SHORT COMMUNICATION

An improved method for kinetic investigations of electrochemical reactions with gas evolution

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1. Introduction

Gas evolution occurs during many electrochemical processes such as electrodeposition, electro-extraction and electrorefining.

The volume measurements and *in situ* investigations of the kinetic changes of gas evolution for the above-mentioned processes may offer the possibility of direct, fast and accurate determinations of kinetic and electrochemical parameters.

The present paper is aimed at improving the equipment and developing a sensitive and precise method for kinetic investigations of gas evolved during electrochemical reactions.

2. Equipment and experimental procedure

The investigations were carried out in a Pyrex electrolytic cell (Fig. 1). Special care was taken to meet the requirements for separation of the cathodic compartment from the anodic space and for hermetic sealing.

The volume of evolved gas was measured using a DAGV 70 2M automatic gas volumenometer [1]. The apparatus (Fig. 2) included bellows (1), an electric motor (8) and a pressure sensor Mechanotron (3) with a sensitive membrane (2). The bellows, membrane and working cell (5) were thermostated and, under operating conditions, this system was hermetically sealed. The volumetric method is based on a conversion (by the Mechanotron) of the gas volume into an electrical current, which, after amplification (9), was fed to the electric motor. As a result the bellows were stretching so that the gas pressure remained constant throughout the experiment.

This apparatus was equipped with a magneto-electric differentiator. However, this differentiation mode did not provide accurate kinetic investigations because it was liable to external influence (temperature, vibrations). The adjustment and calibration were also complicated and the sensitivity was rather poor. Thus, in order to eliminate these shortcomings and increase the possibilities of the instrument, an improved differentiating method was developed in which a frequency compensated differentiating circuitry containing a capacitor, C, and an operational amplifier type 741 was used (Fig. 3). In order to ensure stable operation and high sensitivity we also used amplification of the input signal (up to 500 times) and elimination of phase lag and frequency distortions of the output signal (by using an additional $R_1 C_1$ circuit).

The operation of this differentiator is described by the following equation:

$$U_{\mathrm{OUT}} = -RC \frac{dU_{\mathrm{IN}}}{dt} \tag{1}$$

providing the following condition is fulfilled:

$$U_{\mathrm{c}} \gg U_{\mathrm{OUT}} \tag{2}$$

where U_{OUT} is the voltage at the output, RC is the time constant of the differentiator's operation, U_{IN} is the voltage at the input and U_{c} is the voltage at the plates of the capacitor.

The operation of the differentiator was tested with low frequency triangular, sine and square-shaped voltages [2, 3].

The gas evolution–time relationship $(V-t)$ and dV/dt curve were recorded by $Y-Y'-t$ recorder (Goerz Electro Company Model RE 520).

3. Results and discussion

The accuracy and sensitivity of the volumetric method was tested in two cases. The first was a measurement of the hydrogen evolved on a platinized platinum electrode in 0.5 M H_2SO_4, during cathodic polarization at 25 °C. It is known that this electrochemical reaction ensures 100% hydrogen yield [4]. Table 1 shows the results obtained for the hydrogen evolution at different cathodic current densities I_{c}. The charge, Q, passed through the solution was about 300 C. The
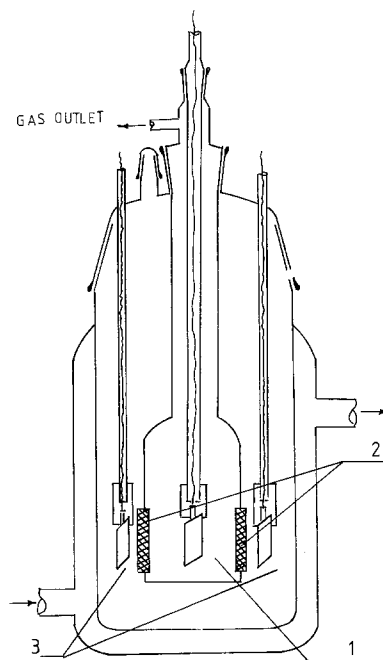

Fig. 1. Thermostated electrolytic cell. (1) Cathodic compartment; (2) porous glass separator; and (3) anodic compartment.
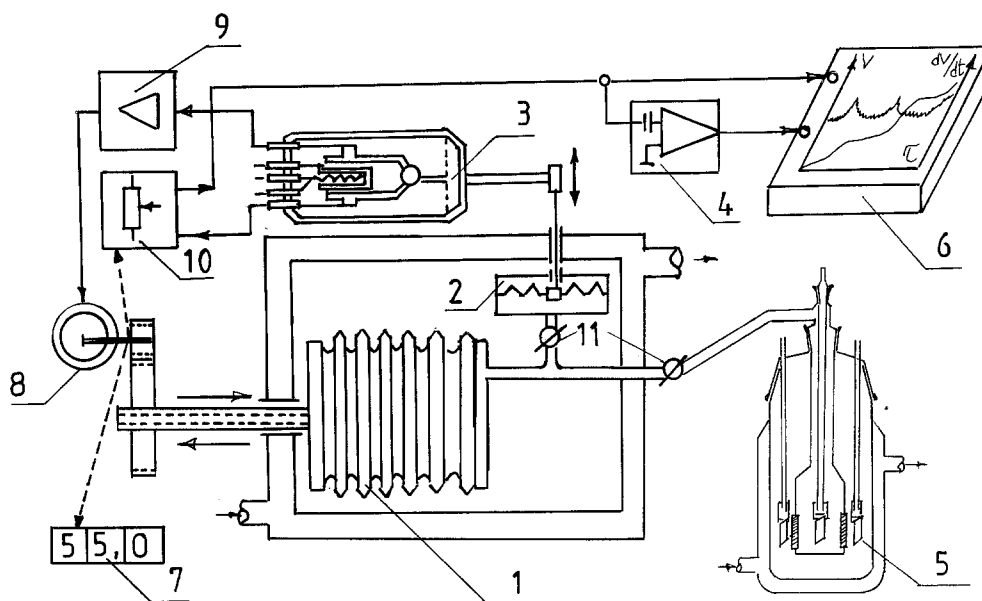
Fig. 2. Measuring unit comprising: (1) Bellows; (2) membrane; (3) pressure sensor Mechanotron; (4) differentiator; (5) working cell; (6) Y-Y'-t recorder; (7) mechanical gas volume counter; (8) electric motor; (9) amplifier; (10) potentiometric block; and (11) stop-cocks.

experimental data was calculated as mean arithmetic values of 3 measurements at each current density.

The volume V_H^{th} was calculated from the electrochemical equivalent of hydrogen $q_{H_2} = 0.116\,cm^3\,C^{-1}$ and the charge Q, and V_H^0 is the hydrogen volume referred to normal conditions ($P = 760\,mm\,Hg$ and $t = 0\,°C$) according to the following equation:

$$V_H^0 = \frac{V_t \times 273.16 \times (P - B)}{760 \times (273.16 + t)} \quad (3)$$

where: V_t is the measured volume (cm^3), P is the atmospheric pressure (mm Hg), B is water vapour pressure (mm Hg) and t is room temperature in (°C).

Comparison between the theoretically calculated values and the experimental data indicated an average error of 3.6%.

The measurement of hydrogen evolved during the electrodeposition of Co was chosen for a second test. It is known that under certain conditions either a αCo of βCo is obtained and different amounts of hydrogen evolve: small for αCo and considerable for the βCo deposit [5-7]. The Co coatings were deposited from electrolyte containing $250\,g\,dm^{-3}$ $CoSO_4 \cdot 7H_2O$ and $20\,g\,dm^{-3}$ H_3BO_3. The operating conditions were: for αCo, temperature $25\,°C$, pH 5 and $I_c = 2.5\,A\,dm^{-2}$; and for βCo, temperature not higher than $5\,°C$,

pH < 1 and $I_c = 2.5\,A\,dm^{-2}$. The deposited amounts were: 0.0694 g. (αCo) and 0.0059 g (βCo). Experimental results and calculated values are presented in Table 2.

It should be noted that the method allowed a fast and accurate determination of the gas volume.

The developed differentiation method was applied for *in situ* kinetic investigations of hydrogen evolution during the electrodeposition of zinc and immersion tin coatings on to aluminium.

The zinc coatings were deposited from the following electrolyte: $10\,g\,dm^{-3}$ ZnO and $100\,g\,dm^{-3}$ NaOH, at $25\,°C$ and $I_c = 2.5\,A\,dm^{-2}$. The surface area of the steel cathode was $3.0\,cm^2$. The V-t (a) and dV/dt (b) curves are presented in Fig. 4. The characteristic steps in the V-t curve were reproducibly observed in all five experiments with zinc platings. These curves may be interpreted in the light of the alteration of the structure and type of cathodic zinc coatings. Within the limits of the first curve region, hydrogen evolution proceeds on the steel and on the growing zinc plating, which partially covers it. Within the second region, where a compact zinc layer is formed, and throughout the third one, where the formation of spongy zinc is observed, it appears that the kinetics of hydrogen evolution depends on the structure and on the
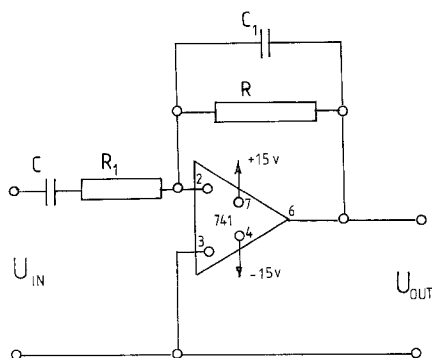

Fig. 3. Frequency-compensated differentiator diagram.

Table 1.

$I_c/A\,dm^{-2}$	Q/C	V_H^{th}/cm^3	$V_H^0\,cm^3$	Relative error/%
0.2	300.2	34.8	35.7	2.6
0.3	297.5	34.5	36.7	6.3
0.4	304.0	35.3	35.7	1.1
0.5	302.5	35.1	36.7	4.5
0.6	300.6	34.9	35.2	0.9
0.7	302.4	35.1	36.9	5.1
0.8	304.8	35.3	37.0	4.8
1.0	300.0	34.8	35.9	3.2

Table 2.

Total charge /C	αCo deposit /C	βCo deposit /C	H_2 evolution /C	V_H^{th} /cm³	V_H^0 /cm³	Relative error /%
240.4	227.5	–	12.9	1.5	1.4	6.6
164.7	–	19.3	145.4	16.9	16.8	0.6

substantially increased zinc deposit. Supplementary studies with another method such as chronopotentiometry, SEM etc. could throw additional light on the experimental results.

The tin immersion deposits were obtained from a solution containing $50\,g\,dm^{-3}$ Na_2SnO_3, $20\,g\,dm^{-3}$ $KNaC_4H_4O_6$ (Rochelle salt), $15\,g\,dm^{-3}$ $C_5H_{12}O_7$ (chelate compound), at $45\,°C$. This process was characterized by the simultaneous deposition of tin and evolution of hydrogen on the aluminium. Depending on the conditions of the immersion treatment, the ratio between the rates of these two reactions can differ substantially [9], and this influences the adhesion between the metal coating and the aluminium. The determination of the evolved hydrogen and the kinetics of this process enable the comparison of these results with the data of the adhesion between the tin coating and the substrate [10]. It should be noted that the main change in the aluminium surface was previously observed [11] during the first sixteen seconds, while the entire immersion process continues up to 50 seconds. Figure 6 shows that two regions in the dV/dt curve exist. At the beginning of the process, corresponding to the first region, the rate of the exchange reaction: aluminium dissolution, tin deposition and hydrogen evolution is predominantly determined by the dissolution rate of the free aluminium surface. After the sixteenth second a considerable portion of this surface is coated by tin, i.e. tin deposition and hydrogen evolution continues, mainly on the tin surface being formed. From curve (b) in Fig. 5 it may be concluded that after 16 s the hydrogen evolu-
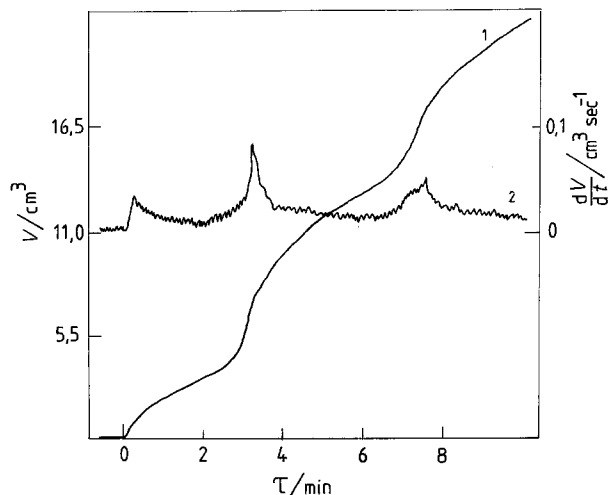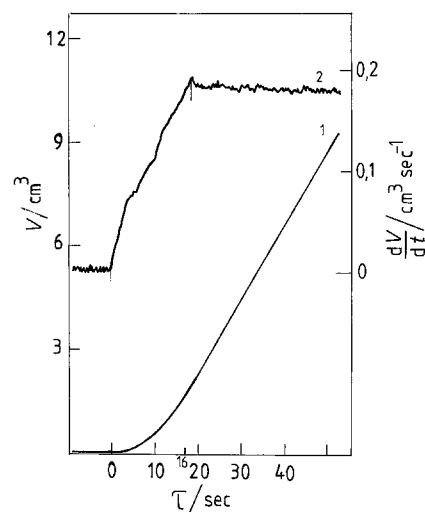

Fig. 5. Change in the amount of hydrogen (curve 1) and its evolution rate (curve 2) for tin immersion coatings on to aluminium from a solution containing Na_2SnO_3 $50\,g\,dm^{-3}$, $KNaC_4H_4O_6$ KNa tartrate (Rochelle salt) $20\,g\,dm^{-3}$, and chelate compound $(C_5H_{12}O_7)$ $15\,g\,dm^{-3}$ at $45\,°C$.

tion rate remains constant. In this sense, an advantage of this method is also the accurate determination of the moment after which the hydrogen evolution rate becomes constant.

4. Conclusion

An improved method has been developed to determine the rate of gas evolution during electrochemical reactions, with the aid of a differentiating circuitry containing a capacitor and an operational amplifier. The method allows *in situ* kinetic investigations at high sensitivity and accuracy of electrochemical processes with hydrogen evolution. It also offers the possibility of checking the thickness of coatings and determination of the current yield during the electrodeposition.

5. Acknowledgements

References

[1] Different. avtom. gas volumometre DAGV 70 2M *Techn. opisanie*, Moscow, Zavod pri Acad. Nauk USSR.

[2] D. Lenk, 'Naratchnik po oper. usilvately', *Technika*, Sofia (1980) p. 102.

[3] D. Klaytan, 'Eksperim. s oper. usilvately', *Technika*, Sofia (1983) p. 30.

[4] A. N. Frumkin, 'Kinetika electrod. procesov', Moscow University, Moscow (1952) p. 118.

[5] S. Vitkova and N. Pangarov, *Izv. po chimia pri BAN*, **4**, 4 (1974) 681.

[6] G. Raichevski and S. Vitkova, 'Zaschita metallov', **9**, 4 (1973) 418.

[7] S. Armianov, S. Vitkova and N. Pangarov, *Izv. po chimia pri BAN*, **5**, 2 (1971) 203.

[8] N. Kudriavtzev, 'Electrolit. pokritia', *Chimia*, Moscow (1979) p. 153.

[9] D. Stoychev and E. Stoyanova, *Bull. Electrochem.* **4**, 7 (1988) 673.

[10] E. Stoyanova, I. Christova and D. Stoychev, *Bull. Electrochem.* **5** (1991) 215.

[11] D. Stoychev and E. Stoyanova, *Surf. Technol.* **23** (1984) 12.

Fig. 4. Change in the amount of hydrogen (curve 1) and its evolution rate (curve 2) for zinc plating on to steel from an electrolyte containing ZnO $10\,g\,dm^{-3}$ and NaOH $100\,g\,dm^{-3}$ at $25\,°C$ and c.d. I_c $2.5\,A\,dm^{-2}$.