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Doctoral Thesis – Abstract

ELECTROCHEMICAL REACTORS WITH ASYMMETRICAL CURRENT DENSITIES

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Key words:
Uncompartmentated electrochemical reactor, asymmetrical current densities, electrochemical active surface, constructive parameters, operative parameters

Chapter 1. Introduction

The modern electrochemical technology of our days is in fact nothing more than the electrochemical reactors' theory. This theory combines a few scientific and engineering fields such as: electrochemistry, physical chemistry, hydrodynamics, the engineering of mass and heat transport phenomena, mathematical modelling and optimisation, chemical kinetics and so on.

Even though the principles that are at the basis of the electrochemical systems functioning are well known and can be used in mathematical modelling, DIN CAUYA of insufficient development of the electrochemical reactors' theory, many times we found ourselves unable to optimise the technological processes by mathematical means.

Taking into account the fact that the electrochemical industry uses more than 6% of the world's electric consumption and that as a result of the electrochemical approach of organic technologies, this industry continues to develop itself, it is obvious that any electrochemical technology must be optimised before it gets to be used in the productive process (because of cost reasons).

Chapter 2. Performance indicators of the electrochemical reactors

The most important performance criteria for an electrochemical reactor are:

- Current ratio (faradic), r_F
- Specific electrical energy consumption, W_j
- Energetic ratio, r_W
- Electrical potential ratio, r_U
- Optimal current density, i_{opt}

Chapter 3. Compartmentated reactors. Uncompartmetated reactors

Beside the important contribution of the separator at the potential drop, the separator raises significant constructive, financial and operating problems. The separator complicates the reactor's design and is often frail, expensive, and sensitive to impurities and it also clogs easily.

The use of the separator is imposed by the possibility of reverse reaction to the counter electrode or by interaction with the reaction media and/or the counter electrode product of the useful product. In any of the above mentioned situations, both the conversion rate as well as the current ratio registers dramatic drops.

Still, considering that the useful product is the oxidised specie (the most frequent situation in the electrochemical practice), its cathode reduction can be diminished by choosing a high cathode current density that favourites the obtaining of a different compound, for example of hydrogen.

$$r_W = \frac{U_e}{U_e + h_a + |h_c| + \Delta U_i + \Delta U_e} \cdot \left[1 - \frac{[O]}{[R]} \cdot \frac{S_c}{S_a} \cdot \frac{D_O / (1 - t_O) d_c}{D_R / (1 - t_R) d_a} \right]$$

Starting from the above formula, one could establish the main possibilities (P) and limits (L) in improving the energetic ratio of the uncompartmentated electrochemical reactors.

- P1: the reduction of the electrode over – potential by using electrocathalitical electrode material. L1: such materials tend to be expensive
- P2: the reduction of the ionic potential drop by increasing the reactants concentration. L2: the solubility limits cannot be surpassed
- P3: the reduction of the ionic potential drop by increasing the working temperature. L3: the increasing of temperature leads to an increase of energetic consumption and can cause decomposing of the product.
- P4: using an anodic current density lower than i_{LA}. L4: low current density implies low productivity
- P5: the reduction of the O/R ratio. L5: in the end O is high and R tends to 0.
- P6: the reduction of the anodic limit layer by relative electrode – electrolyte movement. L6: this movement is difficult to be generated in practice due to the very short inter-electrode distances.
- P7: the reduction of the ionic potential drop by reducing the inter – electrode distance. L7: the surfaces ratio depends upon the inter – electrode distance.
- P8: the reduction of the electronic potential drop by ensuring good electrical connections. L8: by doing so, the price of the reactor increases.
- P9: the reduction of the S_c/S_a ratio. L9: there are problems concerning the uniform primary current distribution.

Chapter 4. The reactors with asymmetrical current densities' theory

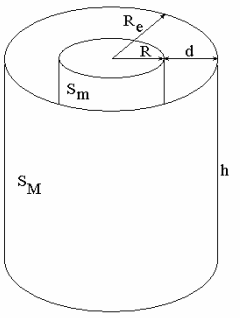
A very important ratio in describing a reactor's performances (regarding its productivity) is the volume current density:

$$i_V = \frac{I}{V_{cel}} = \frac{i_m S_m}{V_{cel}} = \frac{i_M S_M}{V_{cel}}$$

Where:
V_{cel} – the electrolysis cell volume
I – the current
i_m – the current density on the small surface electrode
i_M- the current density on the large surface electrode
S_m – the surface of the small electrode
S_M – the surface of the large electrode

Moreover, it is important to ensure uniform current distribution and this implies the use of equal, plane, parallel electrodes. But the uncompartmentated reactors function on the basis of unequal surface electrodes and therefore the above mentioned practical solution cannot be applied.

A different way of solving this problem is the usage of a cylindrical, concentric reactor.



This type of reactor is bulky and needs lots of material. The radius R of the cathode cannot be too small as the reactor must have a reasonable volume. In the same time, in order to ensure a S_M/ S_m ratio, a bigger inter – electrode distance d is needed, and this leads to increased energy consumption.

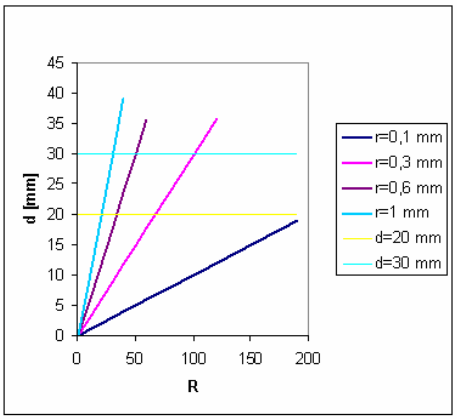
Taking into account the above, we have offered the solution of a cellular reactor of honeycomb type similar to multiple hexagonal cells connected together. By doing so, we eliminate the disadvantages of the cylindrical concentric reactor and obtain the following advantages:

- The primary current density is almost ideal
- The anodic surface is large enough
- For the same surfaces ratio, the volume productivity of the reactor increases and the specific energy consumption decreases
- The honeycomb structure is rigid and allows the use of thinner metal sheets and therefore generates a reduction of the metal consumption.

We have established the formula for obtaining the constructive parameters of the small surface electrode:

$$d = r(R-1)$$

Where:
r- The radius of the small surface electrode
d- Interelectrode distance
R – The surfaces ratio
This formula applies for R>1.
For r taking values between 0.01 and 1 mm, the following chart is valid:



By accepting an inter – electrode distance of maximum 30 mm, the small surface electrode's radius as function of surfaces can be found in the chart under the corresponding horizontal line.

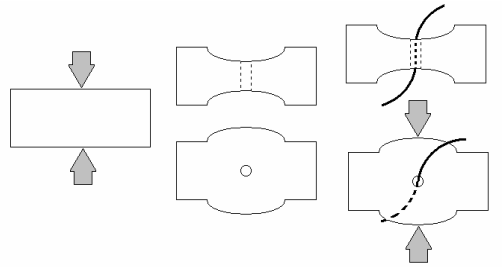
Because the inter – electrode distance cannot be bigger than 20 mm (in order not to increase too much the potential drop), for a S_M / S_m ratio of 200 (ratio imposed by the functioning of a reactor used in the oxidation of the kalium ferrocyanide), the diameter of the cathode d is of maximum 0.1 mm.

We have proposed a new way of manufacturing in practice the small surface electrode, by respecting the following principles connected to this procedure:

- The existence of an exterior wire (namely the electrode itself) that ensures the electrochemical active surface
- The current conduction is ensured by a thread that is isolated from the reaction media and is thick enough and made of such a material as the potential drop through the electrode to be neglectable.
- Because of the small diameter of the electrode itself and the big heights of industrial reactors, multiple contacts of the exterior wire are needed.

As a support, we shall use an isolated conductor made of a material that has good electrical conducting properties, and as an electrode, we shall use a wire of a material chosen in respect to that process.

The way the multiple connections is realised is presented in the chart below:



One can observe that we eliminate the welding (hard to realise because of the very small diameter) and the contact is done by pressing. Moreover:

- The electrochemical active surface is ensured at the necessary dimension (no matter how small)
- The potential drop in the electrode is eliminated
- The manufacturing of reactors at the necessary height is permitted

- The constructive problems that appear at other electrodes are eliminated.

The functioning principle of the electrochemical reactors with asymmetric current densities involves the making of an active surface of the electrode where the useful reaction, much bigger than the active surface of the counter – electrode, takes place.

This purpose can be achieved in two different ways:

- By choosing for making the big surface electrode a material that has an electrochemical active surface bigger than its geometrical surface.
- By a special design of the electrodes block.

Even though both the screen and the perforated plates leave the impression of having an electrochemical active surface bigger than their geometric surfaces, many times, in practice this theory does not apply. Because they are both usually used in filtration or sorting procedures, their classification according to parameters that do not show the ratio between the geometric and real surface, considered electrochemical active, has become imperative.

By using these screens and perforated plates in making the electrodes, it became important to interconnect the constructive parameters of these materials (thickness of the screen's wires, perforation dimensions, number of perforations on surface unity) with the parameters that are relevant to using screens and perforated plates in electrochemistry (electrochemical active surface, relative weight).

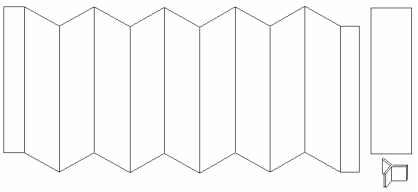
The way of calculating the constructive parameters of the big surface electrode had been established. The formulas for obtaining the constructive parameters of this electrode were elaborated. The screens, the perforated plates with a symmetrical factor of 4 and those with a symmetry factor of 6 were studied.

The use of screens in making big surface electrodes has the following constructive disadvantages:

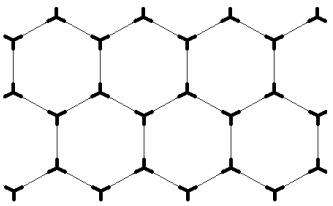
- Ensures a maximum ratio (theoretical one) between the electrochemical active surface and the apparent surface of only 1.59
- Because they are made by knitting threads that are very thin (sensitive to erosion/ corrosion) and the inter – electrode distance is small, there is the risk of short-circuits.
- The small mechanical resistance (lack of rigidity) of the screens makes it difficult to manufacture electrodes at industrial dimensions.

The use of perforated plates eliminates all of these disadvantages but keeps all of the advantages. Therefore it is advisable to use perforated plates in making the big surface electrode.

According to the above aspects we have proposed an original constructive way for the big surface electrode block. The components and the assembling way are presented below:

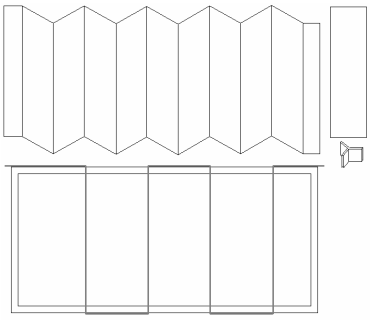


The components of the big surface electrode block.

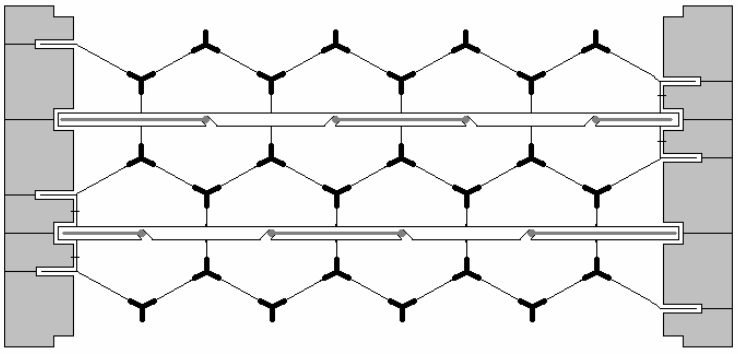


The assembled big surface electrode block.

According to the aspects presented already, we have developed an original constructive solution for an electrochemical reactor with asymmetrical current densities.



The components of the electrode block.



The way for assembling the electrode block

The real number of individual cells, their distribution on rows, the height of the electrode block, are established by calculus in respect to the electrochemical process taken into account.

The contacts between the electrodes are made on the upper side, above the fixing blocks. The electrode block is placed into a parallelepiped cell and is supported in the inferior part of the fixing blocks.

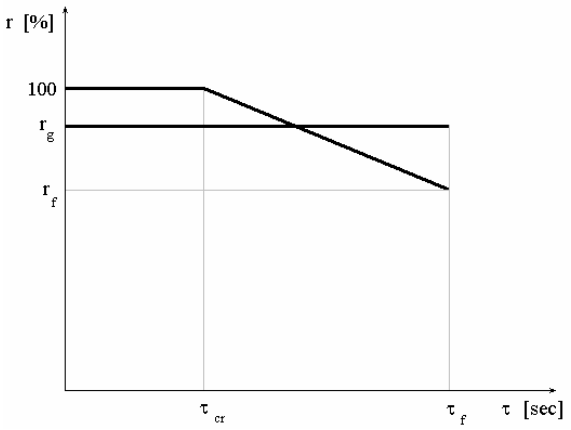
This constructive method has all the advantages of a honeycomb reactor. Moreover, in order to get into a cell from the electrode block, there is no need to disassemble all of the block: the fixing blocks allow the individual disassembling of the cell rows.

Chapter 5. Practical applications of the reactors with asymmetrical current densities' theory

By using as an example the electrochemical obtaining of the kalium ferricyanide we have offered an original approach to the connecting of the working current density to the global current ratio, to the final instantaneous current ratio, to the initial/ final concentration of ferrocyanide, to the final concentration of ferricyanide.

The limiting anodic current density in the first part of the process bigger than the working anodic current density. By decreasing the ferrocyanide concentration, the limiting anodic current density decreases and goes under the value of the working anodic density.

The critical moment t_{cr} is the moment when the limiting anodic current density is equal to the working anodic current density. The final moment t_f is the moment when the process is interrupted. The final concentrations of ferrocyanide and ferricyanide are obtained at this moment.

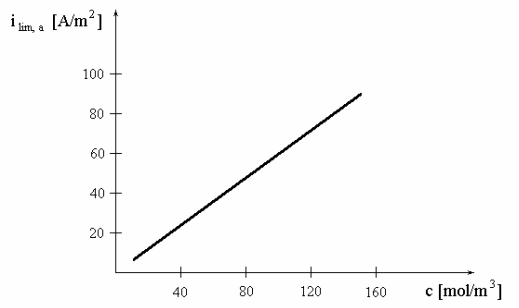


$$\frac{(c_i - c_f)* r_g}{(c_i - c_{cr})*100} = \frac{100 - r_f}{2 * r_g - 100 - r_f}$$

Imposing the following:

- Global current ratio 90%
- The final instantaneous current ratio is 65%
- The initial concentration of ferrocyanide is 160 mol/m^3
- The final concentration of ferrocyanide is of 15 mol/m^3
- The conversion rate is therefore higher than 90%

one shall obtain c_{cr} = 104 mol/m^3.



By tracing the anodic polarisation curves for different ferrocyanide concentrations we had obtained the above presented graph.

By using the c_{cr} value determined as well as the graph one can obtain a working anodic density of 60 A/m^2.

From the instantaneous current ratio formula (chapter 3), for the final moment, considering that K1=K2 and imposing that the final target concentration of the ferricyanide is of 985mol/m^3 we obtain a ratio of the electrodes surfaces of 192 (aprox. 200).

So, by conducting the process at an anodic current density of 60A/m^2, starting from a ferrocyanide concentration of 160mol/m^3, we ensure a global ratio of 90% and a degree of depletion of the electrolyte solution above 90%.

According to the original formulas, the constructive parameters of the electrode block were determined and the reactor was used to electro-oxidise the kalium ferrocyanide into ferricyanide.

There were made calculus and experiments in order to electro- oxidise the kalium manganate into kalium permanganate.

The experiments have proven the correctitude of the calculus method for working anodic current density and of the formulae for constructive parameter determination. The great advantage of this method is that is simplifies the very complicated experimental activity to the tracing of the polarisation curves for different concentrations of electrolyte solution.

Chapter 6. General conclusions

1. The main ways of improving the energetic ratio were established as well as their limits.
2. We have concluded that the development of a rentable reversible electrochemical process in uncompartmentated reactors with asymmetrical current densities is possible.
3. We have studied the primary distribution of current in different types of electrochemical uncompartmentated reactors. We have concluded that the optimal constructive way of the reactor must ensure a primary current distribution as uniform as possible.
4. The highest volume current distribution is offered by the honeycomb reactor (cellular reactor) with hexagon cells.
5. This kind of reactor (honeycomb reactor) with hexagon cells offers a uniform primary current distribution that is close to the optimum.
6. We have studied the small surface electrode. We have offered original formulae and correlation charts between the constructive parameters of the small surface electrode, the inter – electrode distance, the electrode surfaces ratio, the electrode material resistivity, the height of the reactor, the potential drop through the electrode. By imposing some parameters, according to the formulae and the charts, we can determine the other parameters.
7. We have offered an original constructive method for the small surface electrode.
8. We have studied the big surface electrode. We have shown that in manufacturing such an electrode the screens and perforated plates are appropriate.
9. For the screens we have established some original formulae and we have drawn up correlation charts between the thread diameters that the screen is made of, the size of the holes of the screen, the geometrical size of the electrode, the electrochemical active surface of the electrode. By imposing some of the parameters, on the basis of formulae and charts, some of the other parameters can be determined.

10. We have studied in parallel (we have compared) the perforated plates with symmetry factor 4 with those of symmetry factor 6. for both we have established original formulas and drown up correlation charts between the number of perforations per surface unity, the radius of the perforation, the thickness of the plate, the geometrical surface of the electrode, the electrochemical active surface of the electrode, the ratio between these surfaces. We have defined and correlated the other parameters with the perforation factor and the perforation ratio. By imposing some of the parameters, on the basis of the formulas and charts, the other parameters can be determined as well.
11. We have offered an original constructive method for the big surface electrode.
12. We have established an original correlation method between the technological parameters of an electrochemical process. By using this method, drawing the graph for the limited current density in respect to the concentration of the electrolyte solution and by imposing the global current ratio, the final instantaneous current ratio, the initial and final concentration of the reactant and the final concentration of the reaction product we were able to determine the optimum working current density as well as the ratio of the electrochemical active surfaces. By also imposing the inter – electrode distance one can determine the constructive dimensions of the electrode block.
13. The advantages of this method consist in the simplicity and significant reduction of the lab work, only being necessary the drawing of the polarisation curves for different concentrations of the electrolyte concentration.
14. On the basis of the original formulas determined in this thesis, we have determined the technological and constructive parameters of the reactor with asymmetrical current densities in order to obtain through electrochemical means the kalium ferricyanide and the kalium permanganate.
15. The experiment successfully proves the validity of the method and of the formulas for obtaining the constructive parameters of an electrochemical reactor with asymmetrical current densities as well as for determining the operational parameters of the reactor. Moreover, the experiment proves the fiability of the original constructive methods of the anode, cathode and electrode block.