Selective Transfer of Charged Species Along Charged Walls

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GTT

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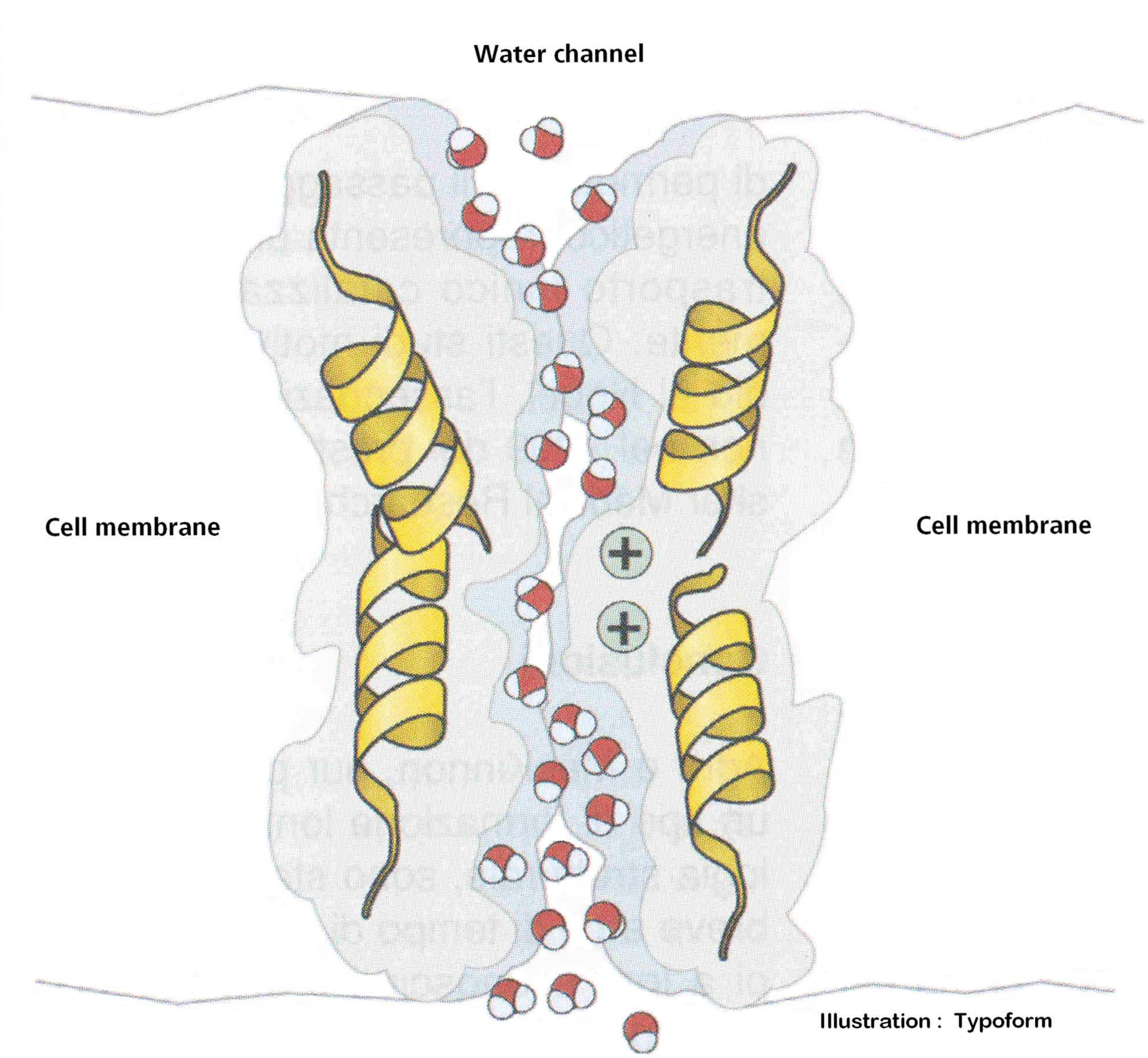

Fig. 1 - Ion Selective Channel.

The knowledge that was generated in the development work done with **electrowinning of titanium at temperatures lower than 900°C**; confirmed that the chloride system is very **complex** under that temperature.

The first main problem of the medium and low temperature titanium electrolysis is the **multivalence of titanium ions**, that is, the **simultaneous presence of divalent and trivalent** ions in the electrolyte: that is represented by the lines on the left side of the diagram of Fig. 2.

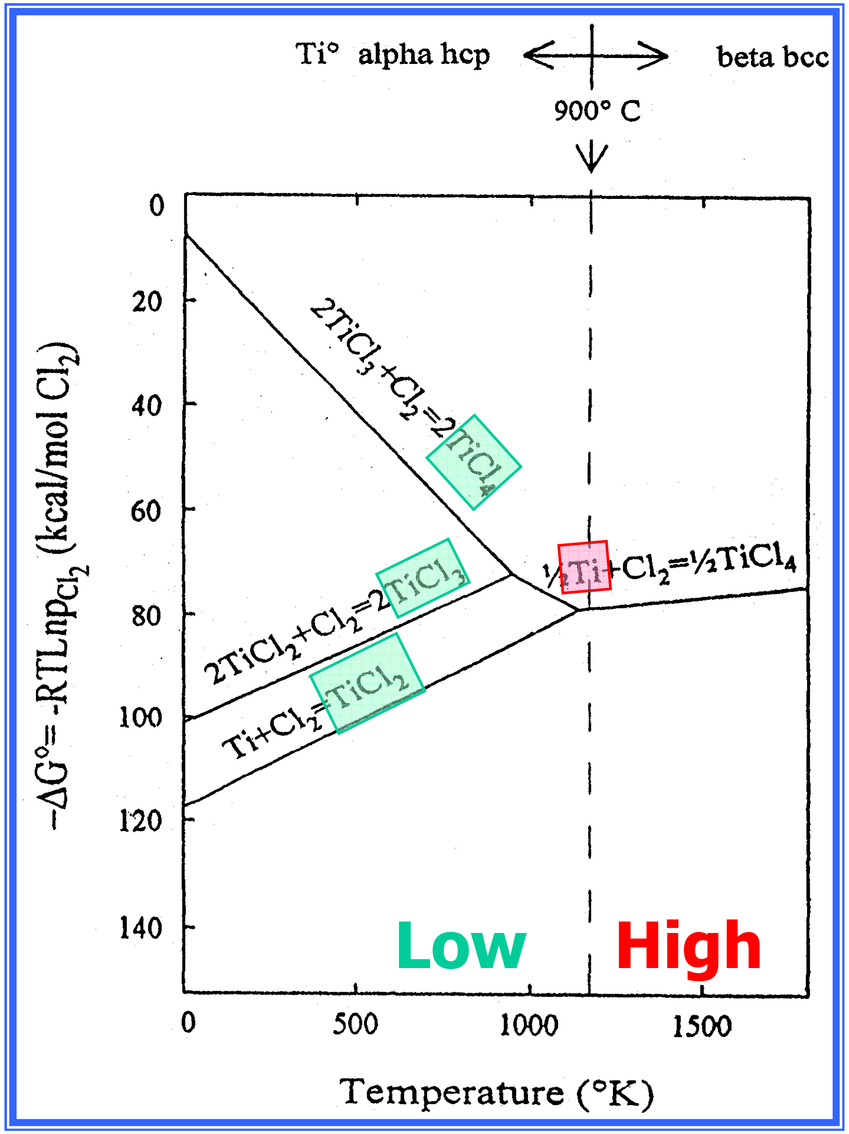

Fig. 2 – Standard free energies of formation of titanium chlorides.

This condition requires that a **separation between anolyte and catholyte** be inserted into the cell in order to avoid the **alternating** oxidation and reduction of titanium ions.

The main difficulty for fulfilling that **requirement** is that, at the same time, we have to **permit to chlorine ions to transfer from the catholyte**, where they enter with $TiCl_4$ feed, **to the anolyte**, where they are evolved as chlorine **gas** from the anode. **Oxides diaphragms** were short-lived because of Ti^{++} **attack** and oxygen ions being released into the electrolyte.

The operation of **intermediate metal electrodes** satisfies the above requirements for a separation **selective for titanium ions**.

Fig. 3 depicts a **GTT intermediate electrode/anode assembly** which is composed of the central graphite anodes with, at **each side**, an intermediate electrode (called TEB).

The TEB **maintains** the **separation** between anolyte and catholyte, by using the **"distal panel" deposition-dissolution mechanism.**

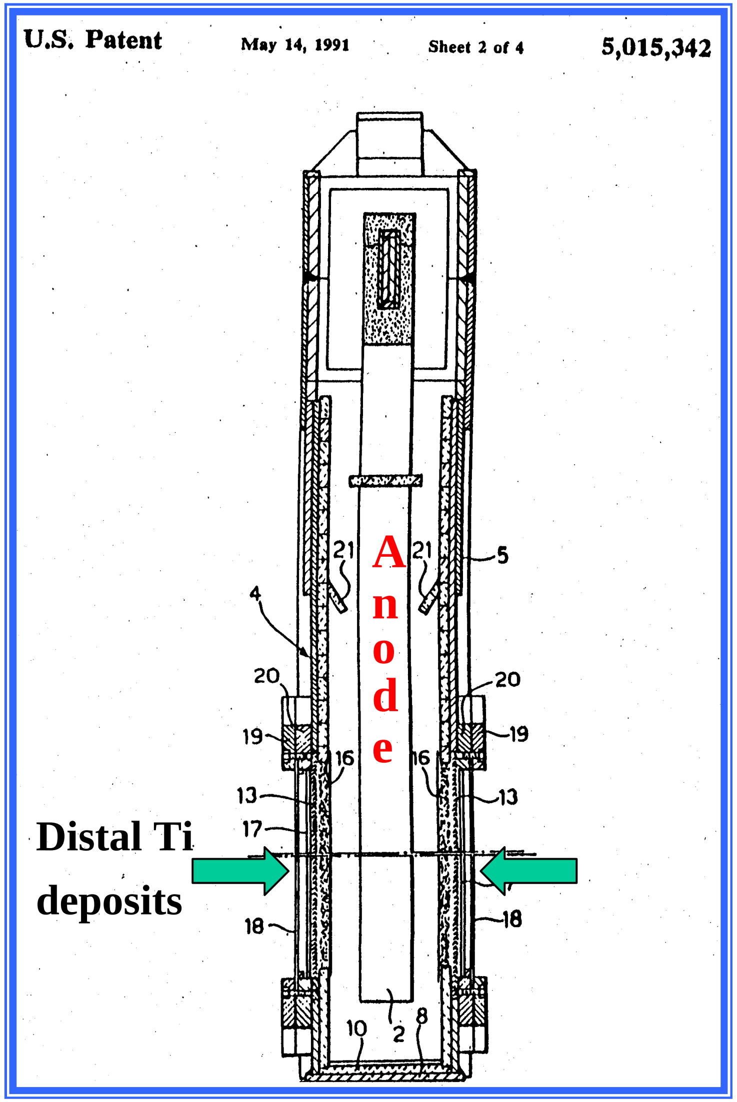

Fig. 3 – GTT Intermediate Electrode and Anode assembly.

Fig. 4 is illustrated the **inner structure** of the GTT intermediate electrode, with the network of iron **wires of decreasing gage** set to **support** the **titanium deposition of nanometric whiskers** which constitute what we call the “**Distal Panel**”.

The distal titanium panel is **grown on the catholyte side,** that is**, on the back side** of the GTT intermediate electrode with respect to the **anodes.**

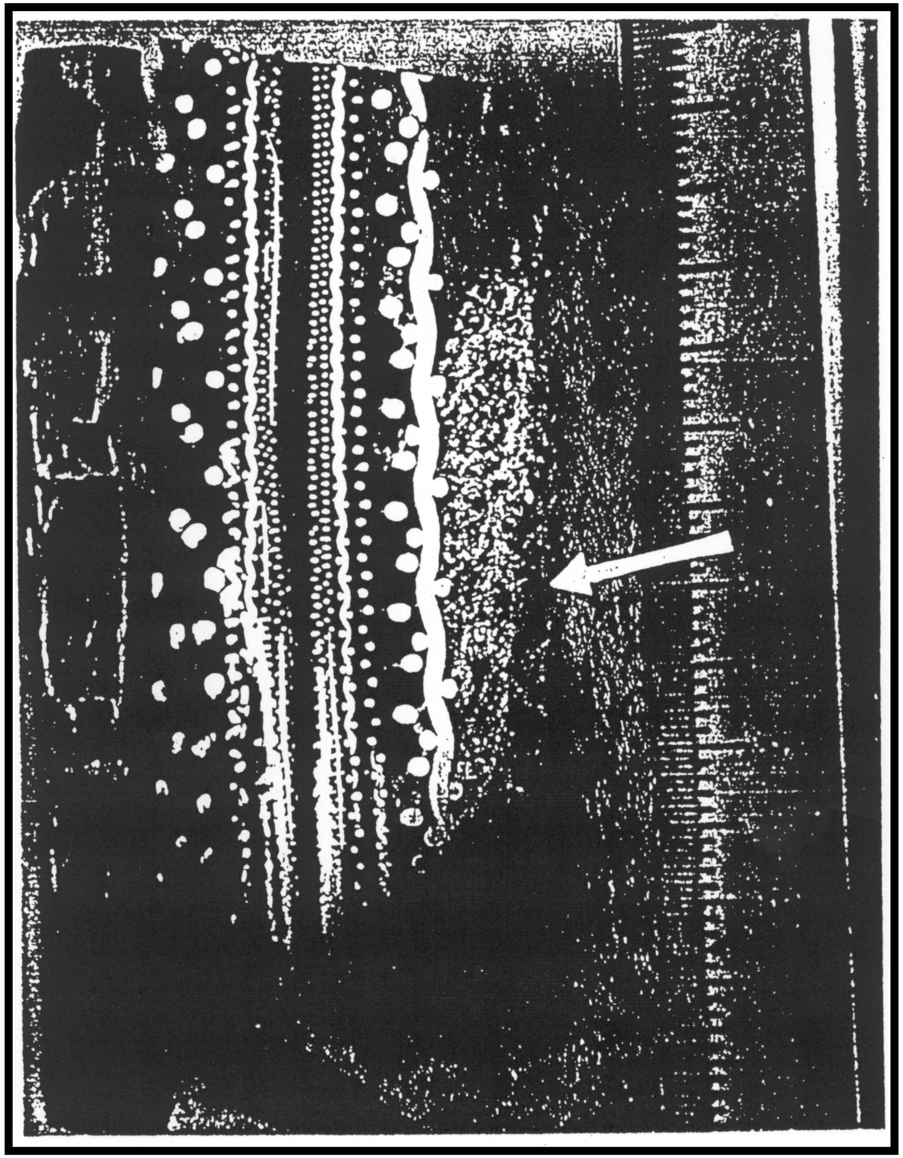

Fig. 4 – Vertical cross section of a working GTT intermediate electrode with the titanium panel (arrow) and the supporting structure.

Fig. 5 shows the **magnification** of the TEB electrode wire net supporting the **nanoporous distal titanium panel.**

The fine titanium structure, **cathodically** connected, that **allows the transit of chlorine anions while blocking the passage of Ti^{++} complexes.**

When I **saw the description** of the system for which the **Nobel Prize** was awarded, Fig. 1, I **immediately thought** of our **Titanium Distal** Deposition mechanism.

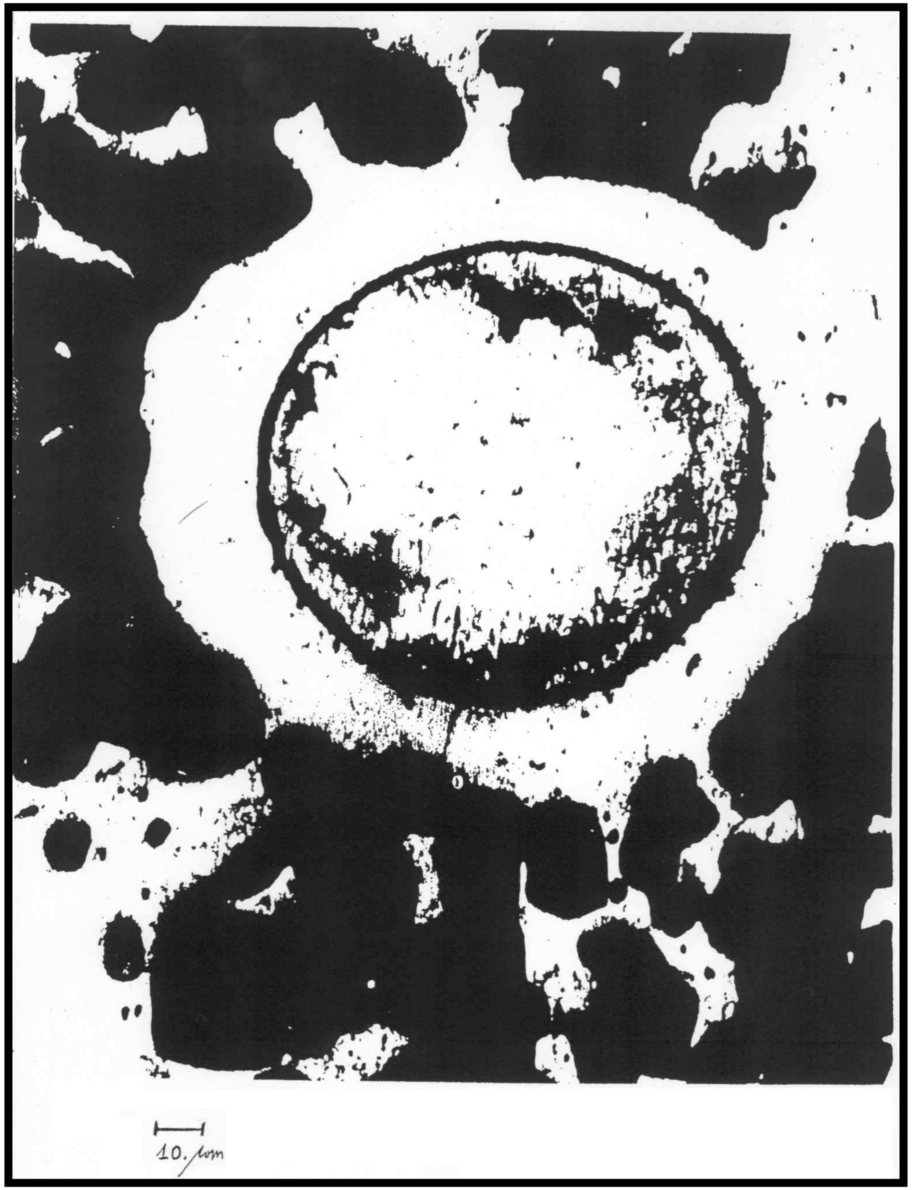

Fig. 5 – Nanoporous structure of the titanium distal panel that permits the passage of chlorine ions while restraining titanium species movement.

This regime is maintained for externally applied approx **5 Volt** between **anodes** and **titanium** working cathodes, and approx **4-5 Volt between anodes and GTT intermediate electrode**.

Fig. 6 depicts a diagram of the **voltage gradient**, from anodes to cathodes, **through the GTT intermediate electrode;** the family of dotted lines from the distal side of the GTT electrode to the front of the cathode depicts the window of voltages for **preventing titanium ions from diffusing towards the anodes**, while the lower line indicate the maximum voltage before sodium reduction starts on the distal side.

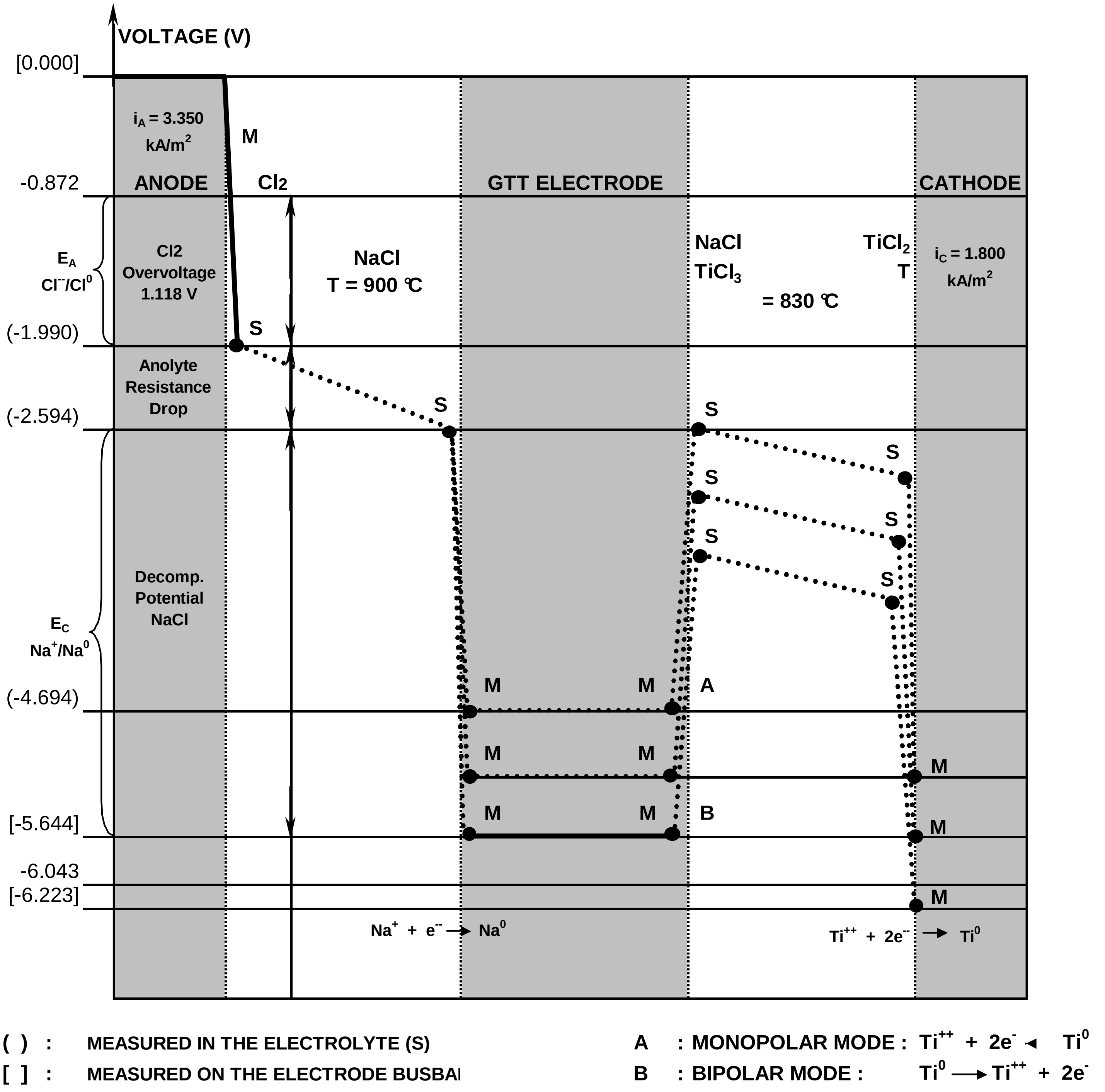

Fig. 6 – Voltage gradient through GTT Intermediate Electrode.

The dotted lines of Fig. 6 represent the **potential existing at different locations within** the **body** of the titanium Distal **Panel** for the various **voltages applied** to the GTT **intermediate** electrode, at the various **current densities** coming from the **working titanium** cathodes.

On the **Frontal** side of the electrode, the **incipient** formation of **Na^0** is **maintained** at all times at the decomposition potential of NaCl, since there is **no $TiCl_2$ in the anolyte**. On the back of the electrode, distal side, depending on the **porosity** and on the **thickness** of titanium Distal Panel, we have a **Window of voltages.**

At the decomposition potential of $TiCl_2$ when the panel has **large porosity** and **small thickness**, and thus the electrode operates as a **monopolar** electrode, that is, in parallel with the main working cathodes.

With the panel conditions of **little porosity** and **large thickness**, the electrode operates as a **bipolar** electrode.

The S**elf-Regulating mechanism** of the GTT intermediate electrode spans from the conditions of **monopolar** behavior, when Ti++ is **cathodically reduced** and titanium is **deposited** on the **distal side** to make the panel less porous and **thicker**.

During **bipolar** behavior when the titanium of the panel is **anodically dissolved** the **porosity** of the panel is **increased.**

In conclusion, with the externally applied voltage of approximately 4-5 Volt, the intermediate electrode is **self adjusting** its electrochemical characteristics in order to follow the requirements of **current density** of the working titanium cathodes. This why we called it “active panel”. The **Chlorine Ions current flux fills the open section of the pores** in the titanium panel, and the **titanium ion complex are not allowed** to diffuse into it.

The **interaction between a Charged Wall, Titanium on the Distal panel**, **with the ions** in solutions is the basis of the **functioning** of the GTT intermediate electrode, which **allows the passage of the Big single charged negative Cl^-** but **blocks the passage of the Small double charged positive Ti^{++} which tightly binds a large complex.** Also this is a practical utilization of the Chemlà effect.

The **experimental results** produced by GTT pilot plants MX3 (1985-1992) shown in Fig. 7, **confirmed** the **selective transfer mechanism**.

In particular, the solidified **anolyte** that was removed from the anode/intermediate electrode assembly (TEB) working at regime conditions was always found to be **colorless**, in the presence of titanium metal crystals inside the assembly, without the slightest amount of Ti^{2+} or Ti^{3+} which would have given a green or purple color to the anolyte.

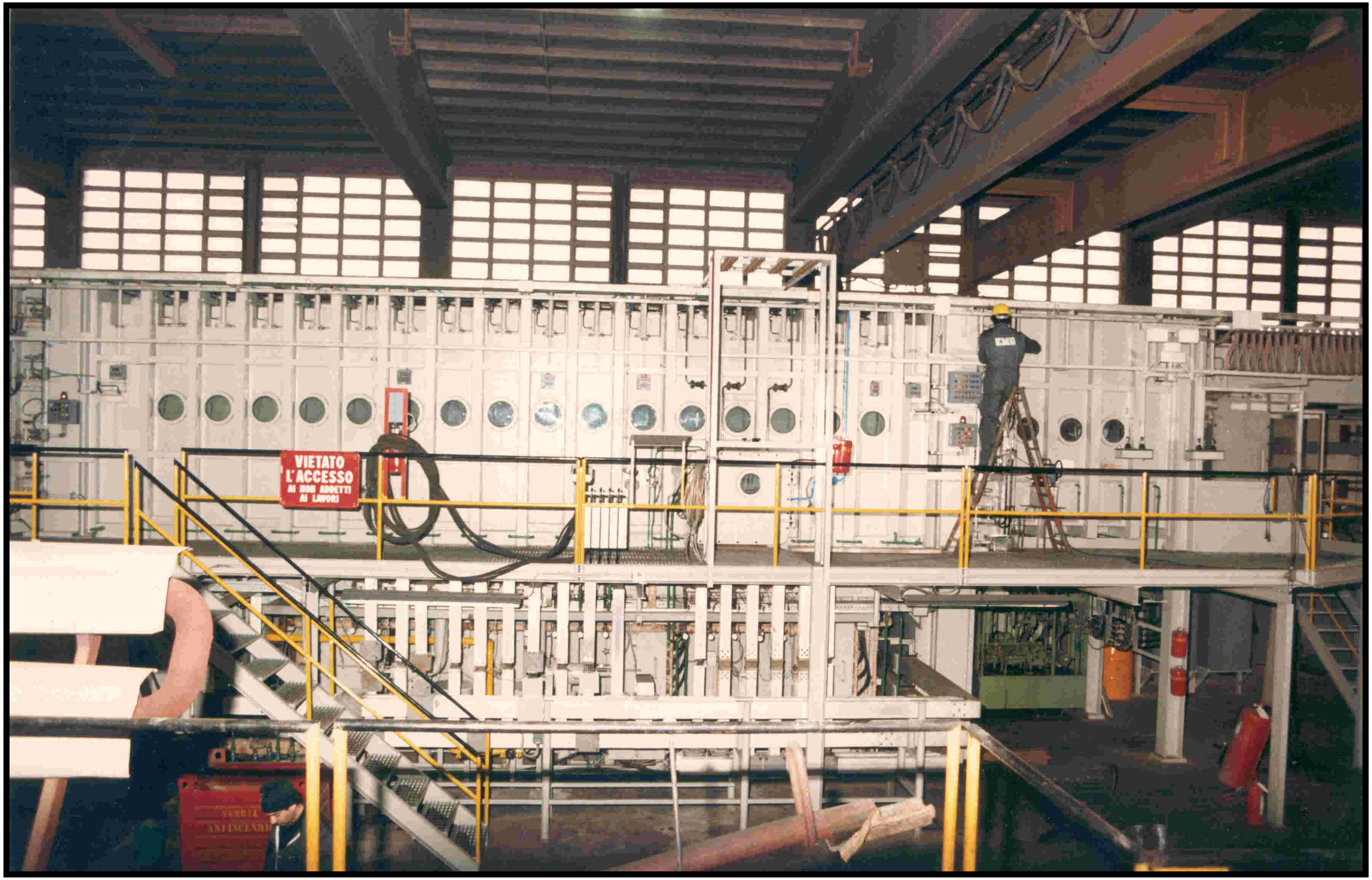

Fig. 7 – Side view of the GTT pilot plant.

CONCLUSION

During the past century very much beautiful powerful **electrochemical technology** has been **produced,** but so much of it is not known and has **not been studied**.

This is a further **proof** of the urgent **need** to **Brake the Barrier between Specialty Fields**

for **theoretical analysis** and **fundamental formalism to be developed**, to be raised up to the level of the industrial **technological progress**.

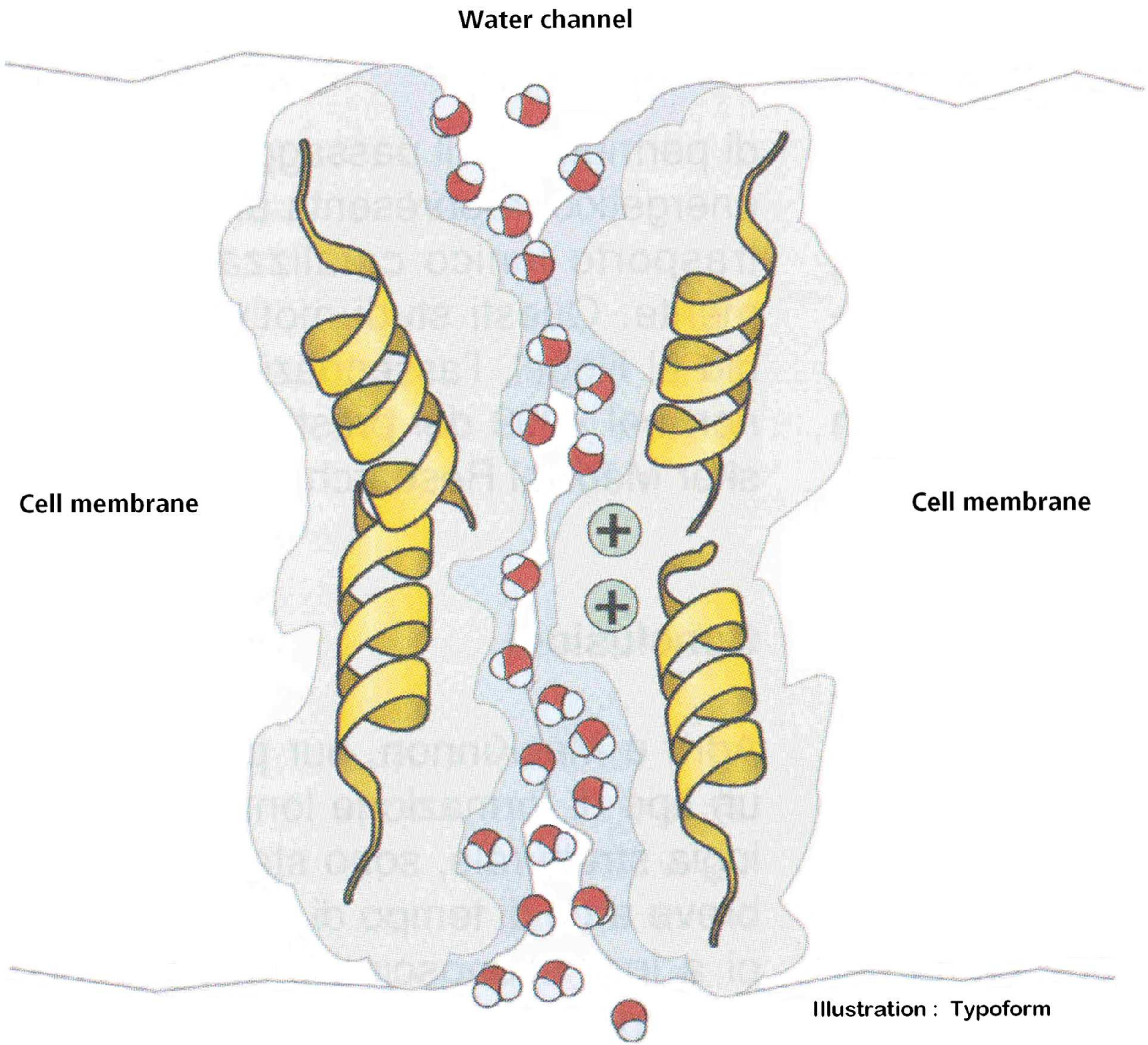

Illustration : Typoform

Fig. 1 - Ion Selective Channel.