

ANODE MATERIAL OF COULOMETRIC GAS GENERATOR

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Ensuring the safety of human life and the requirements of industrial sanitation put forward strict requirements for means of monitoring the air environment. Continuous monitoring of carbon dioxide content using the most reliable monitoring means – amperometric-type electrochemical sensors - requires devices for periodic testing of sensors. Coulometric dispensers make it possible to generate a clearly defined amount of detectable high-purity gas and to carry out a quick check of monitoring devices.

It is shown that the use of an electrically conductive inert support frame made of titanium with a deposited layer of a catalytically active coating allows a controlled course of the reaction of formation of carbon dioxide by oxidation of oxalate acid. A high current efficiency of the generated gas can be obtained using a catalytically active titanium coating on which platinum has been thermochemically applied. This electrode is easily reproducible, technologically advanced and inexpensive due to low platinum content. Compared with other types of electrode materials, the use of platinized titanium will allow the generator voltage to be 0.5 V less. The addition of an indifferent compound in the working solution increases the ionic strength of the solution and allows a minimum of 100 mV to reduce of CO₂ formation potential.

Monitoring of carbon dioxide content in the municipal economy and the food industry requires periodic monitoring of control devices - amperometric sensors, which allow selective determination of the exact gas content in a relatively narrow range of concentrations. The verification of gas analyzers of various types is carried out using standard gas mixtures that can be prepared by static and dynamic dosing methods. The metering device of the gas-detectable component can be an appropriate gas cylinder, or, more often, a coulometric generator, which is highly effective. Coulometric production of carbon dioxide is possible by electrolysis of oxalate acid solutions to obtain a gas of sufficiently high purity (about 90%) [1]. The material of the anode of such a coulometric generator must satisfy a number of requirements: manufacturability; low overvoltage of the main process and high

overvoltage of the by-product of oxygen evolution; chemical and mechanical stability. In general, such properties can correspond to titanium, characterized by considerable stability in a significant number of aggressive solutions [2, 3].

Research Methodology

The choice of the anode material was carried out on the basis of analysis of anode polarization curves, which was obtained in a saturated solution of oxalate acid. Polarization curves were obtained in the potentiodynamic mode in a three-electrode cell using a complex of devices consisting of a PI-50-1.1 potentiostat, a PR-8 programmer and a two-channel PDA-1-01 potentiometer. A saturated silver chloride reference electrode was used. Potentials in the work are given relative to the standard hydrogen electrode.

Dioxide lead electrodes were fabricated by electrochemical deposition of PbO₂ onto a titanium or nickel base from a nitrate electrolyte. On the surface of the lead electrode, the PbO₂ layer was formed by anodic polarization at the anode potential of +2.0 V in a sulfuric acid solution. Some of the electrodes were made on a titanium base, on which thin layers of platinum or ruthenium dioxide were applied by thermochemical decomposition of the corresponding chlorides.

Results and Discussion

Widespread use of inert electrodes in the oxidation of organic compounds, among which titanium and carbon materials are distinguished by their low cost and corrosion resistance. However, the oxide film on the surface of titanium causes a low rate of oxidation of oxalate ions



and the flow of significant currents occurs only at potentials corresponding to the release of oxygen



Further anodic polarization leads only to an increase in the thickness of the oxide layer on the titanium.

On carbon materials, such as graphite and glassy carbon, anodic polarization leads to an almost proportional increase in current (curves 2 and 3, Fig. 1), while the slope of the polarization curve is slightly larger for graphite due to its higher electrical conductivity. However, a disadvantage of this type of electrodes is the possibility of simultaneous reaction with the reaction (1) of the process of material destruction due to oxidation



which is confirmed by the presence of an inflection on curve 3 (Fig. 1) at a potential of about 0.2 V. The current that is observed at potentials less than 0.2 V can be associated with the oxidation of hydrocarbon residues included in the composition of glassy carbon. Although the reaction (3) will not lead to contamination of CO₂, which should be generated by the coulometric generator, but it will lead to a change in the effective surface of the working electrode and a decrease in its service life.

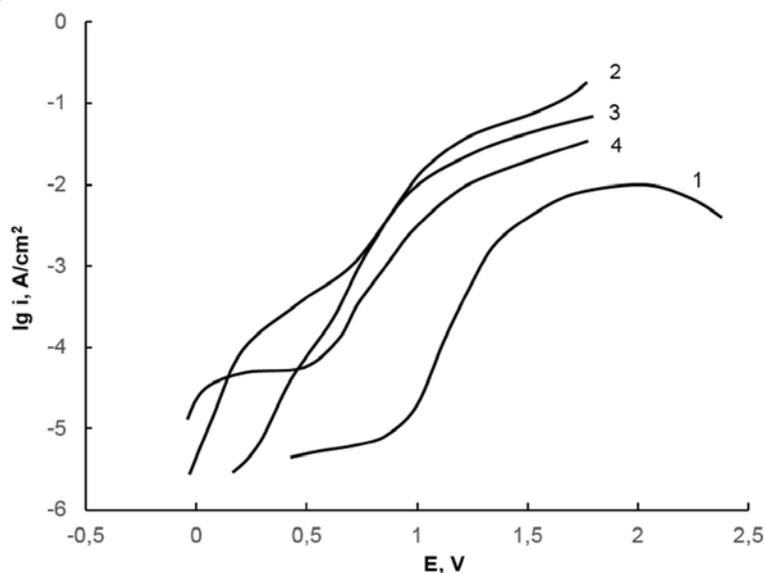
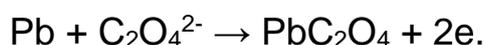


Fig. 1. Anodic polarization curves in a saturated solution of H₂C₂O₄
 1 – titanium; 2 – graphite; 3 – glassy carbon; 4 – titanium powder (2 g) with addition of graphite (0,2 g)

To ensure greater stability of the area of the electrode surface, it is possible to create a volume electrode with a conductive frame made of an inert metal. Electrodes in the form of disks with a diameter of 18 mm were made by pressing the titanium powder with a fraction of 0.05...0.1 mm with the addition of graphite grade C-1. However, the rate of oxidation of the oxalate-ion was low (curve 4, Fig. 1), and at current potentials positive 0.5 V there was a current increase associated with the reaction (3). The slope of the curve almost coincided with the slope of the anode curves on pure graphite and glassy carbon, which indicates an identical mechanism of the process. On all carbon-containing electrodes at potentials more positive than 1.2 V, current growth is associated with the release of oxygen (2).

On the surface of the lead electrode in a saturated solution of H₂C₂O₄, the value of the current potential of -0.2 V corresponds to active dissolution of the base with the formation of lead oxalate, which, due to low solubility, blocks the surface of the electrode (curve 1, Fig. 2). Anodic polarization of the lead electrode does not allow the production of CO₂ due to the binding of oxalate ions to the insoluble compound [4]



The lead electrode with formed PbO_2 -layer has a high flow overvoltage for all possible processes, therefore it is characterized by low currents during anodic polarization (curve 2, Fig. 2). The use of a more electrically conductive base, such as nickel or titanium, leads to an increase in the currents at the anodic polarization (curves 3 and 4, Fig. 2), but some of the current is consumed to oxidize the titanium current base, which will reduce the current efficiency of carbon dioxide.

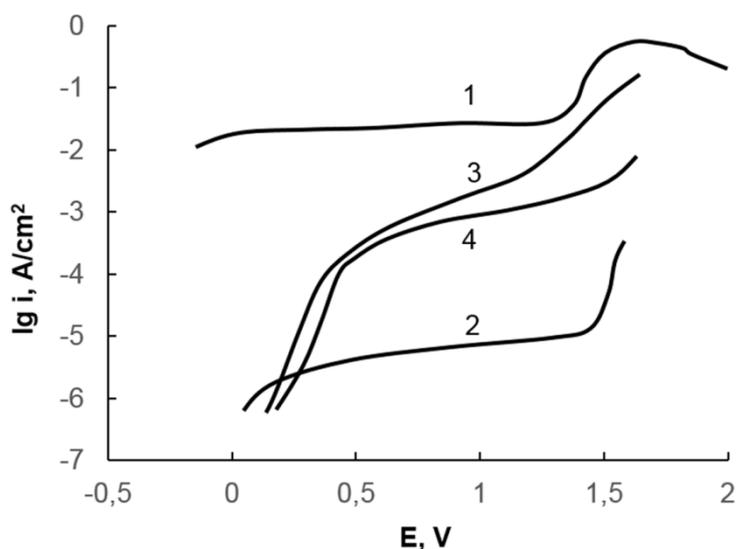


Fig. 2. Anodic polarization curves on dioxide-lead electrodes in a saturated solution of $\text{H}_2\text{C}_2\text{O}_4$

1 – Pb; 2 – PbO_2/Pb ;
3 – PbO_2/Ni ; 4 – PbO_2/Ti

Avoiding problems with the destruction of electrodes with intensive formation of gaseous products is possible using frame structures where the current-conducting inert base will be titanium, which must be applied with a catalytically active coating with a high oxygen overvoltage. Such catalytically active materials can be platinum and dioxide-ruthenium coatings, applied thermochemically to titanium powder. Both materials are characterized by a high overvoltage of oxygen release, and carbon dioxide formation occurs at high speed. At the electrode from platinized titanium (curve 2, Fig. 3), the intensive formation of CO_2 begins at potentials of almost 400 mV less than for the dioxide-ruthenium electrode (curve 1, Fig. 3), which indicates a higher catalytic activity of the platinum coating.

The use of electrode materials, on which the target process proceeds with high speed and low overvoltage, will allow to reduce the voltage on the coulometric generator. In particular, it is possible to reduce the oxidation potential of oxalate-ions by addition of indifferent ions (curve 3, Fig. 3), which increases the ionic strength of the solution and its electrical conductivity.

Conclusions

The operating parameters of the coulometric generator of carbon dioxide significantly influence both the material of the electrodes used

and the composition of the solution. The results obtained make it possible to recommend, as an electrode material, a pressed titanium structure on which a catalytic layer of titanium activated by thermochemically deposited platinum is pressed. This material is characterized by high overvoltage of oxygen release and low overvoltage of oxalate-ion oxidation, which allows to produce a high purity target product with a stable current efficiency. It is possible to reduce the voltage on the generator by increasing the electrical conductivity of the solution by introducing into the working solution an indifferent ion.

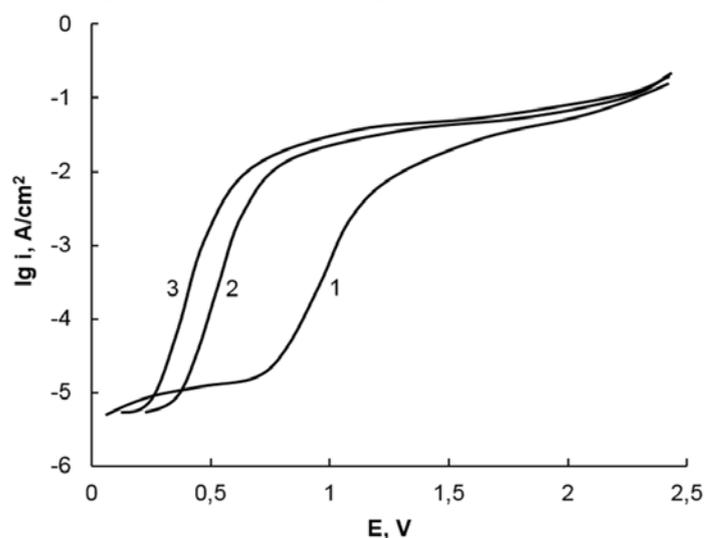


Fig. 3. Anodic polarization curves on RuO₂/Ti (1) and Pt/Ti (2, 3) electrodes in a saturated solution of H₂C₂O₄ (1, 2) and with addition of 0,1 mol/l Na₂SO₄

References

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