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DISSOLUTION OF ZINC IN ACETIC ACID SOLUTION AT POLARIZATION BY NON-STATIONARY CURRENT

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ABSTRACT

In this paper for the first time the process of electrochemical dissolution of zinc electrodes in acetic acid at polarization by alternating current of 50 Hz has been investigated. The effect of acetic acid concentration, temperature and duration of the electrolysis on current efficiency for zinc electrodes dissolving has been studied. It has been established that the increase of electrolyte concentration to 300 g/L apparent current efficiency of metal dissolution increases to 125%, and with increasing of electrolysis duration up to 1.5 hrs current efficiency of zinc dissolution decreases. At temperature of 80^{o}C current efficiency makes 166%.

It is established that as a result of electrolysis zinc acetate [$Zn(CH_3COO)_2$] is formed, composition and structure of which were identified by X-ray diffraction and electronic microscopy.

Key words: Alternating current, Polarization, Electrode, Acetic acid solution, Electrolyte.

INTRODUCTION

The present stage of chemical industry development requires increasing of production efficiency, on which depends the pace of scientific and technological progress in this field[1]. In this regard, low-tonnage chemistry occupies one of the central place providing improved product quality. This also concerns to the production of nonferrous metals, particularly zinc compounds, without which it is impossible for the modern industry.

Zinc compounds having an interesting combination of various physical and chemical properties are widely used in electronic, aerospace, chemical industry and medicine[2].

Existing in the world practice methods of production of zinc compounds, are based either on the sublimation and oxidation of zinc vapor, or on decomposition of oxygen-

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containing zinc salts at elevated temperatures. It uses either a zinc-containing raw material, from which zinc is recovered directly as a vapor in various types furnaces, or branded zinc burnt in a muffles. Compounds obtained by such methods do not differ by sufficient purity due to the low quality of the starting raw materials and characterized by low activity, because they do not have a developed surface, although the presence of active surface is one of the basic requirements for substances used in various industries[3]. With its state and dimensions many properties are related that determine behavior in the process. Naturally such products can not meet the needs of industry. To meet the needs of the industry it is required to obtain zinc compounds with specified properties of surface, particle shape and size[4]. For the development of new methods, it is necessary to be able to produce different varieties of zinc compounds on one plant.

In recent years more sophisticated and future directions in this area have been developed, one of which is the preparation of zinc compounds by electrochemical polarization with stationary and non-stationary currents[5,6]. The main advantage of the electrochemical method is the possibility of production of very pure products, as well as shaping of the developed active surface at certain parameters of the process, which enhances their practical value. Improvement of sanitary working conditions of maintenance staff is also positive.

The aim of our work was to study electrochemical dissolution of zinc in acetic acid at polarization by industrial alternating currents to synthesize zinc acetate.

EXPERIMENTAL

Experiments were performed in glass 50 mL electrolyzer. Zinc plate with a purity of 99.9% were used as electrodes. Acetic acid was used as electrolyte.

The influence of different parameters on the electrolysis process, in particular the current density at the electrodes, the electrolyte concentration, the duration and temperature of the electrolysis solution was studied. All reagents used for the experiments were fit to degree of purity "pure" and "chemically pure". Used solutions were prepared on the base of distilled water. Current efficiency of zinc dissolution was calculated on the anodic half-period of alternating current.

RESULTS AND DISCUSSION

The process of chemical dissolution of the zinc electrodes in acetic acid has been previously investigated, but the value of the degree of dissolution of zinc was insignificant.

At polarization of zinc electrodes by alternating current it was found that zinc dissolves with high current efficiency. This is because the polarization of the zinc electrode by industrial alternating current in acetic acid solution in the anodic period of the alternating current zinc oxidizes to form a bivalent ions. In the near-electrode space possibility is created to interact with zinc acetate ions followed by the formation of zinc acetate:

$$Zn^{2+} + 2\ CH_3COO^- \leftrightarrow Zn(CH_3COO)_2 \quad \ldots(1)$$

In the cathodic half-period at the zinc electrode recovered hydrogen ions:

$$2H^+ + 2e \rightarrow H_2 \quad \ldots(2)$$

Thus, in acetate solution in the anodic half-period of alternating current each zinc electrode is dissolved to form a zinc ion followed by formation of the zinc acetate, while in the cathodic space on the zinc electrode hydrogen is released by the above reaction (2).

The effect of current density on the current efficiency of zinc electrodes dissolution in acetic acid was studied in the range of from 30-300 A/m^2. The maximum value of the current efficiency of zinc electrodes dissolution is observed at a current density of 30 A/m^2 - 138.5%. It should be noted that at higher current densities the current efficiency decreases, moreover the electrolyte begins to heat so conducting the electrolysis at a high current density is not economically feasible. This is because surface electrode partially passivated by oxide or salt film in the anodic half-period. As a result, with current density increasing rate of zinc dissolution increases (Fig. 1).

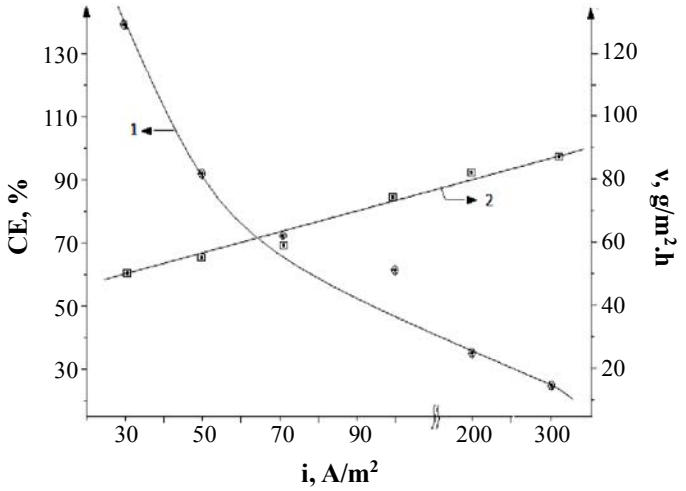

Fig. 1: Effect of current density of the zinc electrode on current efficiency (1) and the dissolution rate of the metal (2) (CH_3COOH = 100 g/L, τ = 0,5 h, t = 20^{o}C)

The effect of acetic acid concentration in the range of 25-300 g/L was studied. The results showed that with concentration of acetic acid increasing current efficiency of zinc acetate (II) formation grows, at a concentration of 300 g/L current efficiency is 125%. The reaction rate of zinc dissolution at acetate concentration of 25 g/L is 37.5 g/cm^2·h, and at 300 g/L is 75 g/cm^2·h (Fig. 2). At the electrochemical dissolution of the zinc electrode in acetic acid current efficiency of dissolution is above 100 % due to chemical dissolution of metal:

$$2CH_3COOH + Zn \rightarrow Zn(CH_3COO)_2 + H_2 \quad \ldots(3)$$

In this case, acetate-ions presented in the solution is actively destroying the crystal lattice of the metal, and because of acid concentration does not allow the oxide formed on the metal film, so electronegative metal dissolves well by chemical way with formation of its ions.

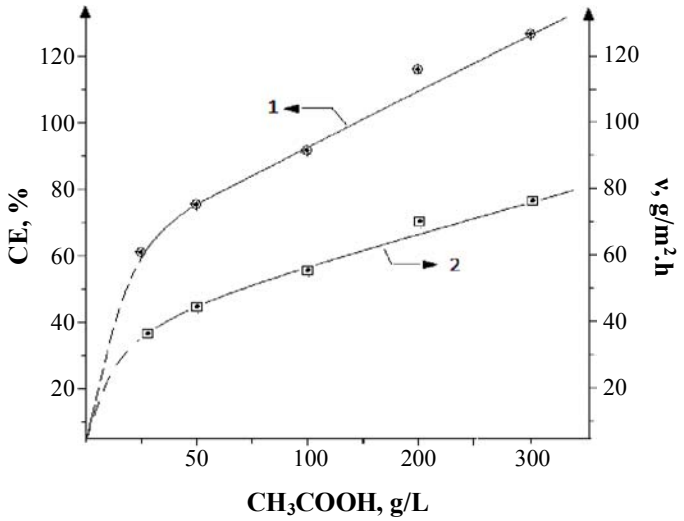

Fig. 2: Effect of concentration of acetic acid on current efficiency (1) and the dissolution rate of the metal (2) (i = 50 A/m^2; τ = 0,5 h.; t = 25^{o}C)

The influence of electrolysis duration on current efficiency of dissolution of zinc electrodes in the range of 0.25-1.5 hr was studied. The results show that with increasing of electrolysis duration current efficiency of dissolution gradually decreases (Fig. 3). This is because the surface of the zinc electrodes is partially passivated by salt film, but the rate of electrodes dissolution increases due to increase of the quantity of electricity.

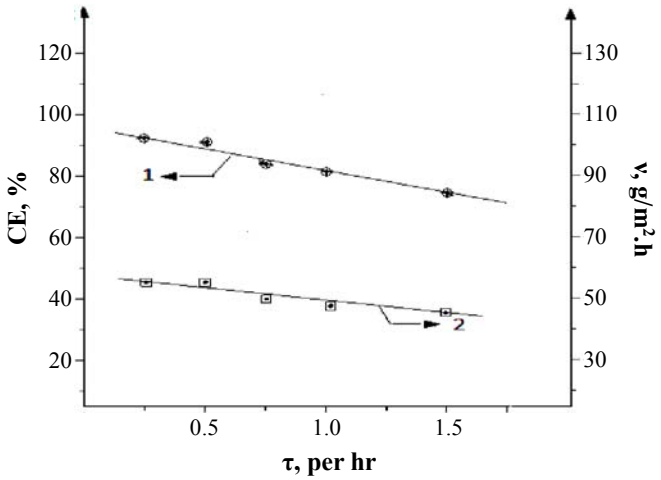

Fig. 3: Effect of the duration of the electrolysis on current efficiency (1) and the dissolution rate of zinc (2) (CH_3COOH = 100 g/L; i = 50 A/m^2; t = 25^{o}C)

At studying the effect of temperature on the current efficiency of zinc dissolution electrodes electrolytic cell was used which equipped with a backflow condenser and a thermostat to maintain the desired temperature. As seen in Fig. 4, with increasing of solution temperature from 25°C to 80°C current efficiency and dissolution rate rise, at 25°C current efficiency is 91.5%, and at 800°C - 166%. Increase of current efficiency of zinc dissolution with increasing of temperature of the solution, apparently connects with the increase in the rate of chemical dissolution of zinc.

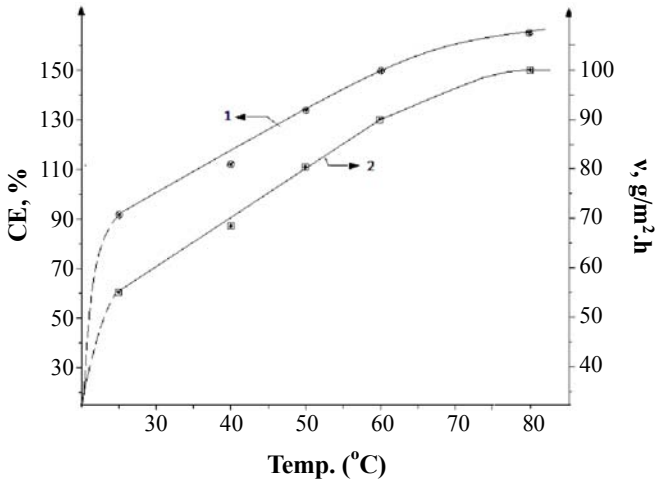

Fig. 4: Effect of temperature on the current efficiency (1) and the dissolution rate of zinc (2) ($C_{CH3COOH}$ = 100 g/L; i $_{Zn}$ = 50 A/m^2; τ = 0,5 h)

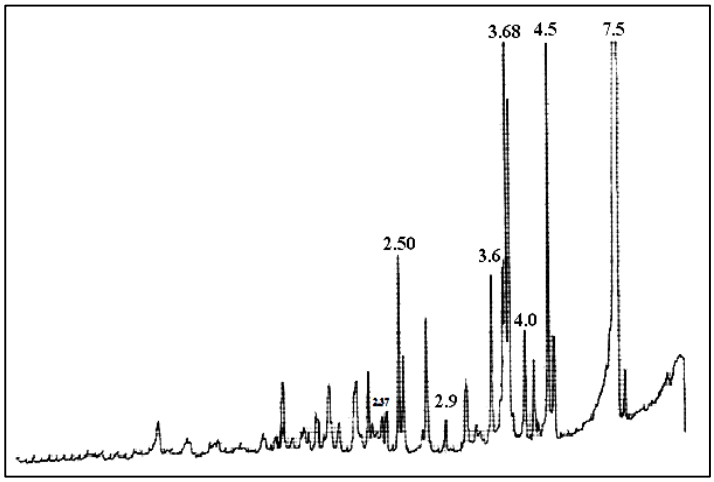

Fig. 5: X-ray picture of zinc acetate, prepared by electrochemical way

CONCLUSION

Thus, for the first time we investigated the influence of various factors on the current efficiency of zinc dissolution at polarization by industrial alternating current with a frequency of 50 Hz in acetic acid solution. It has been established that zinc oxidizes to form a bivalent ions that interact with acetate-ions with subsequent formation of zinc acetate - $Zn(CH_3COO)_2$, composition and structure of which were identified by X-ray analysis (Fig. 5).

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