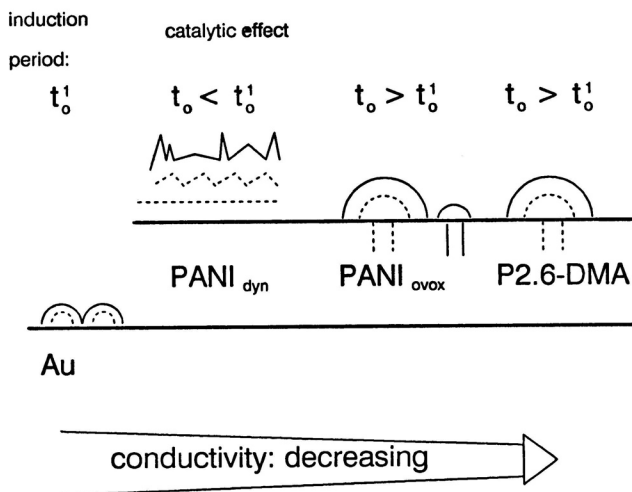


Figure 5. Schematic interpretation of the results.

The initial deposition of a PANI layer »catalyzes« the film growth, because the electronic conductivity and the large number of growing centers can be used to build up the second layer without an induction period. The small increase of the current density is caused by the formation of a rough surface. In the case of the insulating layers the induction period is enlarged, since nucleation occurs in pores only. The following strongly decayed growth on the top of the polymer is characterized by the exponent n (see Figure 5).

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SAŽETAK

Depozicija metalnih faza na polimerima s različitim elektronskom vodljivošću i katalitičkom aktivnošću

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Proučavana je kinetika rasta metalne faze na polimernim supstratima s različitim elektronskom vodljivošću i katalitičkom aktivnošću. Takvi supstrati pripremljeni su prekrivanjem elektroda različitim polimernim filmovima (osnova: polianilin s metalničkom vodljivošću), a vodljivost i broj mjesta na površini za rast faze kontrolirani su prisutnošću monomera u polimernoj fazi, ili elektrodnom polarizacijom. Pokazano je da je broj centara važan parametar koji se može podešavati u supstratu. Modifikacija supstrata s poluvodičima ili izolatorskim polimerima usporava rast. Opisana je primjena elektrokemijske kvarcne mikrovage za mjerenja rasta deponiranih slojeva u uvjetima potencijostatički kontrolirane elektrolize.