

HISTORICAL NOTE

A flow-through porous electrode patented 100 years ago: the Hulin process

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1. Introduction

Exactly one hundred years ago, in 1893, Paul Léon Hulin patented a process along with several electrolytic cells which employed the concept of the 'flow-through porous electrode'. As reference to this patent is never made in the literature, it is possible that, among the numerous patents taken out by Hulin, this contribution is unknown. Because of historical scientific interest, and to mark the 100th anniversary of the patent, the present communication has been prepared. English terms and meanings corresponding to the terminology used by Hulin are expressed in italics.

2. The Hulin process*2.1. Historical*

On 25 November 1893, P. L. Hulin took out a patent [1] entitled 'Procédé et appareil électrolytiques pour la séparation immédiate des produits d'électrolyse liquides ou dissous' which, in English, translates as '*Electrolytic process and equipment for the immediate separation of liquid or dissolved electrolysis products*'. (An addition to this patent was made on 23 November 1894.) This process was recommended for the industrial production of chlorine (or of chlorhydric acid) and soda by electrolysis of aqueous solutions of sodium chloride. Due to the ready availability of the cheap raw material NaCl, and because of the large industrial consumption of soda and chlorine, many inventions were made toward the end of the nineteenth century with a view to improving the industrial electrolysis of NaCl.

The rights for industrial use of the Hulin process were transferred to the Société des Soudières Electrolytiques in 1898, although they were ceded back to the inventor in 1900. Thus it seems that the process had been operated industrially for only two years.

2.2. Aim of the patent

In his patent specification Hulin wrote: '*The starting point of my process is based on the fact that the electrolysis products (the ions) are formed exclusively at the electrodes.*' Clearly, he was aware of the Faraday concept (1834) of ions. He projected the continuous extraction of these ions from the cell as soon as *they are formed*. This was in order to avoid mixing the products of electrolysis with the unreacted electrolyte, thus avoiding secondary reactions and the formation

of undesired products. Hulin may have been seeking conditions for minimum hypochlorite formation.

Thus, by accepting that the ions were formed at the electrodes exclusively, and only when a current was flowing (such a notion agreed with the Grotthus hypothesis (1805), while the Arrhenius theory (1887) considered the ionic dissociation of the solutions irrespective of any current flow), Hulin thought of extracting *the liquid layer containing the electrolytic products (the ions)* through the electrode itself.

To do that he conceived electrodes as filters. These *electrode-filters* were made of sheets of very small porous grains of specially prepared carbon. The name *porous electrode* was used by the inventor; also he used the term *electrolyfilters* to describe the cells involving these 'electrode-filters' and the term *electrolyfiltration* for the process that, according to him, associated the electrolysis (the *production of ions*) and the filtration (the *separation of ions from the electrolyte*).

Figure 1(a) shows one of the schemes in the patent. It represents a two-compartment cell with a porous separator, a solid anode and a 'cathode-filter'. This cell was designed for the continuous production of NaOH and chlorine by electrolysis of aqueous solutions of NaCl. Other cells represented in the patent involved two electrode-filters (vertical or horizontal). One of these cells is shown in Fig. 1(b). In Hulin's arrangement the 'electrode-filter' was a wall of the electrolytic vessel: one face, called 'active', because the inventor considered that the ions appeared on it, was in contact with the electrolyte; the other face, called 'inactive', served *for the discharge of the products formed on the active face and flowing through the porous medium*.

As shown in Fig. 1(a) and (b), the electrolytic flow through the electrode-filter was due to a hydrostatic pressure difference. The presence of a nonconducting and chemically inert mask along the upper part of the electrode-filter is also worth noting; this created the necessary hydrostatic pressure difference and also allowed a sufficiently uniform filtration velocity across the uncovered electrode surface. In the words of the inventor, the process was a *mechanical filtration of the electrolyte through a porous electrode*, with a filtration velocity proportional to the current. Associations of cells in filter-press systems were suggested.

3. Discussion

The Hulin 'electrode-filter' was a forerunner of

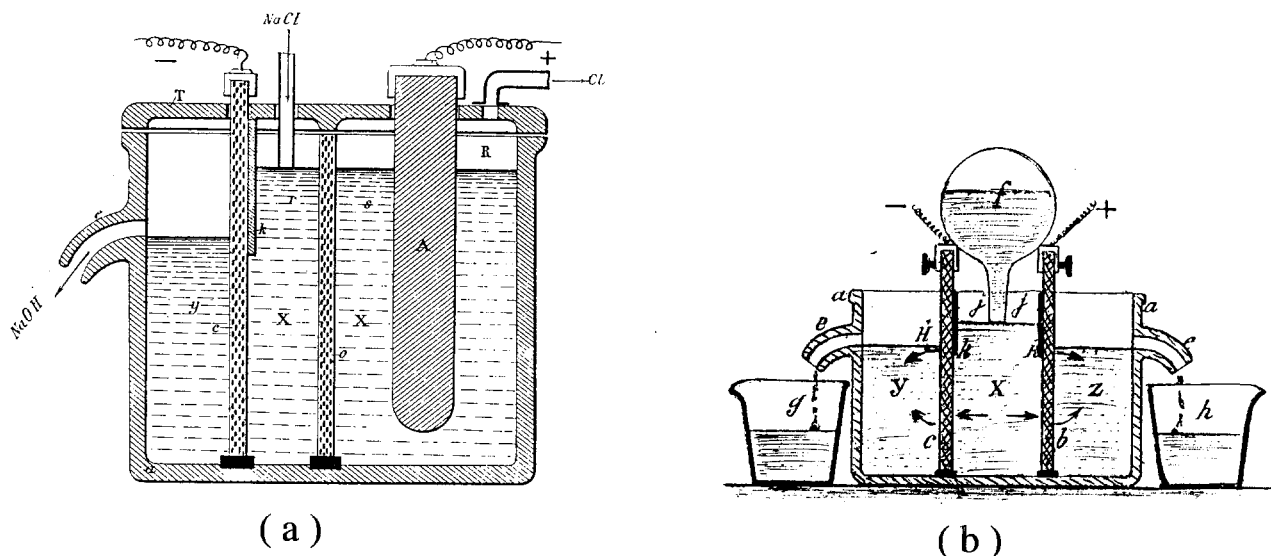


Fig. 1. Views of two cells presented in Hulin's patent.

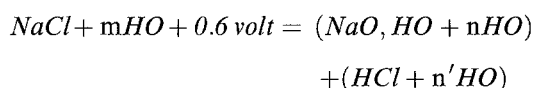
what is currently known as the 'flow-through porous electrode' or 'axial percolated porous electrode' in which the percolating velocity is in a direction parallel to the general electrical current flow. However, the term 'porous electrode' used in the patent did not have strictly the same meaning as that used today. Indeed, only the electrode boundary immediately facing the counter-electrode was considered to be electrochemically active; the rest of the porous volume was thought only to act as a filter.

The following points may be of value to a reader of the original (handwritten) patent:

- (i) The Arrhenius theory of ionic dissociation was not accepted by Hulin, and probably it was unknown to him. This concept was severely criticized, particularly by chemists, following its communication in 1887. In any case discussion of Arrhenius's work took place far from the industrial environment in which Hulin worked. Instead, Hulin relied on the theoretical ideas of the first half of the nineteenth century, namely that ions are 'formed' at the electrodes when the applied cell voltage is sufficiently high to allow the decomposition of molecules to their elements.
- (ii) The use of a porous material working both as electrode and separator, in order to extract the reaction products immediately after their formation, was innovative. In other respects, the term 'electrofiltration' is reminiscent of the term 'electro-ultrafiltration' used to describe a separation process in which ultrafiltration through a membrane is combined with the effect of an electric field.
- (iii) Various materials were advanced for the construction of the electrode-filter: porous sheets of carbon, spongy metal, agglomerated conducting structures, stacks of porous metallic sheets, etc.
- (iv) If the inventor indicated that the filtering element could be made of an electrochemically

and chemically inert material, he suggested also that the ideal electrode-filter should be one in which all the porous material would be of the same material as the electrode. This recommendation clearly showed that an empirical observation led the inventor to consider that the filtering volume could be electrochemically active. Because he ignored (or was unaware of) Arrhenius's theory of ionic dissociation, he also omitted the possibility of ionic conduction within the pores of the conducting filter and, consequently, he could not consider three-dimensional electrode behaviour.

- (v) An electrochemical engineer reading this note will appreciate that the inventor recommended to make equal the ion production and the ion discharge by acting either on the current (production rate) or on the hydrostatic pressure difference (discharge rate). The recommended proportionality between filtration velocity and current satisfied the condition necessary to maintain a constant conversion through the porous electrode.
- (vi) According to Hulin, the overall reaction for the production of sodium hydroxide and hydrochloric acid from an aqueous solution of sodium chloride continuously feeding a cell like that shown in Fig. 1(b) is



In this equation HO represents a molecule of water, where $\text{O} \equiv 8 \text{ g}$ in accordance with the Daltonian concept of atomicity and in accordance with the theory of chemical equivalents (for which H was taken as 1). These ideas were often unrecognized until the latter decades of the nineteenth century. As the measured weight of oxygen relative to hydrogen in water was 8 g, and as two elements (H

and O) were detected, the water molecule was written HO , i.e. with only two atoms. Thus, for Hulin, NaO , HO represented sodium hydroxide, $NaOH$ (with $O \equiv 16$ g according to the atomic theory which began to be fully accepted after 1860). Some attention was given to the erroneous chemical notation of Hulin 30 years after the acceptance of the atomic theory.

(vii) It is perhaps surprising that no mention was made by Hulin of hydrogen evolution at the cathode. In the author's opinion, the presence of evolved hydrogen within the pores of the electrode-filter might well have been the cause of the industrial failure of the process.

4. Conclusion

Although the Hulin process appears to have been applied for only a relatively short period, and therefore of little significance on an industrial scale, it is hoped, nevertheless, that this short account will help to rectify due credit to the originator.

References

- [1] P. L. Hulin, *French patent 234.327* (25 Nov. 1893 and 23 Nov. 1894): 'Procédés et appareil électrolytiques pour la séparation immédiate des produits d'électrolyse liquides ou dissous'.