

EQUIPMENT FOR THE STUDY OF ANODIC OXIDATION OF ORGANIC COMPOUNDS

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In the paper an equipment is briefly described which was used in the study of anodic oxidation and adsorption of organic compounds on Pt electrode.

In the research of the electrochemical oxidation of organic compounds the information on the adsorption is essential. Among the methods used for the determination of adsorbed materials, the MPP (multipulse potentiodynamic) method proved to be the most suitable [1]. This method was applied not only in the investigation of adsorption of organic materials but also in the case of Li^+ , Cs^+ , Cd^{++} , Zn^{++} , Cl^- [2—5]. By this method the extent of the surface coverage and the amount of charge necessary for oxidation of the adsorbate can be determined.

In this paper we describe the method applied in our measurements of electro-oxidation of different organic compounds.

The electrolytic cell used (Fig. 1) had separated anodic and cathodic compartments and was equipped with a water distillation unit and a solution storage recipient. With these the base solution could be prepared in a closed system. The organic material was introduced to the cell through the cap "B" by means of a syringe. The working electrode could be rotated up to 3000 r.p.m. To deoxygenate the cell and the solution, N_2 gas of 99.999% purity was used.

The electrical circuit (Fig. 2) contained the G and VG impulse generators besides the usual potentiostatic components. The impulse generator G was triggered by the generator VG . Generator G controlled the potentiostat by producing sawtooth potential impulses. The speed and amplitude of the impulses could be changed. Furthermore the gener-

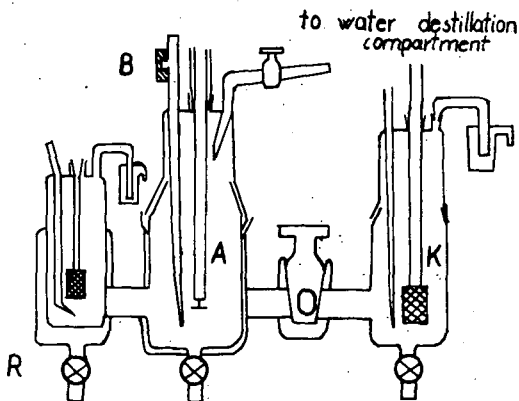


Fig. 1. Electrolytic cell. R: reference electrode; A: anodic compartment; K: cathodic compartment; B: cap for introduction of organic material.

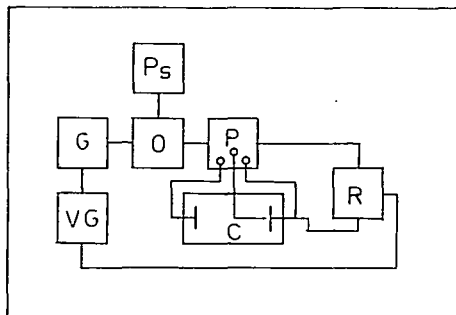


Fig. 2. Electric circuit. *C*: electrolytic cell; *P*: potentiostat; *G* and *VG*: impulse generators; *Ps*: potential switch; *O*: coupling bridge; *R*: XY recorder and/or oscilloscope.

to the value E which was necessary for the examination of oxidation. After the pre-set time t , the generator VG automatically triggered the generator G which produced the cathodic or anodic impulse in order to measure the adsorption. The potential impulse and the current were led to the oscilloscope used as an XY recorder and was photographed. Later the current was directly integrated.

From the hydrogen deposition current, measured during the cathodic impulse, the amount of H deposition charge can be calculated. The value of coverage (θ) is

$$\theta = \frac{Q_H^0 - Q_H}{Q_H^0}$$

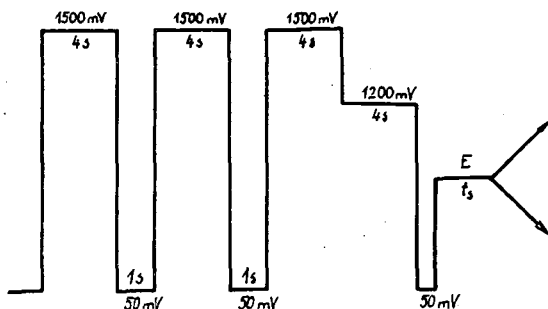


Fig. 3. Potential sequence for cleaning the electrode surface and the measurement of the adsorption.

where Q_H^0 is the charge necessary for producing a H atom covered surface without organic adsorbate, and Q_H is the charge necessary for producing a H atom covered surface in the presence of organic adsorbate. Since the covering of the surface with hydrogen is considered to be complete [6] at the current minimum preceding the H_2 evolution (Fig. 4), the real surface area can be calculated on the basis of the ratio 1 H atom: 1 surface Pt atom (1 cm^2 real surface: 0.21 mC). The 0.6 cm^2 geometric area of our electrode is proved to correspond to 1.6 cm^2 real surface.

By using anodic potential impulses, the charge of oxidation of the adsorbate (Q_R) can be obtained by subtracting the charge (Q_M) necessary to the oxidation of the clean electrode surface from the charge necessary to oxidation of the surface containing the organic adsorbate (Q_{R+M}). Nevertheless, this is applicable only in the cases, when the adsorbate is completely oxidized before the oxygen evolution starts, and the surface is covered only with oxide layer.

ator VG controlled the photoequipment of the oscilloscope. Later an improvement was carried out by integrating the current electronically; in this way the subjective errors in the evaluation of the value of charge could be avoided. The integration of the current was controlled by the generator G .

In order to clean the surface of the electrode, oxidative and reductive conditions were established on it by using the potential sequence shown on Fig. 3. The repeatedly applied 1500 mV and 50 mV produced by the potential switch Ps served the cleaning, and from the last 50 mV the potential was switched over

By applying anodic and cathodic impulses we can obtain information about the changes taking place on the surface if there is no material-transport between the surface and the solution during the impulse. This condition can easily be fulfilled by increasing the speed of potential-change of the impulse. Measuring the charges with different speeds, it was found that the values of both the oxidation and the H deposition charges were independent of the speed above 10 V/s. In the experiments 30 V/s was used.

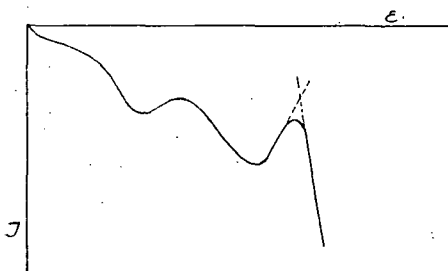


Fig. 4. Current of H deposition.

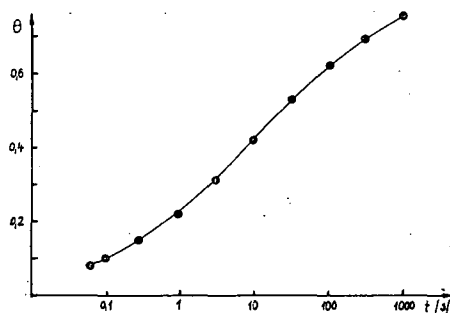


Fig. 5. Increase in coverage with time at 400 mV in *n*-propanol solution. The base solution is 1 *N* H₂SO₄, electrode rotation: 1000 r.p.m.

By this method the adsorption of *n*-propanol was investigated in 1 *N* H₂SO₄ solution at 400 mV (Fig. 5).

The surface coverage increased linearly with the logarithm of time, showing the same relationship which was found by BAGOTZKY for different organics [7].

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ПРИБОР ДЛЯ ИЗУЧЕНИЯ АНОДНОГО ОКИСЛЕНИЯ ОРГАНИЧЕСКИХ СОЕДИНЕНИЙ

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