

SUCTION REMOVAL OF GASES AND LIQUIDS THROUGH POROUS ELECTRODES

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Nearly all electrochemical processes differ from ordinary chemical reactions in one important respect — the over-all reaction effected in the cell is divided spatially into two interconnected reactions taking place at the respective electrodes. On the one hand, this is an important advantage of electrochemical methods, whereby valuable products can be obtained. On the other hand, spatial separation of the electrode reactions leads to certain technological and design difficulties because of the need to use various diaphragms or other devices for separation of the products formed at the electrodes. Permeable porous electrodes can be used with success instead of diaphragms in some cases for separation of the electrode products. The products formed at the electrode surfaces must then be drawn off through the pores.

Heise [1] and Janes [2] have described a number of electrochemical processes in which porous electrodes operating on this principle are used. For example, by the use of porous electrodes with removal of the electrolysis products by suction through the pores, it is possible to effect relatively simply the anodic oxidation of manganate to permanganate, ferrous to ferric iron, arsenite to arsenate, etc.

If the system undergoing electrolysis is homogeneous and no new phases (such as solid or gas) are formed in the process, the action of a permeable electrode reduces in the hydraulic sense to simple filtration. Conditions of filtration through a permeable electrode become considerably more complicated if gaseous electrolysis products are drawn off through the pores together with the electrolyte. However, this case is extremely interesting from the practical standpoint.

Suction of air bubbles through porous electrodes can be arbitrarily separated into two stages: 1) removal of bubbles by the stream of electrolyte from the electrode surface, where they were held by capillary forces, and 2) filtration of the aerated liquid through the electrode pores.

The course of the first stage of this process is determined by a very complex combination of different factors which cannot be taken into account in advance. The second stage has been studied in greater detail. For example, Khristianovich [3] and Lapuk [4] have shown that filtration of an aerated liquid conforms to Darcy's law, but the liquid and gas have a retarding effect on each other. Certain preliminary experiments for study of the conditions of gas evacuation through porous electrodes were carried out in our laboratory [5]. The present communication contains the results of experiments on evacuation of insoluble and soluble gases formed at porous graphite electrodes of various structures.

EXPERIMENTAL PROCEDURE

The apparatus used for investigating the performance of porous electrodes with evacuation of the electrode products is shown schematically in Fig. 1. In these experiments sulfuric acid solution (concentration $C = 2N$) was drawn through a porous graphite electrode (a disk 36 mm in diameter and 8 mm thick). The electrode was cathodically polarized, and the hydrogen formed on it was partly drawn downward by the electrolyte stream and partly collected in the measuring buret. The results were used for plotting curves for variations of the degree of evacuation and pressure drop at the electrode (Δp) with the flow rate of the electrolyte (v) at different current

Electrode type	Density	Porosity	Pore con- volution coef- ficient *	Permea- bility coef- ficient (cm/hr)**	Number of pores*** per cm ²	Mean pore dia- meter*** (μ)
PT	1.18	46	2.02	53.2	6800	65.2
Ts	1.27	42	1.82	12.9	32000	30.3
SS	1.18	46	2.98	5.3	21300	30.4
ChEZ-30	1.01	54	2.34	7.6	42000	26.4
ChEZ-40	0.884	50.5	2.06	27.0	21000	41.7

*Determined by the conductivity method [6].

**For 1 cm specimen thickness, liquid viscosity 1 centipoise, and hydrostatic pressure 1 cm H₂O.

***Calculated by the method described in the literature [7].

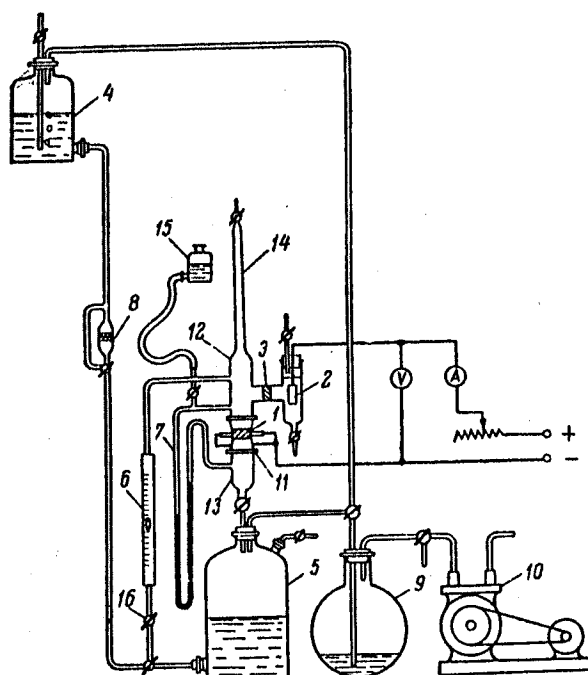


Fig. 1. Apparatus for investigating the performance of porous graphite electrodes with suction removal of the electrode products: 1) test electrode; 2) anode; 3) diaphragm; 4) header vessel; 5) receiver; 6) rotameter; 7) differential manometer; 8) filter; 9) buffer vessel; 10) vacuum pump; 11) connection; 12) upper part of cell; 13) lower part of cell; 14) measuring buret; 15) leveling vessel.

of these electrodes are given in the table.

RESULTS AND DISCUSSION

The experimental results are presented in Fig. 2-9 (results for electrodes of the ChEZ-30 type are not given; these electrodes are similar in properties to electrodes of the PT type).

It follows from the graphs for the pressure drop at the electrode as a function of the electrolyte flow rate

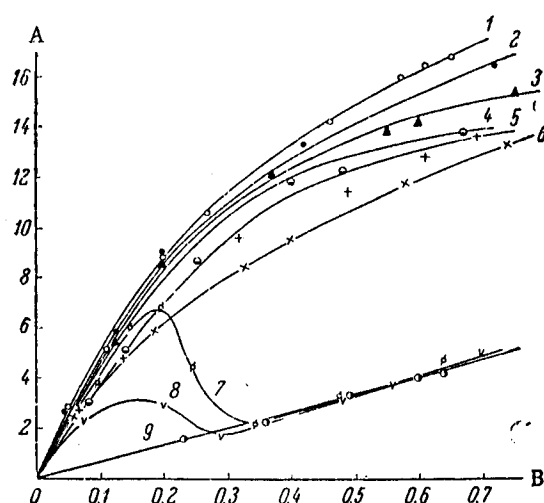


Fig. 2. Variation of the pressure drop in a porous electrode type PT with the electrolyte flow rate: A) pressure drop Δp (cm Hg/cm); B) electrolyte flow rate (ml/cm²·second); current density (amp/cm²): 1) 0.5; 2) 0.4; 3) 0.3; 4) 0.2; 5) 0.1; 6) 0.05; 7) 0.03; 8) 0.02; 9) 0.

densities. The degree of evacuation was defined as the ratio of the volume of the gas drawn off to the total volume of liberated gas.

The specimens investigated consisted of experimental porous graphite made at the Chelyabinsk Electrode Factory (ChEZ-30 and ChEZ-40). Brief details of the physical properties

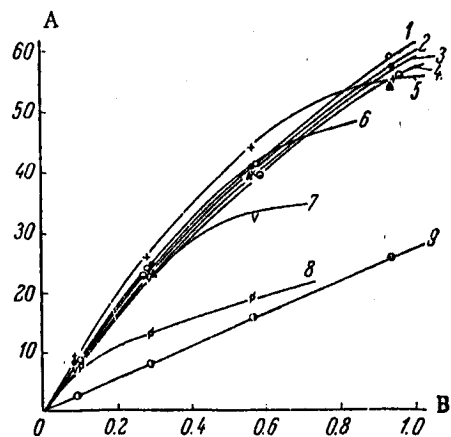


Fig. 3. Variation of the pressure drop in a porous electrode type ChEZ-40 with the electrolyte flow rate: designations as in Fig. 2.

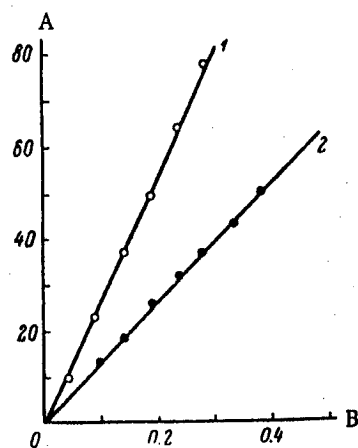


Fig. 4. Variation of the pressure drop in a porous electrode type SS with the electrolyte flow rate: A) pressure drop Δp (cm Hg/cm); B) electrolyte flow rate (ml/cm² · second); current density (amp/cm²): 1) 0.5-0.02; 2) 0.

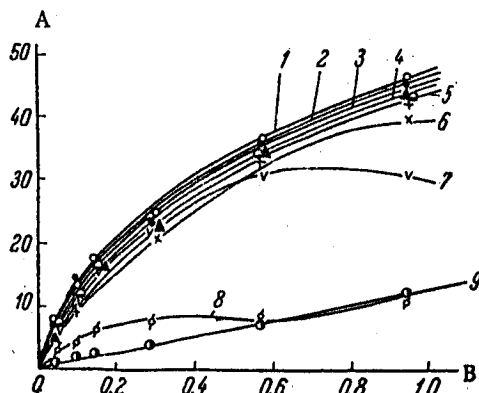


Fig. 5. Variation of the pressure drop in a porous electrode type Ts with the electrolyte flow rate: designations as in Fig. 2.

that in absence of current the filtration of electrolytes through porous electrodes conforms to the Darcy law in all the cases studied, showing that the flow of liquid in the pores is streamline (Werkling [8] observed a gradual transition from streamline to turbulent flow at high flow rates through electrodes with coarse pores).

When the current is switched on the electrode permeability falls sharply, and the filtration rate ceases to be a linear function of the pressure difference.

The current density has relatively little influence on permeability. It is only at very low current densities at electrodes with the coarsest pores (PT, Ts, and ChEZ-40) that the Δp - v relationship is of a peculiar character—when a definite flow rate is reached the hydraulic resistance of

the electrode falls to a value which corresponds to absence of current.

The form of the Δp - v curves indicates that the ratio of the gas and liquid volumes in the electrode pores is highest at low flow rates. The gas then exerts a strong retarding effect on the liquid. As the flow rate increases the pores become less saturated with gas and its retarding effect diminishes accordingly. If the current density is low, then at a sufficiently high flow rate the saturation of the pores with gas diminishes to such an extent that it no longer has any appreciable retarding effect on the liquid.

The close similarity of the curves for different current densities seems to indicate that the gas: liquid ratio at a given flow rate depends little on the current density.

The curves for the degree of evacuation as a function of the electrolyte flow rate are similar in general character for different electrodes, but they have appreciable quantitative differences from each other. Electrode type Ts has the best properties (with regard to degree of evacuation). With these electrodes, at a flow rate of 1 ml/second · cm², the degree of evacuation reaches 90% even at a current density of 0.5 amp/cm². At current densities below 0.2 amp/cm² evacuation is almost complete.

With other electrodes, such as ChEZ-40, PT, or ChEZ-20, the degree of evacuation at 0.5 amp/cm² and $v = 1.0$ ml/second · cm² is about 25-50%, and complete evacuation is observed only at current densities of

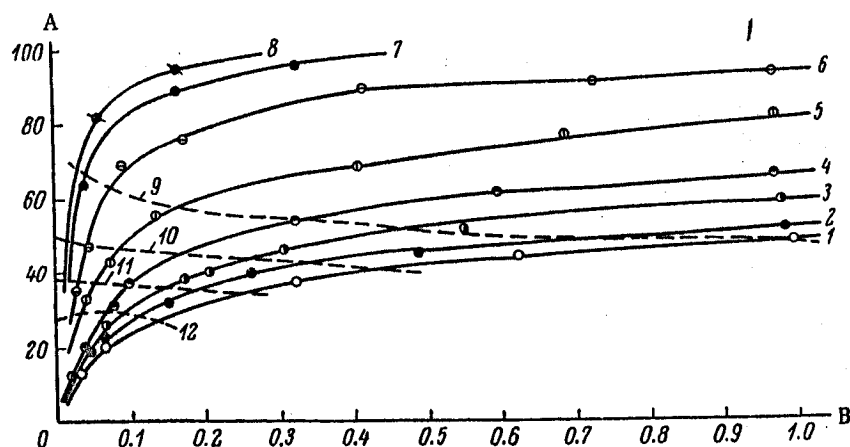


Fig. 6. Variations of the degree of evacuation of the gas with the liquid flow rate and current density for electrode type PT: A) degree of evacuation (%); B) electrolyte flow rate (ml/cm²·second); current density (amp/cm²): 1) 0.5; 2) 0.4; 3) 0.3; 4) 0.2; 5) 0.1; 6) 0.05; 7) 0.03; 8) 0.02; solubility of chlorine (g/liter): 9) 0.1; 10) 0.25; 11) 0.5; 12) 1.

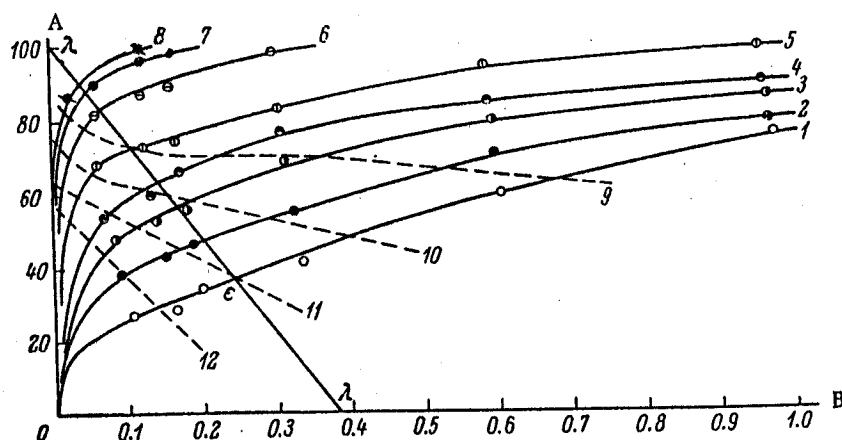


Fig. 7. Variations of the degree of evacuation of the gas with the liquid flow rate and current density for ChEZ-40 electrode: designations as in Fig. 6.

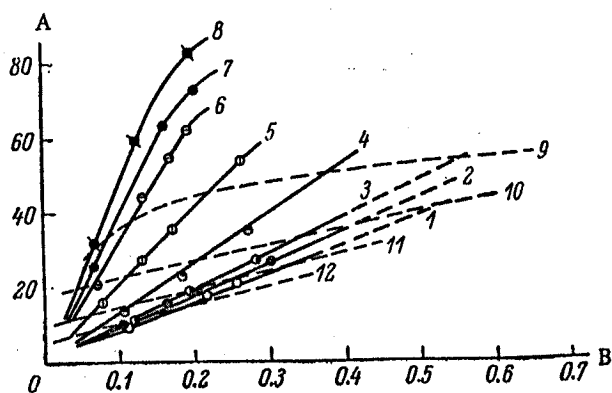


Fig. 8. Variations of the degree of evacuation of the gas with the liquid flow rate and current density for electrode type SS: designations as in Fig. 6.

0.02-0.03 amp/cm². The evacuation conditions are even worse with SS type electrodes. This type of electrode was studied only up to flow rates of about 0.3 ml/second·cm², as its hydraulic resistance is very high. For the investigated region the flow rate-degree of evacuation curves are much flatter than for the other electrodes.

Therefore virtually complete evacuation of an insoluble gas through the electrode pores is possible in principle even at relatively high current densities, but the quantity of electrolyte required for this is very large. For example, to remove hydrogen from the surface of a type Ts electrode (the best with respect to evacuation conditions of all the electrodes studied) at a current density of

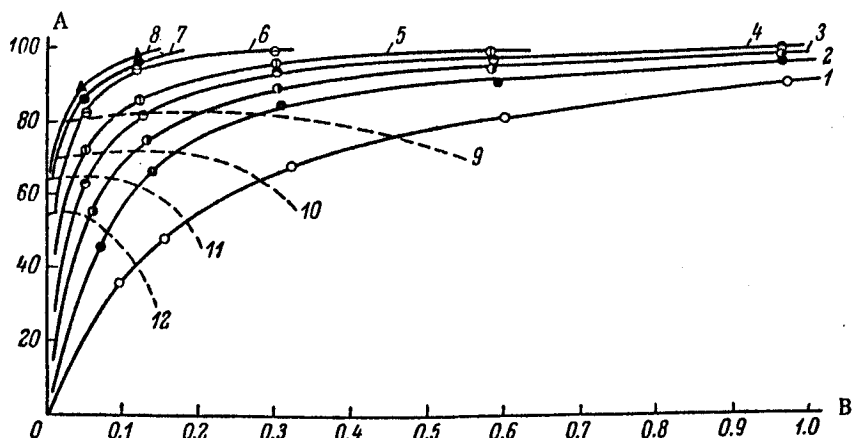


Fig. 9. Variations of the degree of evacuation of the gas with the liquid flow rate and current density for electrode type Ts: designations as in Fig. 6.

0.1 amp/cm² about 0.7 ml of electrolyte per cm² electrode area per second is required. This fact restricts the possibility of technical application of processes involving the use of porous electrodes with suction removal of gaseous products at the electrodes.

The spatial position of the electrode surface (horizontal facing upward, vertical, horizontal facing downward, etc.) should not have any significant effect on the evacuation conditions. It is clear from the pressure drop-flow rate graphs that when an aerated liquid is drawn off the pressure drop required to produce a given flow rate is greater by 10-40 mm Hg than that required for a pure liquid. This excess pressure drop is required for removal of the gas bubbles. The force acting on a bubble in a pore is approximately equal to the pressure drop multiplied by the cross-sectional area of the bubble. The force of hydrostatic upthrust is proportional to the bubble volume. For a bubble 1 mm in diameter the first of these forces is roughly two orders of magnitude greater than the second, and even greater than this for smaller bubbles. It follows that the role of hydrostatic forces is small in this case.

If the gas liberated at the electrode is soluble in the electrolyte, it is removed in two ways from the active electrode surface — by dissolution and by entrainment of the bubbles in the liquid stream. The amount of liquid required for evacuation of the gas should be correspondingly less. The influence of gas solubility on the conditions of its removal by suction can be determined, with some degree of approximation, from data on evacuation of an insoluble gas.

The amount W_d of gas carried away in the dissolved state by the electrolyte may be assumed proportional to the flow rate v and the solubility C of the gas:

$$W_d = v \cdot C. \quad (1)$$

The total quantity of gas liberated at the electrode in unit time at current density D is:

$$W = \frac{M \cdot D}{n \cdot F}, \quad (2)$$

where M is the molecular weight.

The quantity of gas remaining undissolved is therefore

$$W_r = W - W_d = \frac{M \cdot D}{n \cdot F} - v \cdot C. \quad (3)$$

Or, as a percentage of the total quantity:

$$\frac{W_r}{W} = \left(1 - \frac{v \cdot C \cdot n \cdot F}{M \cdot D}\right) \cdot 100. \quad (4)$$

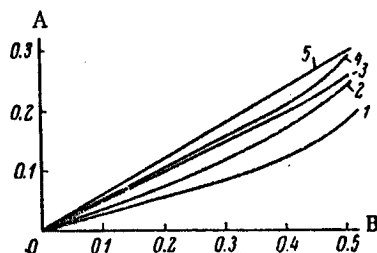


Fig. 10. Variation of the electrolyte flow rate with current density when the solubility of chlorine in the electrolyte is 0.5 g/liter: A) electrolyte flow rate (ml/cm²·second); B) current density (amp/cm²); electrodes: 1) Ts; 2) ChEZ-40; 3) PT; 4) ChEZ-30; 5) SS.

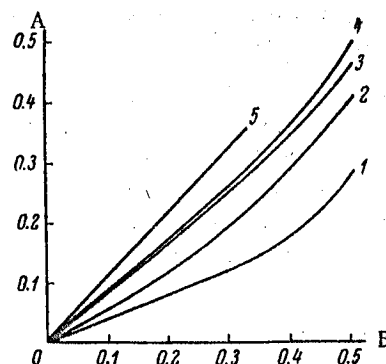


Fig. 11. Variation of the electrolyte flow rate with current density when the solubility of chlorine in the electrolyte is 0.25 g/liter: designations as in Fig. 10.

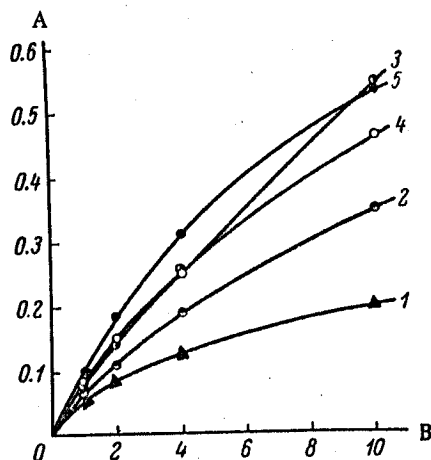


Fig. 12. Variation of flow rate with the solubility of the evacuated gas at current density of 0.3 amp/cm²: A) electrolyte flow rate (ml/cm²·second); B) (solubility)⁻¹ (in liters of solution per g chlorine); curve numbers as in Fig. 10.

If this expression is plotted in flow rate-degree of evacuation coordinates, a sloping line is obtained which runs from the point $y = 100\%$, $x = 0$ to its intersection with the abscissa axis at a point corresponding to dissolution of all the gas liberated at the electrode.

Consider a concrete example. Suppose that chlorine ($M = 71$, $n = 2$) is liberated at the electrode. Its solubility is taken as 0.5 g/liter ($C = 0.5 \cdot 10^{-3}$ g/ml). Then at current density 0.5 amp/cm² equation (4) is represented by the line $\lambda - \lambda$ (Fig. 7). The point of intersection of this line with the evacuation line for the same current density (ϵ) evidently corresponds to complete removal of chlorine from the electrode surface. In this case 63% of the chlorine is removed by dissolution and 37% by entrainment of bubbles in the liquid stream.

Points of complete evacuation for other current densities and solubilities were determined similarly. In Fig. 6-9 the geometrical positions of these points are represented by dash lines, which we shall term, for brevity, lines of complete evacuation. Lines of complete evacuation are drawn for the following chlorine solubilities (in g/liter): 0.1, 0.25, 0.5 and 1.

The position of the lines of complete evacuation on the graph gives a direct indication of the relative proportions of chlorine removed by dissolution and mechanical entrainment respectively under given conditions.

It is evident from the graphs that evacuation conditions are much more favorable for soluble than insoluble gases. For example, with an electrode type Ts at current density 0.1 amp/cm² removal of an insoluble gas required an electrolyte velocity of about 0.7 cm/sec. If the solubility of the gas (chlorine) is 1 g/liter, a velocity of about 1/30 of this, approximately 0.03 cm/second, is sufficient for complete evacuation. The fraction of chlorine removed by dissolution is then only about 45%. Gases of high enough solubility can be removed completely even at very high current densities.

The evacuation conditions are somewhat worse with electrodes of other types, but the difference between them is less pronounced than it is in the removal of an insoluble gas. This is illustrated more clearly by the curves in Fig. 10 and 11, which represent the flow rate at which complete evacuation is obtained, as a function of current density. It is seen that this function is approximately linear, at least for current densities up to 0.4 amp/cm². For the least permeable of the electrodes studied (type SS) the flow rate necessary for complete

evacuation is approximately double the rate for specimen Ts, which shows the best evacuation conditions. The electrodes of the other types are intermediate in properties between the Ts and SS types.

The ratio between the amounts of gas in the dissolved state and in bubble form differs for different electrodes. Thus, when the solubility is 0.5 g/liter and the current density is 0.1 amp/cm² this ratio is approximately 1:2 for electrode type Ts. This ratio increases with increasing solubility and current density. The same rule holds for other electrodes apart from SS, but the ratio between the amounts of dissolved and mechanically entrained gas is somewhat greater, from 1:1 to 2:1. For the SS electrode this ratio reaches 8:1 under the same conditions. In this last case up to 80-90% of the gas is removed by dissolution.

The electrolyte flow rate necessary for complete evacuation of the gas rises rapidly with decreasing solubility of the gas. Figure 12 represents the variation of the required flow rate with the solubility of the gas (chlorine), reciprocal solubility being taken along the abscissa axis. The curves for the different electrodes are approximately of the same general form.

SUMMARY

1. Total evacuation of an insoluble gas through a porous electrode is possible only at very high liquid flow rates and relatively low current densities, i.e., with a very low degree of utilization of the electrolyte.
2. The conditions for evacuation of a soluble gas are considerably more favorable. In the case of chlorine, when its solubility in the electrolyte is 1 g/liter and at a current density of 0.1 amp/cm² a liquid velocity of about 0.03 cm/second is sufficient; this is about 1/30 of the velocity required for removal of an insoluble gas at the same current density.
3. The best results are obtained with electrodes of homogeneous structure and a low degree of pore convolution (type Ts).

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