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MODIFICATION OF COPPER WITH SELF-ASSEMBLED THIOL MONOLAYERS

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ABSTRACT

Self-assembled monolayers (SAM) make the creation of new types of protective layers possible, concerning corrosion, with which ecologically damaged procedures would be replaced for the protection of metal constructions from corrosion. Self-assembling is a spontaneous process which is developed by submerging of suitable metal substract into the melt with surface organic active substance, which is absorbed and self-assembled, forming a highly decorated moleculary monolayer.

Self- assembled monolayers are very suitable system for exploration of inter-phased process, relations between constructions and junctures, they are highly-technologically used as sensors, biosensorss, biomembranes and as protective layers.

In this work, the copper surface is modificated with 1-dodecanethiol of self-assembled monolayers. Characterisation of surface is done by using cyclic voltammetry and contact-angle method.

Keywords: copper, 1-dodecanethiol, self-assembled monolayer

1. INTRODUCTION

Self-assembled monolayers enable the creation of new types of protective layers, concerning corrosion with which ecologically damaged procedures would be replaced for the protection of metal constructions from corrosion. Characteristics and reactivity of monolayer are controled by closing groups of organic molecule, which form the film, so self-assembled monolayers are suitable for fundamental research of surface phenomenon and inter-phased process.

SAMs are highly used [1,2,3]: for production of chemical and biochemical sensors, for metal protection of corrosion, microelectronics, preparation of surface for crystal's controled growth, for DNA's imobilisation, adhesion of living cells on metal surface, for increasing of implant's biocompatibility which is placed in the human organism.

2. SELF-ASSEMBLED MONOLAYERS – THE STRUCTURE

Self-assembled monolayers are formed by displaying metal substracts to organic molecules with functional groups. Those are highly dense packed monomolecular arranged layers.

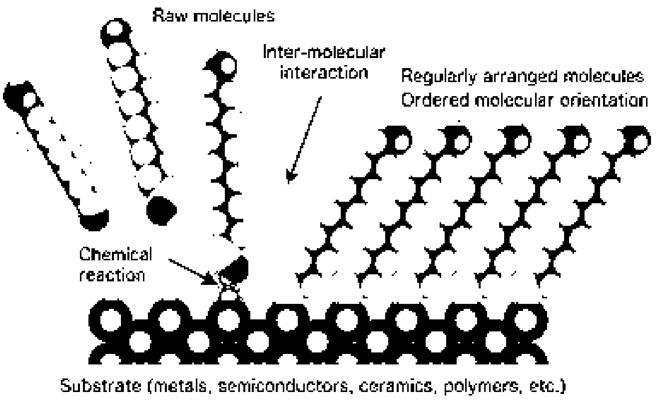

Figure 1. Self-assembled monolayer on copper surface

Adhesion group is absorbed on the substract surface, which is responsible for inhibitonal characteristics of formed monolayer. While alkyl chains are netting, during self-assembling - decorated dense packed monolayer is made. This monolayer enables mechanical stability and defines inter-phased characteristics of formed monolayer. Closing groups can be changed additionally, so that characteristics of monolayer could be changed according to its use. [1,4,5].

Self-assembling consists of two separated process [4,6] :

fast absorbance of adhesion group on metal surface and slow organization/orientation and alkyl chains with Van der Waals intramolecular interactions.

After adding gold to alkanethiol melt in absolute ethanol, link between the gold and sulfur is quickly created, during few minutes.

3. EXPERIMENTAL PART

3.1. Monolayer's synthesis

Self-assembled monolayer is made by using 1-dodecanethiol ($C_{12}H_{25}SH$) , produced by «Fluka», molar mass of 202, 4 g/mol, and density of 0,844 g/cm^3. The tile, made of polycrystalic copper, has the surface of 1cm^2, is used as a substract.

Copper tiles are worked by using mechanical and chemical treatments.

Self-assembling process of 1 dodencatiol on copper tiles :

After preparing the copper surface, copper tiles are submerged in 1mM of 1-dodecanethiol melt in absolute ethanol. The tiles are held in a melt for 20 hours, and after taking it out, they are washed by absolute ethanol, to avoid the remainings of monomers, out of melt which does not participate in a creation of monolayers. Tiles prepared ih this way are left for one day in atmosphere and are enriched by nitrogen, so the surface could be well dried.

3.2. Experimental methods

Copper electrode, as well as copper electrode covered by self-assembled monolayer of thiol, (Cu/SAM) is tested by using the contact angle method and cyclic voltametrics.

3.2.1. Measuring of contact angle

The method of contact angle is based on the surface energy of interaction between hard phase and fluid. That interaction is characterised by adhesion work, which depends on submerging angle. The value of contact angle gives the information about hydrophobity and hydrohility of surface. Measurements are done on «Dataphysics instruments- contact angle system OCA» device, with digital camera, and with mechanism for dosing, which is informatically managed, and which enables reproducible adding of volume drop of 1 mL. On digitally produced drop picture, it's possible to define the angles of wetting, by using computer.

On previously prepared copper electrode, as well as on Cu/SAM electrode, the water drops of 1 μL of volume are added, and contact angles measures are valued, as shown on the table 1.

With this procedure of measurement, the structure od SAM is defined, so that autophobic reaction of surface is observed, as a cosequence of closing hydrophobic groups.

Table 1. Values of measured contact angles on the copper electrode and Cu/SAM electrode.

Example	Contact angle θ / º
Cu	64,8
Cu / SAM	121,8

The high value of contact angle wetting on Cu/SAM electode is a proof that the chains of monolayer are very well oriented, so only the closing group of chain is in a contact with surrounding fluid. In the presented example that is (-CH3) group [3,7].

3.2.2. Cyclic voltammetry

The method of cyclic voltammetry was used for knowing general electrochemical behaviour of copper electrode and copper electrode covered with self-assembled monolayer of thiol (Cu/SAM). The reaction signal of this method is the linear change of potential from starting until final potential, and back, with defined speed of changing potential. The measurement are done in a wide range of potential : from cathod limit potential of E k.g. = - 1,2 V to anhod margin potential of E a.g. = 0,5 V vs Ag/AgCl.

The measurements are done on device managed by computer, which was consisted of «potentionstate/galvanostate» EG & GPAR model 273 and personal computer.

Working electrode is a copper tile which has a surface of 1cm^2. Before measuring cyclic voltammetry, we use not only mechanical and chemical treatments, but also elecrochemical treatment of electrode surface : after submerging into electrolite, electrode is cathodically polarised on the potential of –1,3 V vs Ag/AgCl in the period of 30 seconds, because of removal of oxydans, which are spontaneuosly created by leaving the electrode in the open air.

As the referent electrode for measuring the potential of working, we used silver-chlorid-silver (Ag/AgCl) electrode in KCl, whose potential is positivier for 0,222 V then standard hydrogen electrode (SHE). All values of potentials in this work are given in the relation to the previously mentioned referent electrode.

The netlike platinum electrode is used as counterelectrode. Platinum electrode is, before measuring, washed with redestitalated water.

Natrium's acetate, CH_3COONa, concentration of 1 mol dm^{-3}, pH = 6, is used as a fundamental electrolite.

The melt is made out of non-water Na-acetate, produced by «Kemika», cleanliness pro-analysi and redestilated water. pH value of this melt is adjusted by adding winegar acid, CH_3COOH, produced by «Kemika».

Voltamogram registered on Cu/SAM electrode in 1M of melt of Natrium-acetate shows reducement of anode's density of electricity melting the copper (approximately 2000 times) in a comparison with cylic voltamogram of copper's electrode registered in the same electrolite.

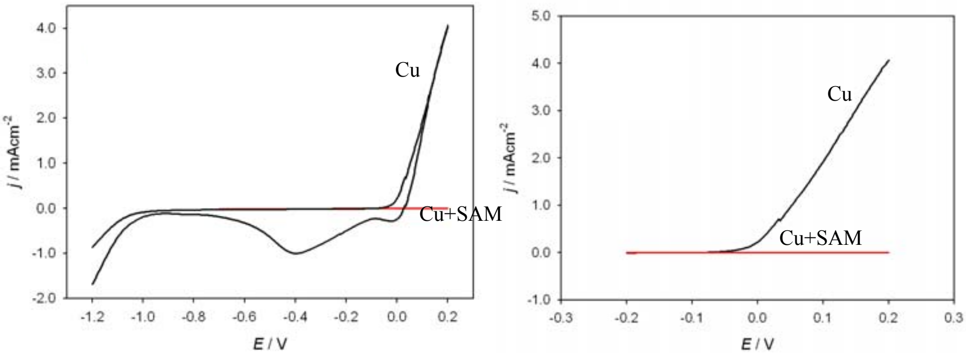

Figure 3. Cyclic voltamograms registered on Cu electrode and Cu/SAM electrode in 1M of melt Na-acecate , pH = 6, with the changing speed of potential, v= 10 m Vs^{-1}.

Efficiency of inhibition of copper's corrosion with monolayer of 1-dodecanethiol in 1 M of melt Na-acetate, pH = 6, is caluculated by next relation:

$$DI = \frac{j_{\mathrm{Cu}} - j_{\mathrm{Cu+SAM}}}{j_{\mathrm{Cu}}} \qquad (1)$$

where j_{Cu} presents the density of anode's electricity seen on experimental part of the curve j vs. E on the potential of 0,1 V, and its value responds to the copper's melting. On the same potential of 0,1 V it is shown the value of density of anode's electricity of Cu/SAM electrode. Efficiency's caluculated value of inhibition of copper's corrosion, E = 0,1 V, to relation (1) is 99,93 %.

4. CONCLUSIONS

Synthesis of self-assembled monolayer of 1-dodecanethiol is done by submerging of previously prepared copper's electrode into the 1 mmol dm^{-3} in the melt of 1-dodecanethiol diluted in absolute ethanole in the period of 20 hours. Characterisation of formed dodecanethiol monolayer is done by measuring the contact angle, which the drop of water encloses with the surface.

The measured value of contact angle has shown increased hydrophoby of the surface, reflected by increasing the value of contact angle. The value of contact angle is increased for about 50% in the comparison to the copper electrode. Monolayer of 1-dodecanethiol, synthesized on the copper electrode's surface, inhibitates copper corrosion in acetate electrolite. The efficiency of inhibition is 99,93 %.

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