JOURNAL OF APPLIED ELECTROCHEMISTRY **20** (1990) 986–988

The effect of the type of electric current on the cathodic corrosion of aluminium

E. SABEVA, I. DOBREWSKY

Higher Institute of Chemical Technology, Bourgas, Bulgaria

P. DINEFF

Higher Institute of Mechanical and Electrical Engineering, Sofia, Bulgaria

Received 15 August 1989; revised 22 February 1990

A comparative experimental study on the cathodic corrosion of aluminium in 0.52 M sodium chloride distilled water solutions is carried out. The electrolysis is conducted using a single half-cycle rectified, direct or industrial frequency current. Characteristic relationships concerning the cathodic corrosion are noted. Attention is drawn to the higher rates of cathodic corrosion observed on electrolysis with single half-cycle rectified current which is combined with lower energy costs.

Nomenclature

w_{k1}	cathodic corrosion rate for direct current electrolysis ($g\,s^{-1}\,m^{-2}$)
w_{k2}	cathodic corrosion rate for single half-cycle rectified current electrolysis ($g\,s^{-1}\,m^{-2}$)
w_a	anodic dissolution rate ($g\,s^{-1}\,m^{-2}$)
w_F	theoretical Faradaic dissolution rate ($g\,s^{-1}\,m^{-2}$)
w	dissolution rate for alternating current electrolysis ($g\,s^{-1}\,m^{-2}$)
j	electric current density ($A\,m^{-2}$)

1. Introduction

Electrocoagulation is a contemporary method for the purification of industrial waste and natural waters. It is based on the formation of a coagulant on electrolysis of the treated water using soluble electrodes.

The results from studies on the electrochemical dissolution of technical grade aluminium electrodes in NaCl solutions were reported in an earlier paper [1]. In these investigations it was experimentally established that, depending on the parameters of the electrical regime, i.e. density and type of current and topology of the electric field, the ratio between the amounts of aluminium dissolved from the anode and from the cathode varied from 1.3 : 1 at low current densities up to 15 : 1 at high current densities. These results are of interest for the practical application of electrocoagulation since they permit, on the basis of the cathodic corrosion of aluminium, a highly efficient technological process for which a comparatively low specific electricity consumption per unit volume of purified water is required.

Various technological solutions aiming at water purification through electrocoagulation are known, some based on direct current while others successfully employ single half-cylce rectified [2–4] and pulsating direct current [5–7].

The present work reflects the results obtained from experimentally investigating the effect of the type of electrical current upon the rate of cathodic corrosion of aluminium.

2. Experimental details

Stationary flat-parallel electrodes of an active geometric surface of $4 \times 10^{-4}\,m^{-2}$ were used in the present investigation. The elctrodes were made of 99.5% aluminium, with 0.26% Fe, 0.14% Si, 0.10% Cu, 0.001% Mg, as impurities, and fixed in specially prepared Teflon holders at a distance of 0.015 m. The electrode surface was mechanically polished prior to electrolysis with emery paper of various grades, the surface was then washed with ethanol, distilled water and the electrodes were dried and weighed. After electrolysis the electrodes were again washed with distilled water, dried and weighed. The amount of removed aluminium from the electrodes was determined by weighing after three experiments conducted in parallel.

Two series of experiments were carried out. In series A the experiments were carried out in 0.052 M NaCl solutions prepared from chemically pure NaCl and distilled water. The pH of the solutions was adjusted to an initial value of 4 with 0.1 N hydrochloric acid. The voltage was applied immediately after immersion of the electrodes in the solution.

Electric sources of direct, single-cycle rectified and alternating current (50 Hz) were used. The electric current density was varied from 10 to 600 $A\,m^{-2}$. The electrolysis was maintained in the galvanostatic regime at room temperature without stirring the solution. The duration of the experiments was 900 s. The changes in pH and the specific conductivity of the solutions were measured.

0021-891X/90 $03.00 + .12

In series B the experiments were carried out using electrodes of similar area, the anode being of platinum. The solutions were of the same NaCl concentration with an initial pH value of 6.3. The interval of electric current densities in this case widened up to 1000 A m^{-2} and the solutions were stirred during electrolysis with a magnetic stirrer.

3. Results and discussion

Figure 1 gives the rates of corrosion of the cathode w_{k1} and w_{k2} when using direct and single half-cycle rectified current, respectively, the rate of anodic dissolution, w_a, the theoretical rate of dissolution (as given by Faraday's law), w_F, and the dissolution rate of the electrodes while using alternating current, w, as functions of the electric current density, j, under the conditions of series A.

At low current densities and the above mentioned distance between the electrodes the rates of anodic dissolution in the cases of single half-cycle rectified current and of direct current remain approximately the same, while at high current densities, in the case of single half-cycle rectified current, the anodic dissolution is slightly reduced. Because of this a generalized curve $w_a = f(j)$ for the anodic dissolution of the two types of current is presented in Fig. 1.

The $w_{k1} = f(j)$ and $w_{k2} = f(j)$ relationships indicate that at low current densities the increase of the latter leads to a rapid increase in the cathodic corrosion rate. In the cases when the electrolysis is carried out with direct current and the current density exceeds 60 A m^{-2} the cathodic corrosion rate, w_{k1}, continues to grow, but very slowly. In the case of electrolysis with single half-cycle rectified current this change in the cathodic rate of corrosion takes place at a higher current density, i.e. above 100 A m^{-2}. Figure 2 shows the relative difference Δw_k between the rates of corrosion as a function of current density for the two types of electric current, calculated from the expression:

$$\Delta w_k = \left(\frac{w_{k2} - w_{k1}}{w_{k1}}\right) \times 100\% \qquad (1)$$

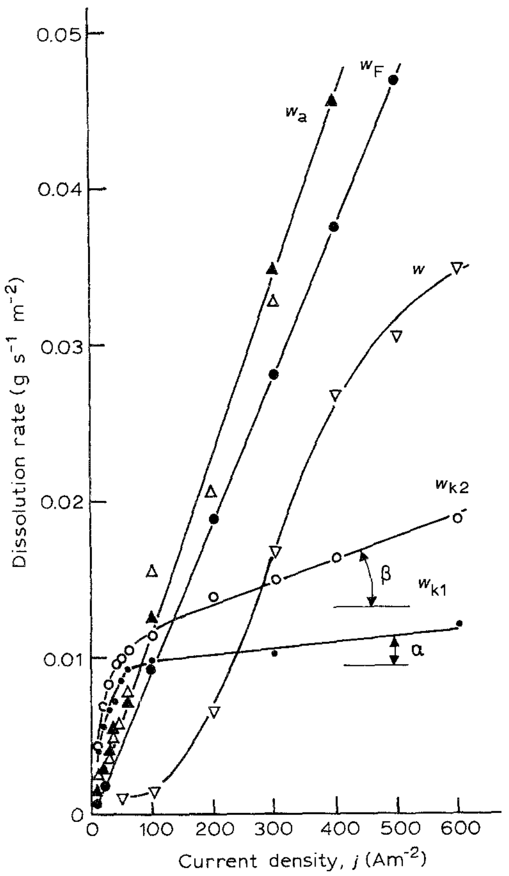

Fig. 1. Rates of corrosion of the cathode w_{k1} and w_{k2} when using direct and single half-cycle rectified current, respectively, the rate of anodic dissolution, w_a, the theoretical rate of dissolution as given by Faraday's law, w_F, and the dissolution rate of the electrodes while using alternating current, w, as functions of the electric current density j, under the conditions for series A experiments.

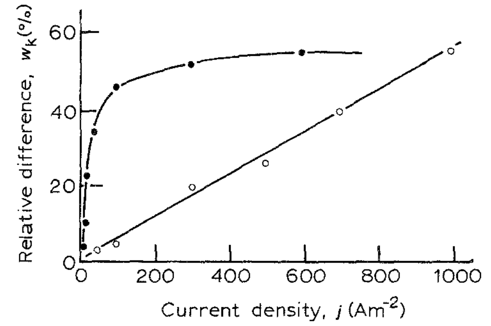

Fig. 2. Relative difference, Δw_k, between the rates of corrosion for direct current and for single half-cycle rectified current as a function of current density. (●) series A, (○) series B experiments.

The comparison between the $w_a = f(j)$, $w_{k1} = f(j)$ and $w_{k2} = f(j)$ dependencies obtained with direct and single half-cycle rectified current as well as $w = f(j)$ obtained with alternating current indicate (see Fig. 1) that, depending the values of the electrode dissolution rates, the considered current density interval can be divided into several regions.

At current densities below 80 A m^{-2} the cathodic rates at the cathode for the two types of current, Δw_k, dissolution, w_a, for the two types of current. At higher current densities the rates gradually become equal and then w_k remains smaller than w_a.

The anodic rate of dissolution, w_a, is always greater than the theoretical rate of dissolution, w_F. In other words, the total quantity of aluminium, removed from two electrodes, considerably exceeds the theoretical amount.

The specific consumption of electric energy per kilogram of aluminium (kWh kg^{-1}) for the two electrodes was computed from the data reflecting the total quantity of aluminium lost from the anode and the cathode and the electric energy consumption at the various current densities.

The variation in the specific electric energy consumption as a function of current density at direct and single half-cycle rectified current is depicted in Fig. 3. The advantage of conducting the electrolysis under the latter conditions with respect to energy saving is obvious. The rate of dissolution of the aluminium electrodes using alternating current varies within 15 to 70% of the theoretical rate w_F.

In the range 200 to 400 A m^{-2} w varies proportionally

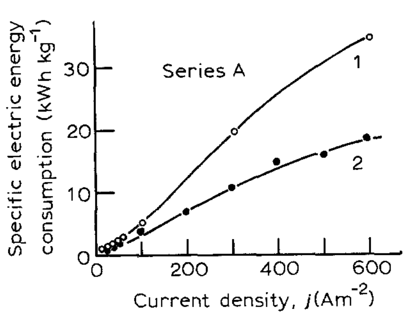

Fig. 3. Dependence of the specific electric energy consumption on the current density: (1) direct current; (2) single half-cycle rectified current.

to the electric current density. The character of the changes of dissolution rates with alternating current is similar to that cited by Mihailovsky [8]. The rate of dissolution with alternating current becomes equal to that of cathodic corrosion using direct current, w_{k1}, and using single half-cycle rectified current, w_{k2}, within the 200 to 300 A m^{-2} range.

$w_{k1} = f(j)$ with direct current, $w_{k2} = f(j)$ using single half-cycle rectified current and $w = f(j)$ at alternating current as well as $w_F = f(j)$ which is the theoretical curve under series B conditions. These are illustrated in Fig. 4.

The variation in the cathodic rate of corrosion of the aluminium electrode as a function of the current density, j, when using direct or single half-cycle rectified current was analogous to the variation observed under the conditions of series A, regardless of the fact that the electrolysis, under series B conditions, was conducted using a platinum anode while stirring the solution.

Some significant differences however, were also noted. The relative difference between the corrosion rates at the cathode for the two types of current, Δw_k, was lower than in the case of series A experiments (Fig. 2).

At higher current densities, i.e. above 500 A m^{-2}, the rate of dissolution of the aluminium electrodes when using alternating current, w, becomes equal to the cathodic corrosion rates, w_{k1}, and is about 25 to 35% of the theoretical rate, w_F, i.e. it is markedly lower than in the case of the series A experiments.

The cathodic corrosion rate of the aluminium electrode will be determined by the hydroxide ion concentration formed in accordance with the reaction [9].

$$H_2O + e^- \longrightarrow OH^- + \tfrac{1}{2}H_2$$

This is in agreement with the view that the corrosion of the aluminium cathode is caused by the alkalinity of the solution in proximity to the cathode due to the evolution of hydrogen [10].

4. Conclusion

The experimental results indicated that, at low current densities, the cathodic corrosion rate increases rapidly with the current density. In this case all OH$^-$ ions formed are consumed in the process of cathode dissolution.

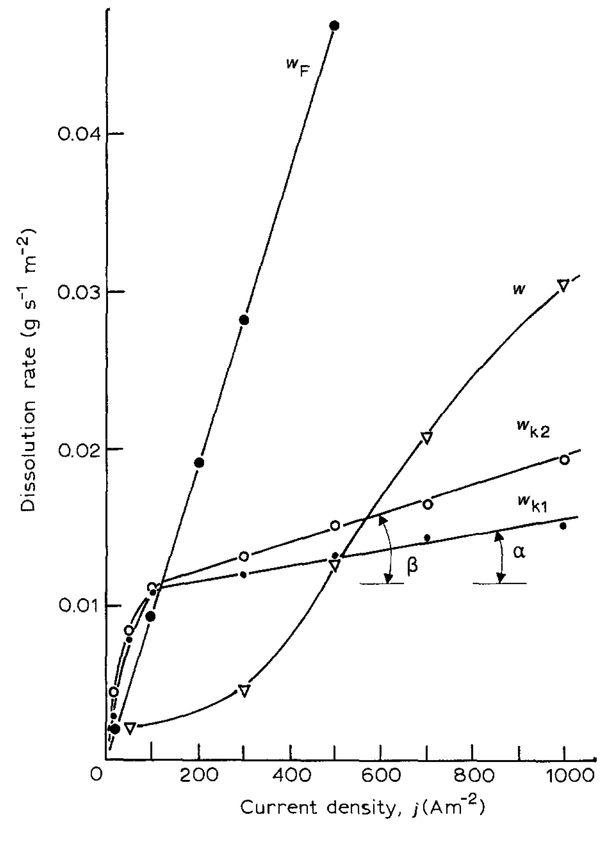

Fig. 4. Dependence of the cathode dissolution on the current density for direct, alternating and single half-cycle rectified current under the conditions of series B experiments.

At high current densities the hydroxyde ion concentration on the surface of the cathode increases and a part of the OH$^-$ are carried away by diffusion or electric migration into the bulk of the solution. With direct or single half-cycle rectified current and high current densities, therefore, no equilibrium is established between the rate of hydroxyde ion accumulation in the cathode film and their rate of diffusion into the bulk of the solution. Because of this, above a certain value of the current density, the cathodic rate of corrosion does not tend towards a constant value, but increases slightly.

References

[1] I. Dobrevsky, E. Sabeva and P. Dinev, *Chimia i Industria* **4** (1984) 160.
[2] P. Dineff. Dissertation, Higher Institute of Mechanical and Electrical Engineering, Sofia (1978).
[3] Bulg. Pat. No. 276171 (1979).
[4] Bulg. Pat. No. 35415 (1979).
[5] Bulg. Pat. No. 27618 (1979).
[6] USSR Pat. No. 645943 (1979).
[7] R. Sh. Shafeev and M. V. Tavdishvili, *Technologia dobychi i obogash chenii poleznych izkopaemych Gruzii,* (1975) 104.
[8] Yu. I. Michailovskii, *sb. Korozii metalov i splavov,* Moskva (1963) 222.
[9] Van de Ven and H. Koelmans, *J. Electrochem. Soc.* **123** (1976) 143.
[10] B. P. Caldwell and V. J. Albano, *Trans. Electrochem. Soc.* **76** (1939) 271.