総　説

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Electrochemical Engineering a Science of Its Own

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개　　요

역사적으로 볼 때, 지난 20년 동안 전기화학공학은 그 자체 하나의 기술과학으로 발전하였다. 최적화와 경제성 산출의 원리는 대안 또는 최적방법 등에 대한 정량적인 분석을 하기 위하여 물질적인 것들을 공통사용수단인 돈으로 환원시키는 것을 수반한다. 맥동전류에 의한 금속도금기술의 개발이 연구되어지고 있다.

전극설계의 발달결과 전기화학공정은 폐수처리와 같은 실제 이용에도 사용할 수 있는 매우 경제적인 좋은 공정이 되어졌다.

ABSTRACT

A glance at the historical development shows that electrochemical engineering became a technical science of its own through the last decades. Principles of optimization and economic evaluation are involved reducing the physical laws to a common denominator, money, in order to perform a quantitative analysis of alternative and optimal routes. Scientific investigations open a window on future techniques of metalplating by pulsating current. Developments in cell design made electrochemical processing quite attractive and competitive to conventional routes, e.g. for waste water treatment.

1. A Glance at the Historical Development

The first applications of electrochemistry might be quite old as a 2000 years old assembly found near Baghdad is believed to have been the first battery.[1] However, the recorded history starts in 1791 with the well known experiment of Galvani. About four years after the discover of the Cu/Zn element(Daniell, 1836) the first fuel cell has already been built by Grove. We remember, it was only recently that fuel cells started to be used: in the Gemini and Apollo Program, NASA.[2] In the middle of the last century a large number of reports on more or less successful plating of metals were published in Europe.

About 1880 the time became ripe for large scale electrolysis with the invention of the dynamo machine. In 1886 the famous patent
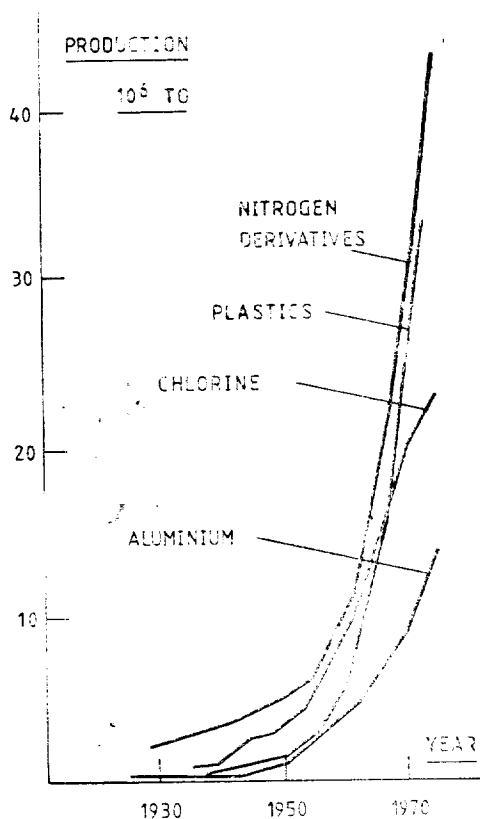
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Fig. 1. World production per year of some important chemical industries(from[1])

of Hall and Héroult were applied(aluminium production). The turn of the century marked for applied electrochemistry the transition from the artisan to the industrial stage. Industrial copper refining, aluminium and chlorine production date back to this time.

For many years teams of industrial chemists and mechanical engineers were the backbone for the expanding industry. In the middle of this century the production rates of many chemical substances have reached enormous figures, the growth has been exponential for many years(*Fig. 1*). Such procution rates can be only achieved in a very rational way. Optimization from an economic and ecological viewpoint is essential. The

problems arising in such systems can be handled only by a professional specially trained for this purpose: the chemical engineer who is neither a chemist nor a mechanical engineer.[3] It was shortly before World War II that this new profession came in sight, in America and England.

The situation in the electrochemical industry was quite similar. In order to achieve optimal solutions to modern problems a specialized electrochemical engineer was needed It is reasonable to regard electrochemical engineering as part of chemical engineering. Indeed, specialization is usually achieved through appropriate elective courses in connection with the regular curriculum in chemical engineering or by a postgraduate study following such a curriculum.

2. Optimization and Economic Evaluations

The electrochemical engineer is expected to make a calculation in order to optimize the current density(cd) at which an electrolytic process has to be operated. Most likely he will balance the energy consumption against the investment.[4,5] At increasing cd the energy cost becomes larger and the investment cost smaller. There are thus two effects acting in opposite direction and the total cost goes through a minimum at a certain, optimum cd(*Fig. 2*).

Assuming linear relationships,

energy cost: $K_E = b \cdot E \cdot A \cdot i$
investment: $K_I = a \cdot A \cdot t$
cell voltage: $E = E_o + Ri$

with b: energy price($/kwh), A: electrode area needed to make a certain amount of product(m^2), i: current density(A/m^2), a: specific investment cost($/m^2h$) and R: ohmic
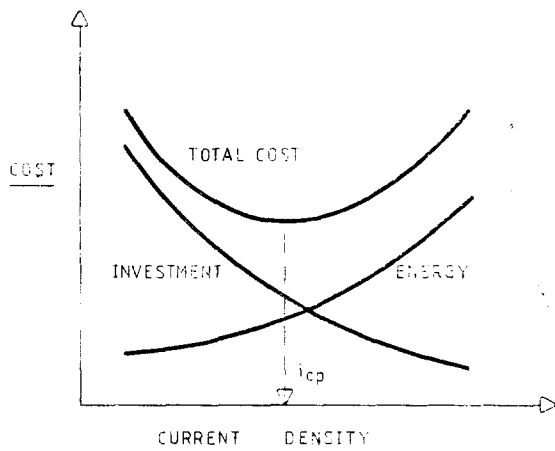
Fig. 2. Principle of optimization of current density

Fig. 3. Optimum current density vs. energy price for copper refining

resistance per electrode area(m²),
assuming also that the current efficiency is independent on the cd, one obtains a simple relationship for the optimum current density

$$i_{op} = \sqrt{a/bR}$$

The specific investment cost consists mainly of two parts: a_1 is given by the metal inventory in the plant which is not consumed, a_2 is given by the invested capital which has to be amortized[6]. a_2 can be calculate by:

$$a_2 = \frac{P \cdot S^n \cdot (S - 1)}{8760 \cdot (S^n - 1)}$$

where P: invested capital per m² electrode area, $S - 1$: rate of interest per year and n: years for amortization.

Fig. 3 shows the optimum cd as a function of the energy price for some values of a. The calculation refer to the copper refining process. As one recognizes, the optimum cd is always much higher than the conventional operating cd for this process. It is therefore of great interest to discuss the feasibility of operating at i_{op}. First of all, it must be kept in mind that one can not operate above the limiting cd which lies at about 650 to
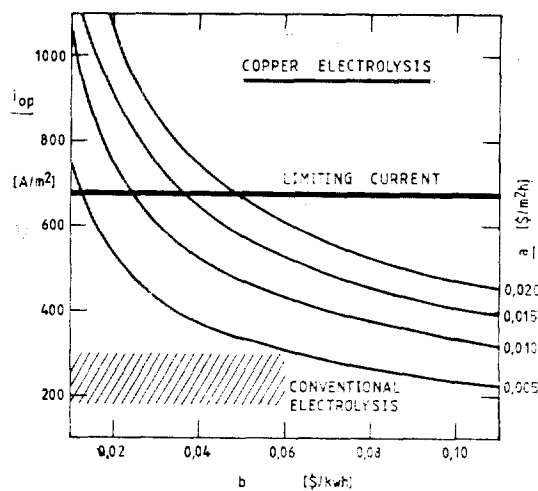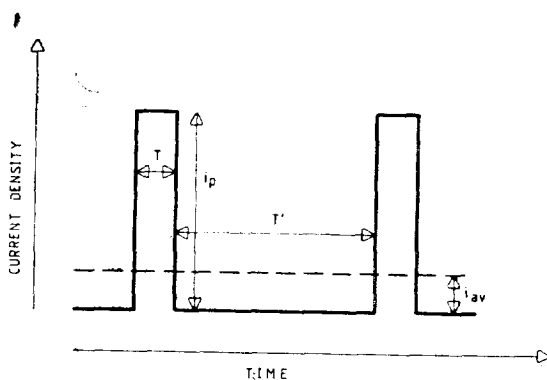

Fig. 4. Electrolysis with galvanostatic pulses (schematic)

700A/m²(natural convection) because the deposited metal becomes then powdery. It is not even possible to approach the limiting cd because already below the deposit gets undesired properties. However, from the economical viewpoint it seems to be worthwhile and commendable to envisage some modifications of the traditional process, (e.g. to consider stirred systems or the use of interrupted current. For a detailed discussion refer to[6]).

3. Metal Plating by Pluse Electrolysis

Modern electronics allow to apply instead of dc short pulses of current followed by an off-time between succeeding pulses(*Fig. 4*). The current density i_p during a single pulse may be as high as several 100A/cm^2 and the length T of a pulse as short as microseconds or less. The three parameters, i_p, T and offtime T', can be varied in a wide range. This allows one to create a variety of mass transfer situations, electrocrystallization conditions and adsorption/desorption phenomena during both, the pulse and the off-time. In addition to an improvement of the properties of the depositions the investigations made so far have also been aimed at saving energy and deposition time.[7,8,9]

In the case of a series of galvanostatic pulses the average cd is given by:

$$i_{cv} = i_p T/(T + T')$$

i_{av} can not exceed the values corresponding to conventional dc electrolysis, even so the cd during a pulse may be 10,000 times higher than i_{av}.

Regarding mass transfer, one distinguish two diffusion layers in pulse electrolysis: One near the electrode which pulsates and an other further outside which is essentially stationary. Applying short pulses of about 1μs one may realize a very thin inner diffusion layer of about 0.02μm. As a matter of fact the thickness of this layer is quite important regarding the properties of a metal deposition.[9] It was found that by pulse plating smooth deposits could be obtained under conditions which would not give such a result applying dc. This was found e.g. for copper, silver and cadmium.[7,8,10]

The cathode potential during a high cd pulse is much more negative than in the dc case, thus favouring the formation of nucleation centers. The initial stage of a deposit can be formed only by some random nucleation at a relatively high overpotential. Investigating the morphology of cadmiuim deposits it was found that an increase of pulse cd decreases the grain size of the deposited metal.[10] This might be explained by the fact that the activation overpotential becomes larger with increasing cd so that a larger free energy is available for the formation of new nuclei, resulting in a less coarse deposit (*Fig. 5*).

Finally, it has to be mentioned that very interesting results might be expected applying pulse electrolysis on the codeposition of two metals. In this technique it is possible to shift the relative parameters of the two processes and thus influence the composition and properties of an alloy.

However, pulse plating is still in its beginnings and its scientific investigation occupies researchers in many laboratories.
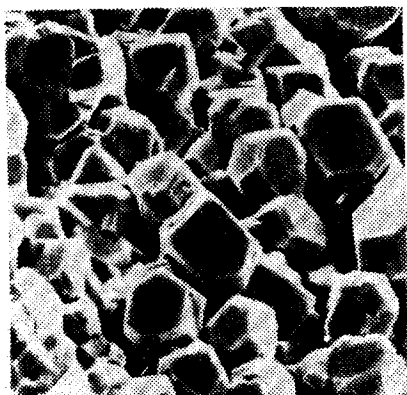
4. Mass Transport in Electrolytic Cells

Mass transport, a classical field of chemical engineering, plays a special role in electrochemical engineering; in all electrolysis the active species have to be transported from the bulk to the electrodes or vice versa. The technique to investigate mass transfer by the limiting current method is well known.[11] The resulting correlatics are usually represented in a dimensionleons form comprising the Sherwood number as characteristic mass transfer quantity.

Thus, electrochemical reactors have the main disadvantage to be heterogenous: the re-

(a)

(b)

(c)

pulse current, i_p

    (a) : 10A/cm²

    (b) : 50A/cm²

    (c) : 125A/cm²

Fig. 5. Deposits of 10μm cadmium(from[10])

    (T : 0.7μs, i_{av} : 75mA/cm², 1200x)

action rates are limited by the diffusion distance for the reacting species. An improvement is therefore to be obtained by decreasing the diffusion layer thickness which can be acheived by stirring the electrolyte. In this respect, electrolytic cells with gas evolution are quite interesting systems.[12] The mass transfer enhancement by gas bubbles is considerable.[13] In some cases it might be even an attractive measure to introduce gas from outside in order to obtain higher mass transfer rates at low pumping cost.[14] Recent developments in the layout of gassing cells are reflected in a new aluminium electrolysis reactor by Alcoa.[15]

An other disadvantage of electrolytic cells is the usually small ratio of electrode area per reactor volume. A possible issue matching these problems might be the so-called 'Swiss-roll cell': high electrode area, high mass transfer rates(specially with cloth separatorstr), low pumping cost and simple construction.[16,17] The Swiss-roll cell is constructed by rolling a flexible sandwich of electrodes and separators around a central axis and placing the roll in a container(*Fig. 6*). If this cell shall be competitive with others, the electrochemical engineer is again asked to make a calculation.

The mass transfer rates for a cell packed with polypropylene cloths as separators between cathode and anode can be calculated by:

$$Sh = 0.26Re^{0.6} \cdot Sc^{1/3} \quad (1 < Re < 3000)$$

and for pumping energy consumption, the fanning friction factor by:

$$f = 75/Re + 0.175$$

Some applications of this novel cell type have already been discussed. In the field of environmental engineering the Swiss-roll cell might be used for waste water treatment.
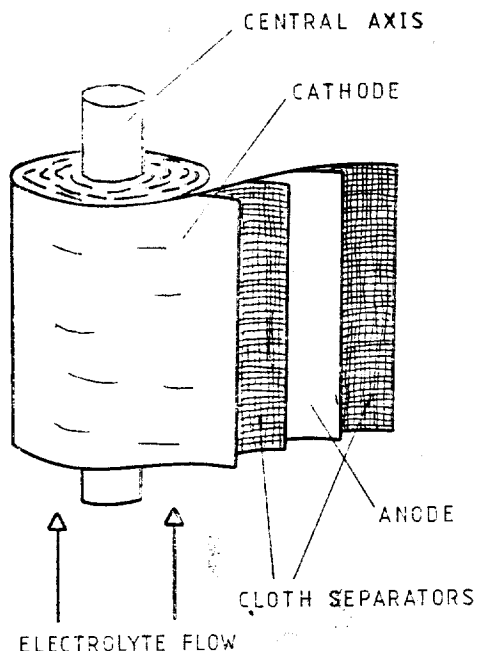
Fig. 6. The 'Swiss-roll' cell(schematic)

Experimental data from laboratory and pilot plants show that with a cell built of Ti cathodes and Ti anodes coated by RuO_2 the concentration e.g. of copper in dilute waste waters may be taken down to under 1ppm and the economical evaluation shows that the process is competitive with other waste water treatment technologies[17].

These examples show that electrochemical engineering is not simply applied electrochemistry, but can be a real science in many aspects by its own. Both the engineer and the scientist are needed in cooperation to achieve the goals of the modern electrochemical industry.

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