

# Anodic electroluminescence accompanying the electrolytic oxidation of cadmium\*

R. DRAGON, R. KRUPA

Physics Laboratory, Institute of Mathematics and Physics, Technical University of Opole, 45-370 Opole, ul. Ozimska 75, Poland

The anodic electroluminescence, accompanying electrolytic oxidation of cadmium in 0.1 M water solution of KOH/K<sub>2</sub>CO<sub>3</sub>, has been investigated. It has been found that the system cadmium-anodic oxide layer-electrolyte displays a stationary electroluminescence, when the cadmium electrode is held at the positive potential. Switching off the voltage in the electrolytic cell and switching it on again causes anode flash. The anodically oxidized cadmium electrode exhibits no electroluminescence when held at the negative potential, relative to the counterelectrode.

## 1. Introduction

The phenomenon of the electroluminescence accompanying the electrolytic oxidation of some metals was the subject of very intensive studies, spurred on by both the purely scientific and technological interest [1]–[3]. It is commonly accepted that the phenomenon may be interpreted as the electroluminescence of oxide layer formed on the surface of the metallic anode. Until now, the exhaustive studies were performed, however, only for the “wet” system Al–Al<sub>2</sub>O<sub>3</sub> – electrolyte and for “dry” system Al–Al<sub>2</sub>O<sub>3</sub> – metallic (or semiconducting) counterelectrode. There are also reports on the investigations of the electroluminescence accompanying the electrolytic oxidation of Al, Ta, W, Zr, Zn, Mg, Bi, Hg and In [1]–[5]. Electroluminescence occurring during the electrolytic oxidation of the other valve metals, including cadmium, has not been the subject of systematic studies.

Cadmium is used as the negative electrode in the nickel-cadmium batteries. During the discharging of the battery, the cadmium electrode is subjected to the electrolytic oxidation. Therefore, the behaviour of the cadmium electrode during anodic oxidation as well as the oxidation products were already studied [6]–[10], but, as far as we know, there are no data in the literature on the electroluminescence accompanying the electrolytic oxidation of cadmium.

The purpose of the paper is to present the preliminary results of the investigations of the electroluminescence of cadmium anodes electrolytically oxidized in 0.1 M water solution of KOH/K<sub>2</sub>CO<sub>3</sub>.

---

\* Work sponsored by the Ministry of National Education (grant DNS–P/04/092/90–2).

## 2. Experimental conditions

The experiments were performed on cadmium plates cut from the industrial cadmium sheets of the purity of 99.95 wt. %, containing admixtures of Zn – 0.010%, Pb – 0.035%, Fe – 0.003%, and Tl – 0.005%. Before the electrolytic oxidation the cadmium plates were chemically cleaned in the water solution of nitric acid (75 ml  $\text{HNO}_3$ , 25 ml  $\text{H}_2\text{O}$ ). Next, the plates were rinsed in running water and then rinsed in the solution containing 30 ml  $\text{H}_2\text{SO}_4$ , 70 ml  $\text{H}_2\text{O}_2$  and 900 ml  $\text{H}_2\text{O}$ . The final step in the cleaning procedure was the rinsing in running and distilled water [11].

The electrolytic oxidation of cadmium plates was carried in the 0.1 M water solution of  $\text{KOH}/\text{K}_2\text{CO}_3$ . During the process of electrolytic oxidation the cadmium plates were used as anodes, the platinum plate being used as the cathode. The oxidation process was carried at a constant voltage of 40 V. In some cases the voltage between the electrodes was gradually increased up to value of 40 V. The cadmium anodes emitted light during the electrolytic oxidation.

The block scheme of the experimental setup used for the electrolytic oxidation of cadmium and for measurements of the intensity of electroluminescence accompanying the electrolytic oxidation is represented in Fig. 1. Part I of the measuring

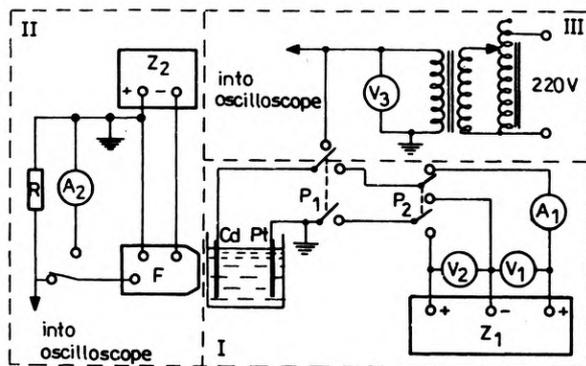


Fig. 1. Scheme of the apparatus for measurements of the electroluminescence accompanying the anodic oxidation of metals:  $Z_1$  – battery,  $Z_2$  – high-voltage supply ZWN-2.5. F – photomultiplier FEU-38

system enabled the oxidation process to be performed, part II was used for measurements of the intensity of electroluminescence, and part III – for observation of brightness waves. The intensity of light emitted from the cadmium plates was measured using an FEU-38 photomultiplier, the sensitivity of which covers the range of light wavelengths from 300 to 800 nm.

## 3. Results of experiments

### 3.1. Electroluminescence during the electrolytic oxidation of cadmium at a constant voltage

The intensity of electroluminescence  $L$  accompanying the process of electrolytic

oxidation of cadmium at a constant voltage (e.g., 40 V) initially increases, reaches some maximum value and then decreases with decreasing rate and after about 20 min becomes constant, whereas the density of current  $j$  flowing through the electrolytic cell rapidly decreases from the value of about  $150 \text{ mA/cm}^2$ , just after switching the voltage and after few minutes reaches its stationary value. Figure 2 represents the

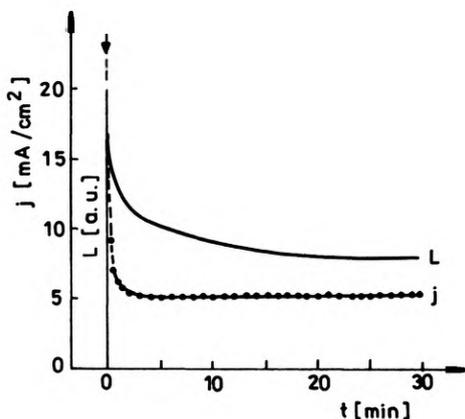


Fig. 2. Time dependences of the intensity of electroluminescence  $L$  and of the density of current  $j$  flowing through the electrolytic cell during oxidation of cadmium in  $0.1 \text{ M KOH/K}_2\text{CO}_3$  aqueous solution at a constant voltage of 40 V

typical time dependence of  $L$  and  $j$ , registered during electrolytical oxidation of cadmium at a constant voltage of 40 V.

The initial part of the time dependence of the intensity of electroluminescence accompanying the electrolytic oxidation of cadmium at a constant voltage was observed using the oscilloscope technique. As it follows from the oscilloscope traces represented in Fig. 3, the oxidized cadmium plate starts to emit the light about

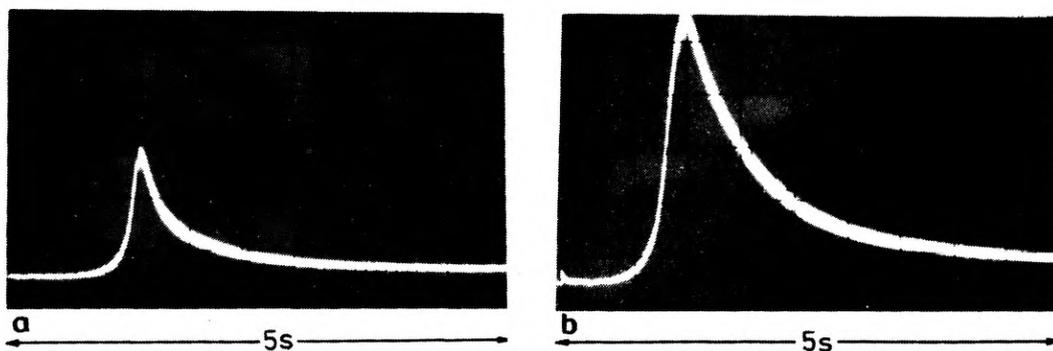


Fig. 3. Oscilloscope traces of the change in the electroluminescence intensity during the early stage of anodic oxidation of cadmium at a constant voltage of 40 V: **a** – Cd plate directly after the chemical cleaning, **b** – Cd plate chemically cleaned and then oxidized by 1 h tempering at  $300^\circ \text{C}$  in air under atmospheric pressure

1 s after switching the electrolytic cell on. It is worth to note that the shape of the time dependence of the intensity of electroluminescence accompanying the early stage of the oxidation process strongly depends on the state of the oxidized cadmium surface – the anode flash of the thermally oxidized cadmium plate (Fig. 3b) is distinctly stronger than that for the chemically clean sample (Fig. 3a).

### 3.2. Electroluminescence of the cadmium electrodes having already been formed

After electrolytic oxidation of cadmium electrodes lasting few tens of minutes, the intensity of the electroluminescence becomes constant (Fig. 2). The thickness of the anodic oxide layer in this stage of the oxidation process is practically constant, too. If, in this stage, the voltage across the electrolytic cell is lowered fast enough, it can be assumed that the changes in the intensity of electroluminescence caused by the changes of the voltage, occur at a constant value of the thickness of the oxide layer covering the cadmium electrode. Figure 4 represents the voltage dependence of the intensity  $L$  of electroluminescence of cadmium plates oxidized at a constant voltage of 40 V. It has been proved (see Fig. 5) that the observed voltage dependence of the

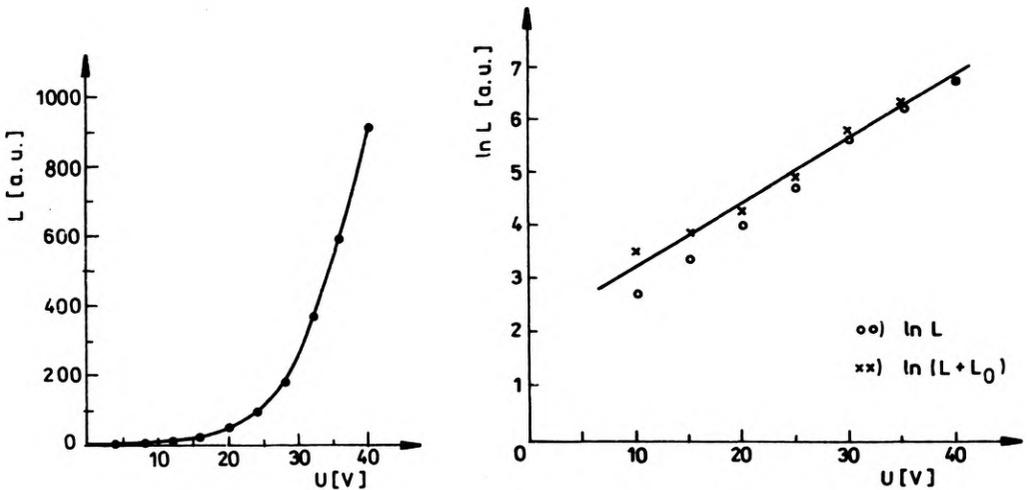


Fig. 4. Voltage dependence of the intensity of electroluminescence of the cadmium electrode after 12 min anodic oxidation at constant voltage of 40 V

Fig. 5. Semilogarithmic plots of the voltage dependence of the intensity of electroluminescence shown in Fig. 4 (...  $\ln L = f(U)$ ;  $\ln(L + L_0) = f(U)$ )

intensity of electroluminescence of electrodes, covered with an oxide layer of a constant thickness, obeys the Van Geel law  $L = L_0(e^{aU} - 1)$ .

Switching off the voltage from the cadmium anode having been formed previously and switching it again causes a flash of radiation due to anode luminescence (anode flash) followed by a few oscillations of the electroluminescence

intensity, after which the intensity of light emitted from the anode reaches its previous stationary value. The density of the current flowing through the electrolytic cell changes in a similar manner (see Fig. 6). It has been found

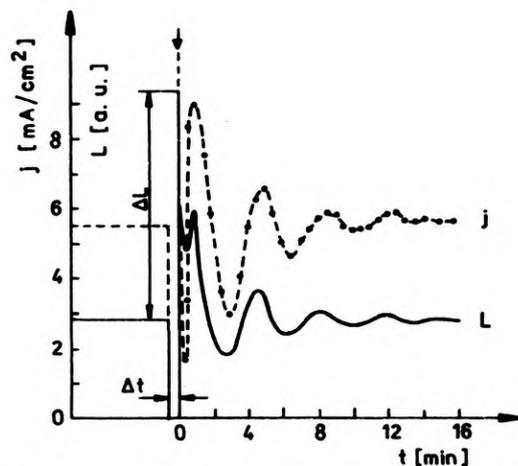


Fig. 6. Anode flash  $\Delta L$  and oscillations of the intensity  $L$  of electroluminescence and the current density  $j$  in the system switched on after 30 s time lapse. Before switching off the cadmium electrode was formed at a constant voltage of 40 V

that the intensity of anode flash depends on the duration  $\Delta t$  of the time lapse between the switching off the voltage across the electrolytic cell and switching it again. The intensity of the anode flash monotonically increases with increasing the time interval  $\Delta t$  up to some saturation value, for  $\Delta t \geq 3$  min (see Fig. 7). It should be noticed that after each anode flash the cadmium electrode was formed anew in 12 min, in order to reach a stationary value of the electroluminescence intensity (see Fig. 6).

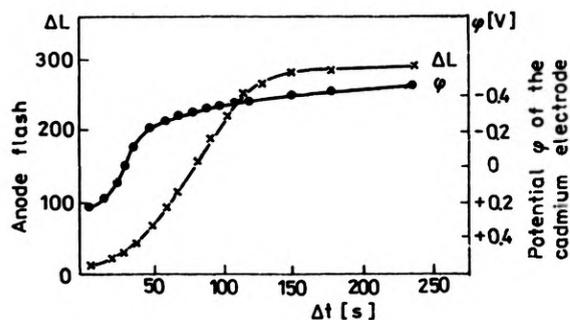


Fig. 7. Anode flash  $\Delta L$  and the potential  $\phi$  of the cadmium electrode versus the duration of the time lapse  $\Delta t$  between switching off the electrolytic cell and switching it on again

It has been found that there exists a correlation between the intensity  $\Delta L$  of the anode flash and the potential of the cadmium electrode relative to the platinum electrode. The potential of the freshly cleaned cadmium plate, relative to the platinum electrode amounts to ca.  $-0.4$  V. After anodic oxidation the potential of cadmium plate becomes positive. Switching off the voltage from the electrolytic cell causes decrease of the potential of the electrolytically formed cadmium plate. After about 4 min the potential reaches the value of  $-0.4$  V (see Fig. 7). This behaviour of the electrolytically formed cadmium plate is, most probably, connected with the dissolution of the previously formed oxide layer and formation of pores in it. Interruption of the process of growth of the oxide layer (switching off the voltage) enables the continuous increase of the pore depth during the direct contact of the metal substrate with the electrolyte.

The negatively polarized cadmium electrode does not exhibit any electroluminescence in the electrolyte (lack of the cathode flash). Figure 8 represents the

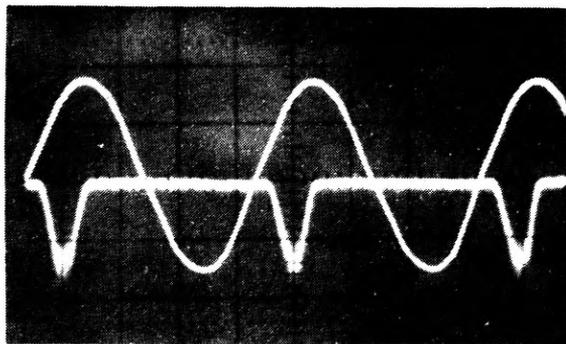


Fig. 8. Oscilloscope traces of the brightness waves of the system: cadmium-anodic oxide layer-electrolyte

oscilloscope trace of the brightness waves of the system cadmium-anodic oxide layer-electrolyte supplied with alternating voltage of the frequency of 50 Hz and amplitude of about 20 V. As it may be seen from Fig. 8 the cadmium electrode emits light only when polarized positively with respect to the platinum counterelectrode.

#### 4. Concluding remarks

From the investigations performed in the present study it follows out that:

- The stationary electroluminescence occurs only when the cadmium plate is held at a positive potential. The intensity  $L$  of this luminescence, at a constant value of the thickness of anodic oxide layer, obeys the Van Geel law  $L = L_0(e^{aU} - 1)$ .
- Switching off the voltage in the electrolytic cell with a cadmium plate having been already formed anodically, and switching it again causes a flash of the emitted light (anode flash). The intensity of the anode flash depends on the duration of the

time lapse between switching off the voltage and switching it on again.

– The system: cadmium-anodic oxide layer-electrolyte does not exhibit electroluminescence when the cadmium plate is held at the negative potential.

The electroluminescence accompanying anodic oxidation of cadmium, similarly as the electroluminescence accompanying the electrolytic oxidation of aluminium and other valve metals, can be considered as the electroluminescence of the layer formed on the surface of the anode (cadmium oxide or other cadmium compound, depending on the electrolyte used in the formation process).

Verified by Hanna Basarowa

## References

- [1] VAN GEEL W. CH., PISTORIUS G. A., BOUMA B. C., Philips Res. Rep. **12** (1957), 465.
- [2] WESOŁOWSKI J., DRAGON R., MOCHNIAK J., Acta Phys. Polon. **24** (1963), 407.
- [3] RUZIEWICZ Z., Wiad. Chem. **17** (1963), 325; **15** (1961), 637 (in Polish).
- [4] MOCHNIAK J., Doctor's Thesis, Wrocław University 1967, Poland.
- [5] DRAGON R., Doctor's Thesis, Wrocław University 1968, Poland.
- [6] HUBER K., J. Electrochem. Soc. **100** (1953), 376.
- [7] LANGE E., OHSE E., Naturwiss. **45** (1958), 437.
- [8] CROFT G. H., Electrochem. Soc. **106** (1959), 913.
- [9] LAKE P. E., CASEY E. J., J. Electrochem. Soc. **105** (1958), 52; **106** (1959), 913.
- [10] YOUNG L., *Anodic Oxide Films*, Academic Press, London–New York 1961.
- [11] TEGART W. J. Mc. G., *Electrolityczne i chemiczne polerowanie metali*, WNT, Warszawa 1962 (in Polish).

Received April 17, 1991

## Электрoлoминесценция при анодном оксидировании кадмия

Исследовано явление электрoлoминесценции при анодном оксидировании кадмия в водном 0.1 м растворе KOH/K<sub>2</sub>CO<sub>3</sub>. Было обнаружено, что система кадмий–анодная оксидная пленка–электролит проявляет стационарную электрoлoминесценцию, если кадмиевый электрод находится на положительном потенциале. Выключение на некоторое время напряжения из образованного кадмиевого электрода вызывает, после его повторного включения, анодную вспышку. Оксидированный кадмиевый электрод не проявляет электрoлoминесценции, когда находится на отрицательном потенциале.

Проверил Станислав Ганцаж