ANNALES
UNIVERSITATIS MARIAE CURIE-SKŁODOWSKA
LUBLIN—POLONIA
VOL. XLI, 13 SECTIO AA 1986

Zakład Chemii Analitycznej i Analizy Instrumentalnej
Instytut Chemii UMCS

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Investigations on the Current Oscillations Observed During the Electrolytic Reduction of the Chromate Ion in Alkaline Solutions

Badania oscylacji prądowych obserwowanych podczas elektrodowej redukcji jonu chromianowego w roztworach alkalicznych

Исследование токовых осцилляций наблюдаемых во время электродного восстановления иона хромата в щелочной среде

Several earlier publications [e.g. 3, 4, 5, 6, 8] dealing with the electoreduction of CrO_4^{2-} have shown that there occur alkalinization of the surface layer of solution as well as local formation of a film of $Cr(OH)_3$ and of basic chromates. The presence of this film affects the circumstances of electrodeposition of chromium and hinders the diffusion of ions to the electrode surface. In this paper, the permeability of this film and its resistance to cracking are briefly described.

A multi-sweep fast polarograph TELPOD, (DME of m=1,31 mg sek^{-1} t = 3,2 s - SCE-mercury pool electrode) and a polarograph LP-60/DME - mercury pool were used. A 1 M NH_4NO_3 - NH_4OH buffer adjusted to pH 8,5 was applied as supporting electrolyte. The solutions were not deaereted because no influence of oxygen on phenomena described were observed.

In such conditions well-formed polarographic waves are observed (Fig. 1) at low chromate concentrations. With increasing concentration the curve develops a depresion. The films of precipitate display mechanical endurance and elasicity, as evidences by the lengthening of the drop time and visible deformations of drops shape. During the drop expansion, cracks develop in the film and oscillations occur on single sweep curves (Fig. 2).

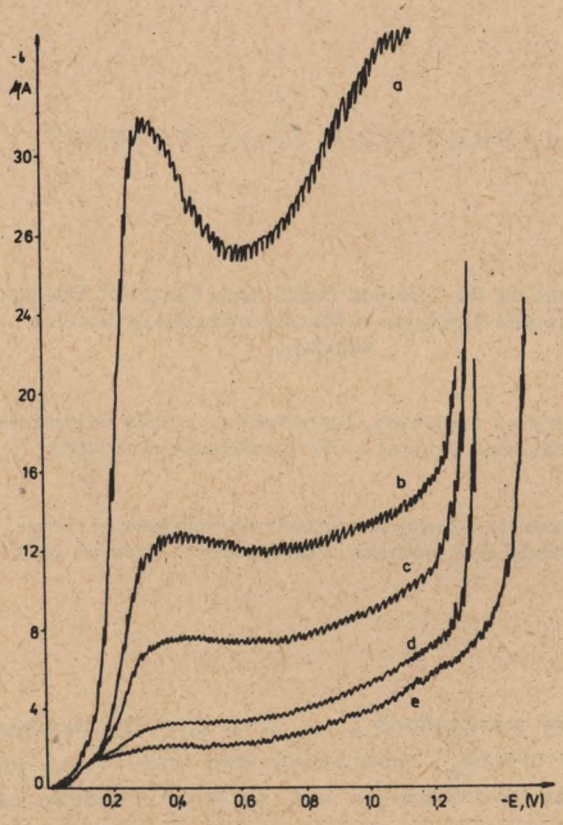

Fig. 1. Polarographic d.c. waves of chromate at variable concentrations ($mol \cdot dm^{-3}$):
a. $2 \cdot 10^{-3}$; b. $4 \cdot 10^{-4}$; c. $2 \cdot 10^{-4}$; d. $6 \cdot 10^{-5}$; e. buffer NH_4NO_3/NH_4OH, pH 8,5 alone

In contrast with the result of works of Sluyters [7] and Fleszar [2], the oscillations are observed in a wide range of potentials, (from -0,3 V to -1,5 V) and are characterized by a pluse pattern of higher

frequency. They appear as separated sharp narrow peaks of current, emering from a flat background. The duration time of each peak is of order of 0,1 s. The ascending part of the peak is remarkably steep, independently of the direction of the potential scan. The frequency and amplitude of the oscillations increase with the chromate concentration. They are smaller and their frequency is higher, when the electrode surface expands faster (initial stage of the drop or shorter drop time) and they do not depend on the rate of the potential scan.

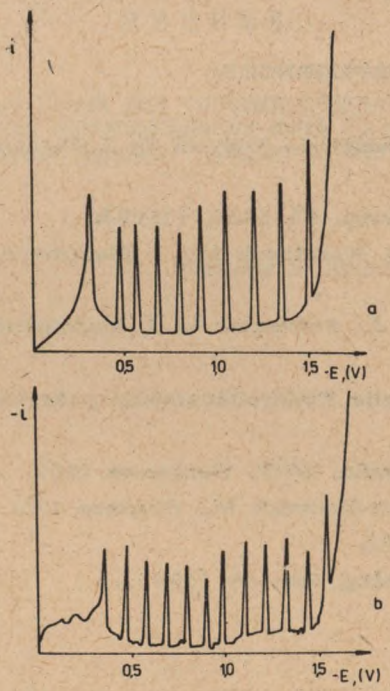

Fig. 2. The oscillations of the current. Solution: $2 \cdot 10^{-3}$ mol·dm^{-3} CrO_4^{2-} in NH_4NO_3/NH_4OH pH 8,5, the rate of potential scan -0,5 V/s., drop time 3,2 s,
a. increasing negative potential,
b. decreasing negative potential

The formation of such peaks can not be connected with gradual dissolving of the precipitate layer: the peaks are obviously caused by the sudden availability of fresh electrode surface to significant amounts of the depolarizer ions, probably coupled with simultaneous changes of the double layer capacity. These sudden breaks of the

film are surely provoked by the expansion of the drop. This explanation is veryfied by the fact that peaks occur within the range of potentials of Cr^{3+} formation and at incidental values in various registrated curves. Parallely to peaks rising, sudden movements of changed solution and of $Cr(OH)_3$ deposit fractions at the electrode surface can be seen 1 by using the phase contrast method. Sharp peaks are also beserved in other solutions provided that the formation of the mentioned film is possible.

REFERENCES

1. Chmiel J., Cięszczak-Chmiel A., Matysik J.: J. Electroanal. Chem. 99, 259, (1979).
2. Fieszar B.: Roczniki Chem. 43, 1805, (1969).
3. Frańczak A., Matysik J, Korolczuk M.: J. Electroanal. chem. 107, 189 (1980).
4. Korolczuk M., Matysik J., Frańczak A.: J. Electroanal. Chem. 71, 229 (1976).
5. Matulis Ya.: Blestiaszczije Elektroliticzeskije pokrytia, Mintis, Wilno, 1969.
6. Milner G.W.C.: Polarografia, WNT, Warszawa 1962.
7. Pieterse M.M.J., Sluyters-Rehbach M., Sluyters J.H.: J. Electroanal. Chem., 105, 269, (1979).
8. Ryan N.E.; Metal Finishing, Jan, 46 (1965).

STRESZCZENIE

Przedstawiono nowy rodzaj oscylacji prądowych powstających podczas elektrodowej redukcji jonu CrO_4^{2-}, Przyczyną ich powstawania jest rozrywanie się filmu produktów elektrolizy na KER.

РЕЗЮМЕ

Представлено новый род токовых осцилляций возникающих во время электродного восстановления иона CrO_4^{2-}. Они возникают в в результате разрыва фильма продуктов электролиза на KER.

Złożono w Redakcji 1986.11.06.