



# Multilayer Electrode Interphase

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An attempt to **rethink the fundamental tools** that we have at our disposal to further our understanding of the electrochemical processes for the **metal electrolytic production**.

The aim is the design of experimental work to generate the data required for **optimizing** the electrowinning processes.

This will be done by, **simulating as close as possible to reality, the electrode processes in molten salts**. From the simulation we will have to develop the necessary **formalism** to obtain a **model** with the **minimum amount of oversimplifications** and unrealistic assumptions.

## State of the art

- **inadequate** state of development of the **theory of molten salts** in fundamental electrochemistry has retarded the industrial progress in general;
- still **incomplete** understanding of the functioning of the **aluminum production cell**; the theoretical formulation is far from a common acceptance;
- insufficient experimental work performed in fundamental electrochemistry; the **formalisms** still used in the published literature is often devoid of a rational base and of a **physical significance**;

- conceived as two-dimensional quiescent **interfaces** at reversible **equilibrium** conditions;
- we need **practical understanding** of the physical meaning of the data which describe the **operative conditions**;
- the **metallurgist** that attempts to interpret the phenomena occurring at a **working single electrode** gets entangled in matters of principles about thermodynamics of electrically charged species;

- we remember how much the electrochemistry has **contributed** to the development of thermodynamics, but it has not received much;
- in published literature we can see that the electrochemists still have **fear to enter deep into the matter**, that is to **abandon** the **reversible** equilibrium in which the metallurgist has no interest and to abandon the two-dimensional **interface unrealistic** model;
- large amount of **work** was done in the past in the determination of values of physicochemical parameters, in the **absence of live electrochemical processes**;

- published works on **cathodic deposition** are concerned in studying how irregularities, dendrites and **whiskers** grow from a nucleation point, but very few works attempt to explain how the **nucleation point is formed** in the first place;
- many **insufficiently understood** electrode process **phenomena**;
- **not enough study** was performed on the large amount of **experimental results** produced by the non-diaphragm full scale electrolytic cells;

- most workers on high temperature electrochemistry are complaining on the **lack of reliable experimental data**, but **very few venture** to speculate on designing the experiments required to generate the new data;

-Fig. 1 lists a collection of **species carrying Al** to the cathode: most of them are indicated as **anions**.

Raman spectra are reporting the presence of  $(\text{NbF}_7)^{2-}$  and  $(\text{Ti}_2\text{Cl}_9)^{3-}$

NMR spectra reported  $(\text{TaF}_7)^{2-}$ .

**It is difficult to simulate a cathodic mechanism that begins with negatively charged species.**

**Table 4.2: Various suggested structural entities in molten cryolite-alumina mixtures.**

Authors	Method of investigation	Species
Abramov, <i>et al.</i> <sup>13)</sup>	Viscosity, density	Al <sup>3+</sup>
Rolin <sup>9)</sup>	Cryoscopy	AlO <sup>+</sup>
Rolin and Bernard <sup>29)</sup>	Cryoscopy	AlO <sup>+</sup>
Petit and Bourlange <sup>42)</sup>	Cryoscopy	AlO <sup>+</sup>
Boner <sup>43)</sup>	Phase diagram, X-ray analysis	AlO <sub>2</sub> <sup>-</sup>
Rolin <sup>9)</sup>	Cryoscopy	AlO <sub>2</sub> <sup>-</sup>
Foster and Frank <sup>44)</sup>	Activities	AlO <sub>2</sub> <sup>-</sup>
Foster <sup>45)</sup>	X-ray	AlO <sub>2</sub> <sup>-</sup>
Abramov, <i>et al.</i> <sup>13)</sup>	Viscosity, density	AlO <sub>3</sub> <sup>3-</sup>
Belyaev, <i>et al.</i> <sup>46)</sup>	Viscosity, density	AlO <sub>3</sub> <sup>3-</sup>
Rolin and Bernard <sup>29)</sup>	Cryoscopy	Al <sub>2</sub> O <sup>4+</sup>
Fréjacques <sup>47)</sup>	Postulate	Al <sub>2</sub> O <sub>4</sub> <sup>2-</sup>
Boner <sup>43)</sup>	Phase diagram, X-ray analysis	AlOF <sub>2</sub> <sup>-</sup>
Grünert <sup>48)</sup>	Electrolysis	AlOF <sub>3</sub> <sup>2-</sup>
Brynestad, <i>et al.</i> <sup>49)</sup>	Cryoscopy	AlOF <sub>3</sub> <sup>2-</sup>
Brynestad, <i>et al.</i> <sup>49)</sup>	Cryoscopy	AlOF <sub>5</sub> <sup>4-</sup>
Grünert <sup>48)</sup>	Electrolysis	AlOF <sub>5</sub> <sup>4-</sup>
Førland, <i>et al.</i> <sup>50)</sup>	CO <sub>2</sub> dissolution	AlOF <sub>5</sub> <sup>4-</sup>
Grjotheim, <i>et al.</i> <sup>51)</sup>	Cryoscopy	AlO <sub>x</sub> <sup>1-x</sup> (x = 3,5)
Førland, <i>et al.</i> <sup>50)</sup>	CO <sub>2</sub> dissolution	AlO <sub>2</sub> F <sub>2</sub> <sup>3-</sup>
Brynestad, <i>et al.</i> <sup>49)</sup>	Cryoscopy	Al <sub>2</sub> OF <sub>x</sub> <sup>4-x</sup>
Sterten <sup>57)</sup>	Activities	Al <sub>2</sub> OF <sub>6</sub> <sup>2-</sup>
Holm <sup>41)</sup>	Calorimetry	Al <sub>2</sub> OF <sub>6</sub> <sup>2-</sup>
Kvande <sup>59)</sup>	Vapour pressures	Al <sub>2</sub> OF <sub>8</sub> <sup>4-</sup>
Førland <sup>4)</sup>	Theoretical considerations	Al <sub>2</sub> OF <sub>x</sub> <sup>4-x</sup>
Holm <sup>41)</sup>	Calorimetry	Al <sub>2</sub> OF <sub>2x</sub> <sup>4-2x</sup>
Ratkje <sup>52)</sup>	Cryoscopy	Al <sub>2</sub> OF <sub>x</sub> <sup>2-x</sup>
Petit and Bourlange <sup>42)</sup>	Cryoscopy	Al <sub>2</sub> O <sub>2</sub> F <sub>2</sub>
Treadwell <sup>53)</sup>	Phase diagram	Al <sub>2</sub> O <sub>2</sub> F <sub>4</sub> <sup>2-</sup>
Sterten <sup>57)</sup>	Activities	Al <sub>2</sub> O <sub>2</sub> F <sub>4</sub> <sup>2-</sup>
Ratkje <sup>52)</sup>	Cryoscopy	Al <sub>2</sub> O <sub>2</sub> F <sub>x</sub> <sup>2-x</sup>
Førland, <i>et al.</i> <sup>50)</sup>	CO <sub>2</sub> dissolution	Al <sub>3</sub> O <sub>2</sub> F <sub>14</sub> <sup>9-</sup>
Holm <sup>41)</sup>	Calorimetry	Al <sub>3</sub> O <sub>2</sub> F <sub>2y</sub> <sup>(2y-5)-</sup>
Brynestad, <i>et al.</i> <sup>49)</sup>	Cryoscopy	Al <sub>x</sub> O <sub>z</sub> F <sub>y</sub> <sup>(y+2z-3x)-</sup>

**Fig. 1 - Grjotheim K. et al., 1982**



## Statements by most regarded scientists

**Prigogine** stressed the current limitations by which it is clear that thermodynamics alone is not sufficient to give a theoretical interpretation of the present experimental information. An **ideal mixture of thermodynamics and molecular physics** is required for each specific case.

**Sanfeld** states that **technological results** in electrochemistry are **beyond comparison** with theoretical progression, because of the lack of coherent **theoretical formulation**.

We are **very far from equilibrium**, thus we must use statistical methods.

It is very difficult to explain **nanoscopic regions** in terms of **macroscopic variables**, such as pressure, temperature.

The major **assumption** of thermodynamic is that all systems are **continuum** is the clearest proof of the **failure** in the treatment of the electrode processes.

The peculiarity of the **real** electrode processes is the **non-uniform distribution of charges and matter** in the region between the body of the metal and the bulk of the electrolyte.

**Van Rysselberghe** stated:

**The Integrity of the Electrochemical Potential.**

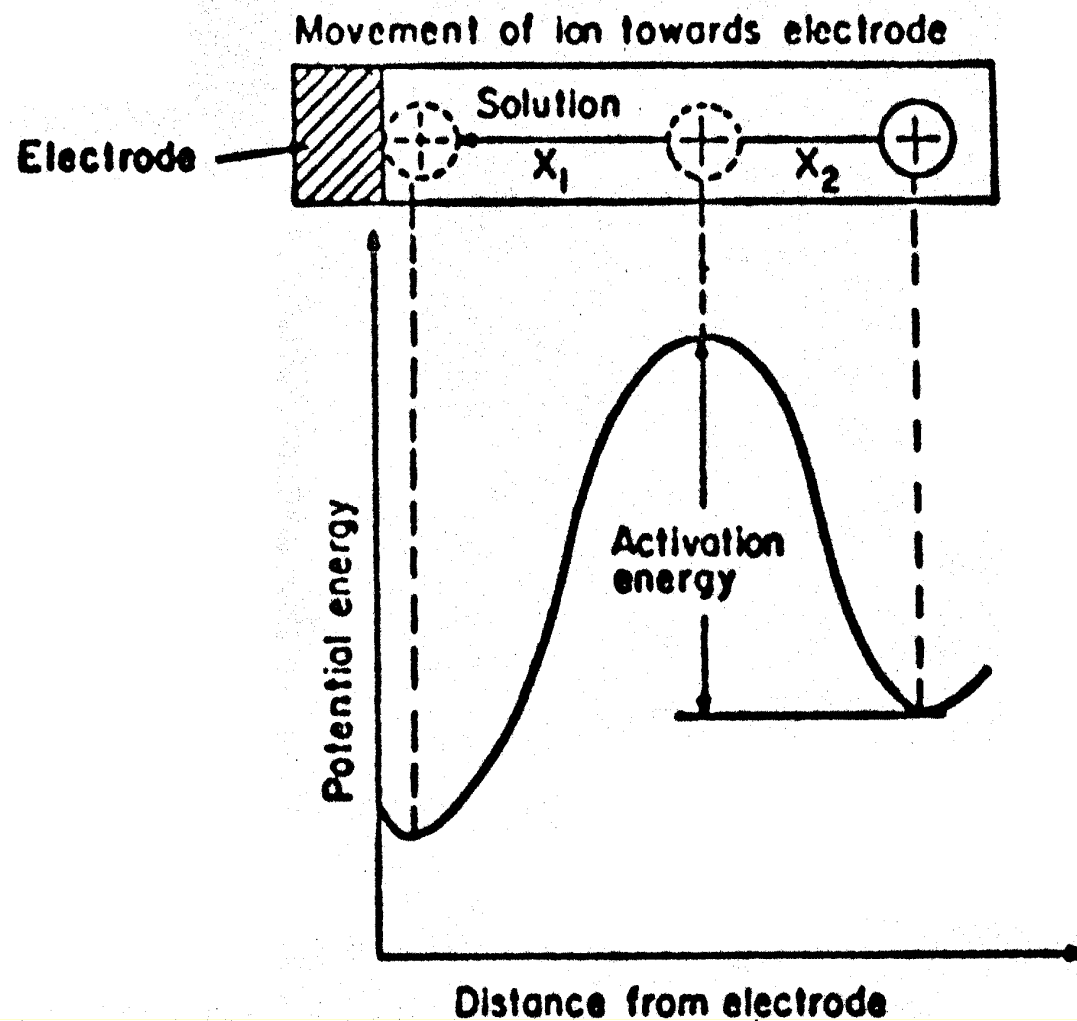
The arbitrary separation of electric and chemical contributions in the electrochemical reacting species, followed by the separated treatment of these contributions cannot be allowed.

**Eastman, on entropy of individual ions** stated:

The mechanism of **conduction of heat** is identical with and **inseparable** from that of **transfer of matter** between regions.

Therefore, the electrochemical reaction must be treated as **non-isothermal process**: another major **assumption** that has hindered the understanding.

**Piontelli** stated: the usual treatment of electrodic kinetics consists in an **intuitive combination** of principles and methods of **chemical kinetics**, with **empirical factors** introduced to take into account the influence of the electric potential difference between electrode and solution. **Qualitative** considerations have been developed on the basis of **arbitrary traced potential energy curves**, while thermodynamic quantities have been introduced without adequate bases. The **transfer coefficient** has never had a definition free from **ambiguity**; while for the **reverse process** it has almost always been assumed to be the **complementary** of the coefficient of the **direct process**.

**Fig. 2**

**Fig. 8.17.** Construction of a potential-energy–distance profile by consideration of the potential-energy changes produced by varying  $x_1$  and  $x_2$ .

[Bockris, 1970]

The curve for the activation energy for electrode processes as illustrated in most textbooks.

The **numerical** values of the **energies** as a function of distance is seldom mentioned, nor is the **distance** scale itself given.

The contribution to this free energy change, that is the **changes** in entropy and enthalpy, this information is also not given.

No data on the origin and the source of the energy and **how** some species are **activated**.

How does the **de-activation** occur?

Since the **energy balance** must be observed, where does the de-activation energy go?

From the shape of the curve one is lead to believe that the **deactivation starts before** the species is physically at the electrode surface: would this mean that the **electron transfer** takes place **away** from the metal surface ? At what distance from the surface ?

In short, the curve as shown has little meaning until the above questions are answered.

On this subject **Dogonadze** attacked **Markus'** theory for not being able to calculate the **exchange current density**, but the expression they proposed is based on **assumptions that over simplify** the real electrodic system.

**Laidler** stated that there are **two classes** of activated **complexes**, those that were reactants and those that were products.

The **flow of complexes in one direction is independent** from the flow of the **other** class of complexes in the **opposite** direction.

The peak of the classical energy-distance diagram is considered the point of no return for the **transient species** which **pass the maximum** of the curve **straight in one direction** during a time of the order of  $10^{-14}$  second.



These authors are among the very few who give **numerical values** for energies and distances, accounting of the various **energies stored, transferred and used** for crossing the barrier and remains stored in the product.

Finally, how the energy stored in the activated complex is **disposed of** during the **de-activation** of the complex.

**Kushner** offered the following explanation for electrode process.

A metal ion in the solution must **surmount** an **energy barrier** to be transformed from an **hydrated ion** to a **metal atom firmly** attached to the lattice. Once the metal ion is over the hurdle, however, it **possess** considerable **excess energy**; a group of such ions will have a higher temperature than their surroundings. As the hot metal atoms deposit on the surface (they will have an average temperature several hundred degrees centigrade higher than their surroundings), the thermal gradient developed is very steep, both into the liquid and into the solid substrate. The very thin **layer of hotter atoms** forms.

The above fundamental reasoning leads us to arrive to an understanding of the physical meaning of the **characteristics of a cathodic interphase** hosting the processes leading to the net deposition of metal atoms at a rate of **1.0 A/cm<sup>2</sup>**, current density.

In order to begin a first stage synthesis, I proposed an improvement on the **graphical representation** of the activation curves with reference to the **electrolytic refining of metals** in Fig. 3.



- $E^*$  = Activation energy level.
- $E_{III}$  = Ground state energy level of anode surface.
- $E_{II}$  = Ground state energy level of the ions in the electrolyte .at large distance from the electrodes.
- $E_I$  = Ground state energy level of the cathode surface, electrons in the Fermi level of the metal.
- $E_0$  = Ground state energy level of the transient entity.
- $\Psi_+$  = Galvani potential at the anode interphase, plus the overpotential, as a function of the distance from the electrode surface.
- $\Psi_-$  = Galvani potential at the cathode interphase, plus overpotential, as a function of the distance from the electrode surface.
- $R$  = Reversible potential curve as a function of the distance from the electrode.
- Act. = Activation energy curve as a function of the distance from the cathode surface.
- Dis. = Dissolution energy curve as a function of the distance from the anode surface.

Besides the cathodic deposition on the left side, in **analogy**, I represented the **anodic dissolution** on the right side, where the **de-electronation** state for the atoms of the metal surface have the lowest energy of the system while loosing their valence electrons.

At the cathode, the **newly formed atom**, just after it has received the electron, is still at the **high energy level** of the activation; we compare the entering of the new atom in the metal structure as a **solidification** process that is **dynamic** process with the atoms continuing leaving and joining the solid.

The **newly formed atoms** must be able to **transfer** to the solid the excess **energy** of activation and the **latent heat of fusion** and be accommodated by the solid; the solidification rate is a function of the **metallurgical characteristics of the solid metal electrode**.

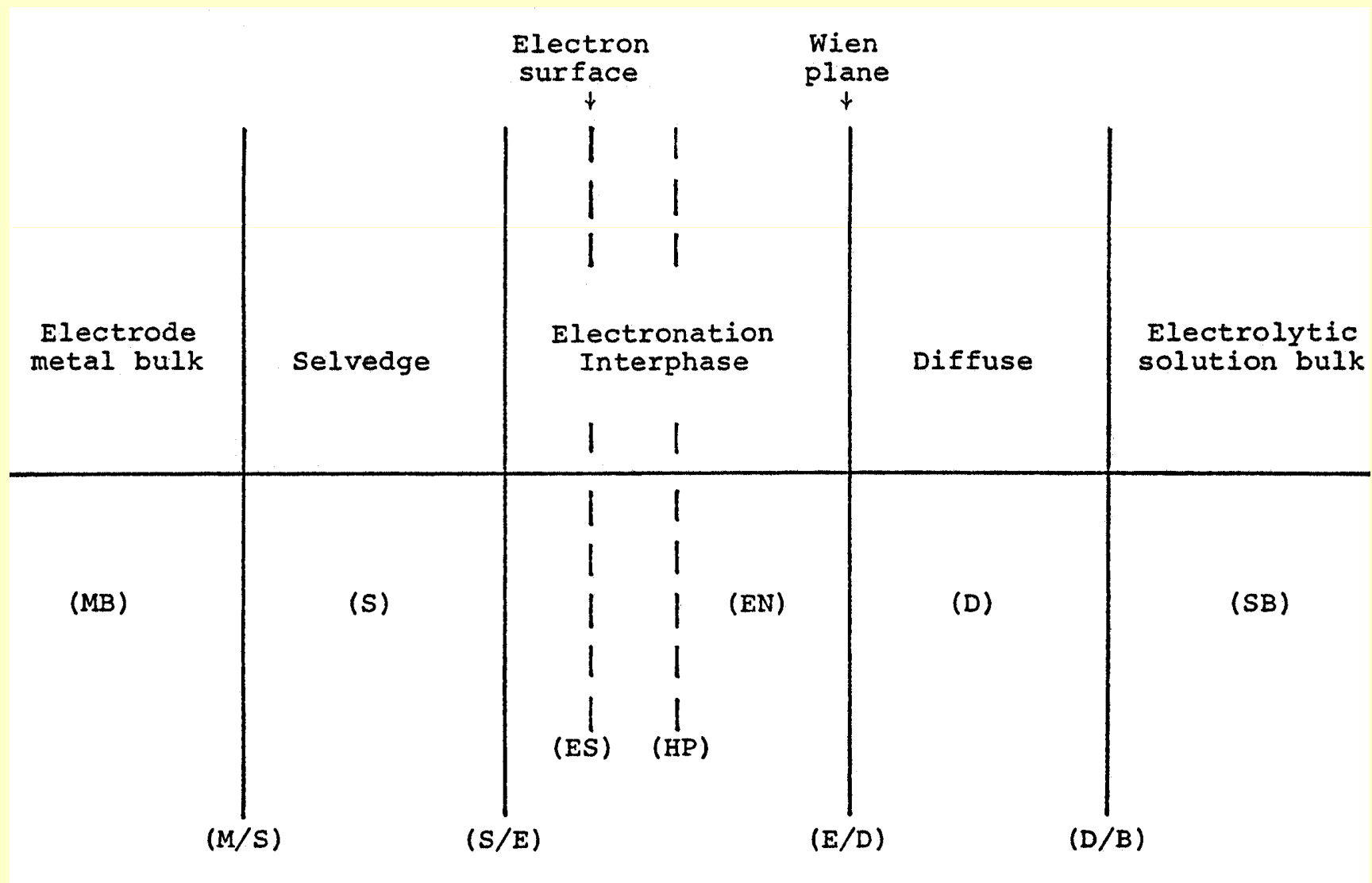
$T\Delta S$  occurring at the **cathodic interphase** and the  $T\Delta S$  occurring at the anodic interphase, are **independent from each other** and are much **larger numbers** than the  $T\Delta S$  of overall electrowinning reaction which is the algebraic sum of the two.

## Multilayer Cathodic Interphase Model

In order to **establish a formalism** for the calculations we must further **detail the structure** of the electrode/electrolyte multilayer **interphase**, to better design the electrolyte characteristics which will **destabilize the ion complex** at the appropriate current density, and to determine the **sequential charge transfer** which is conducive to the most effective metal ion cathodic reduction.

A multilayer interphase composed of **five regions** describes the **electrode/electrolyte transition**, as sketched in Fig. 4 where the **metal electrode** is on the **left** while the **electrolyte** is on the **right**.





**Fig. 4:** One dimensional arrangement of the electrode/electrolyte interphase.

The idealized planar interfaces between regions of the interphase are labeled as follows:

- (M/S) - interface between metal body and selvedge;
- (S/E) - interface between selvedge and electronation region;
- (E/D) - interface between electronation region and diffuse region, Wien plane;
- (D/B) - interface between diffuse region and electrolyte bulk;
- (ES) - cathodic electron surface;
- (HP) - anodic hydration point;
- (MB) - electrode metal bulk;
- (S) - selvedge region;
- (EN) - electronation region;
- (D) - diffuse region ;
- (SB) - electrolyte bulk
- (EP) - electronation point ; ?
- (IC) - incoming ion position ; ?

**Selvedge** region where metallic atoms have **energies** and **spatial** arrangements different from those of the **metal body**. Its thickness depends on the current density and **thermal conductivity** of the metal.

**Electron surface:** since the velocity of electronic motion is **much faster** than the **ions motion**, we consider the electrons available at all times at the **plane** for the transfer on the incoming activated ions.

**Wien plane:** point in which the metal ion is completely **free** of its complexing anions, under the local electric field strength, starts to **accelerate** towards the electron surface.

**Diffuse region:** is the place where all the **mass transport phenomena** have **origin**.

We have very many excellent treatments from the Interphase into the bulk of the electrolyte, but this diffuse layer, within the interphase, is characterized by a metal ions concentration **non-uniform** and with the symmetry of the complexed ion present a different **degree of distortion**.

Beneath the apparent **lack of macroscopic motion**, charged species pass constantly to and from across the interphase between electrode and electrolyte, at a rate of **several thousands of atomic layers per second**, which increases with temperature.

The two contrary **flows are independent** from each other, and since the flow **cross section** is fixed, constant  $1 \text{ cm}^2$ , the only way we can envisage this **enormous rate of exchange** is by **increasing the thickness of the interphase**, so to allow this heavy two-way dodging traffic.

We have a **dynamic accumulation** of various species in particular **regions** of the interphase, under the **effect of the externally applied** electron potential difference.

Some ions act as structure makers, or order formers, while other **ions** act as **structure breakers**, for the metal ion species to be reduced.

The total **thickness of the interphase** must be significant in order to have reasonable electric **potential gradients** within the various regions of the interphase. A 3.0 V potential applied corresponds to an average electric field strength of 1'000 kV/m on a interphase 3'000 nm thick.

For low electrical field strengths **Ohm' law** applies; that is the **velocity of migration** of the charge carrier is **independent** of the strength of the externally applied field increasing the voltage. The result is an increase in number of charge carriers, the current, not the velocity, which remains **constant** at  $10^{-6}$  m/sec.

For **field strength** of above  $10^6$  V/m, the conductivity of strong electrolytes increases with increasing field strength: the **Wien effect**.

Very **high ion velocities**, of the order of 1 m/sec, and **complete dissociation** of all species exist within the Interphase.

We can venture to talk in terms of **local temperature**: it is difficult to use this macroscopic parameter in the **nanoscopic treatment**.

The effects on the **results** of the electrochemical processes are those of high temperature.

**Peltier** heat is **directly** proportional to the current; not as the Joule heat that is proportional to the square of the current.

In the electrochemical systems there are **two types of Peltier effects**: one between the **ionic conductors**, that is the bulk of the electrolyte and the Interphase; the other between the **electronic conductors**, that is the body of the electrode and the Interphase.



Another **effect** generated by the **superimposition** of the **electric field**: the **pressure** within the Interphase.

Macdonald calculated pressure values of 6'000 atm.

The **external** electric field can be seen as **shifting the electrons cloud** into the interphase region.

**Trasatti**, determined the “**electrochemical**” **work function**, were the **metals** with **high** work functions have a **large electron density** in the surface layer and this would favor strong **interactions** with **cations**. Instead, metals with low work functions possess electrons with low kinetic energy in the Fermi level, and this would favor a large interaction with anions.

This approach allows the dissociation of the **entropy exchange** from the **entropy production**.

In the cathodic interphase for a metal **deposition**, we have a **negative  $\Delta S$**  within the **Diffuse** region, with the corresponding **heat** being **released** at the **Selvedge** region.

The contrary occurs in the anodic interphase for a metal **dissolution**, where we have the positive  $\Delta S$  in the Diffuse region with the corresponding heat being absorbed from the Selvedge region.

The electrode systems need a **volume** between the metal electrode and the electrolyte, where the various electrode processes can occur, that is a **three-dimensional Interphase**.

We deal with **reactions between electrolyte and interphase** and **reactions between the interphase and the metal electrode**.

The Interphase is composed by a **series of non-homogeneous regions** with changing chemical identity and energy of the species, along the thickness dimension.

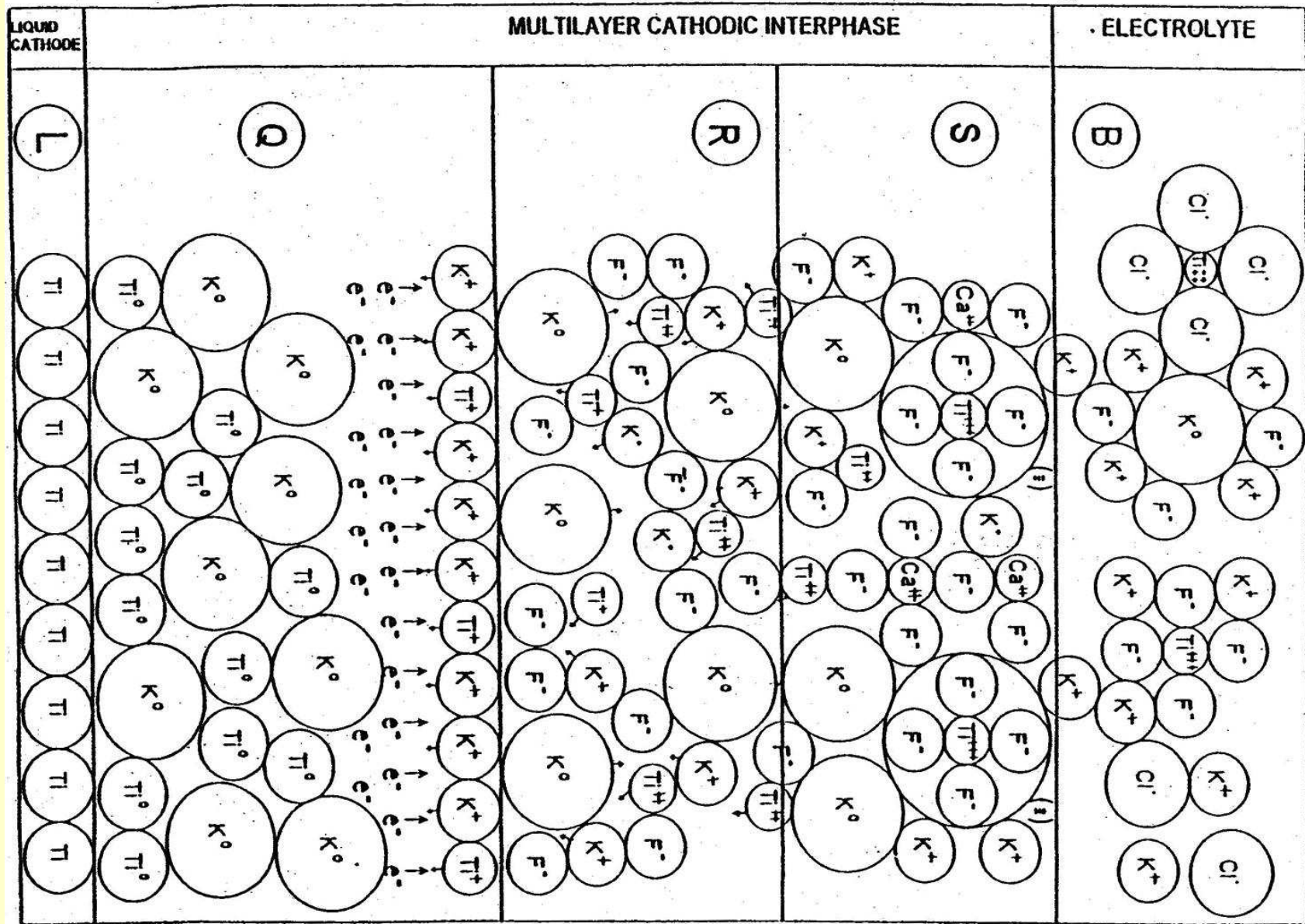


Fig. 5: Multilayer Cathodic Interphase.

## Simulation to Model

We imagine the electrode process occurring at the Interphase, **as accurately as possible**, the experts of Models will set up the formalisms.

The **mechanism is proposed** for the molten salt titanium reduction depicted in Fig. 5.

- Layer Q includes the Ti electrode surface and the accumulated alkali or alkaline earth metal
- Layer B is formed upon injection of  $\text{TiCl}_4$ .
- Under the electric field in layer S the **synproportionation** of Ti complex occurs.

- At the operation current density, layer R is formed where the complex carrying the Ti species are distorted and destabilized for the charge transfer reaction.

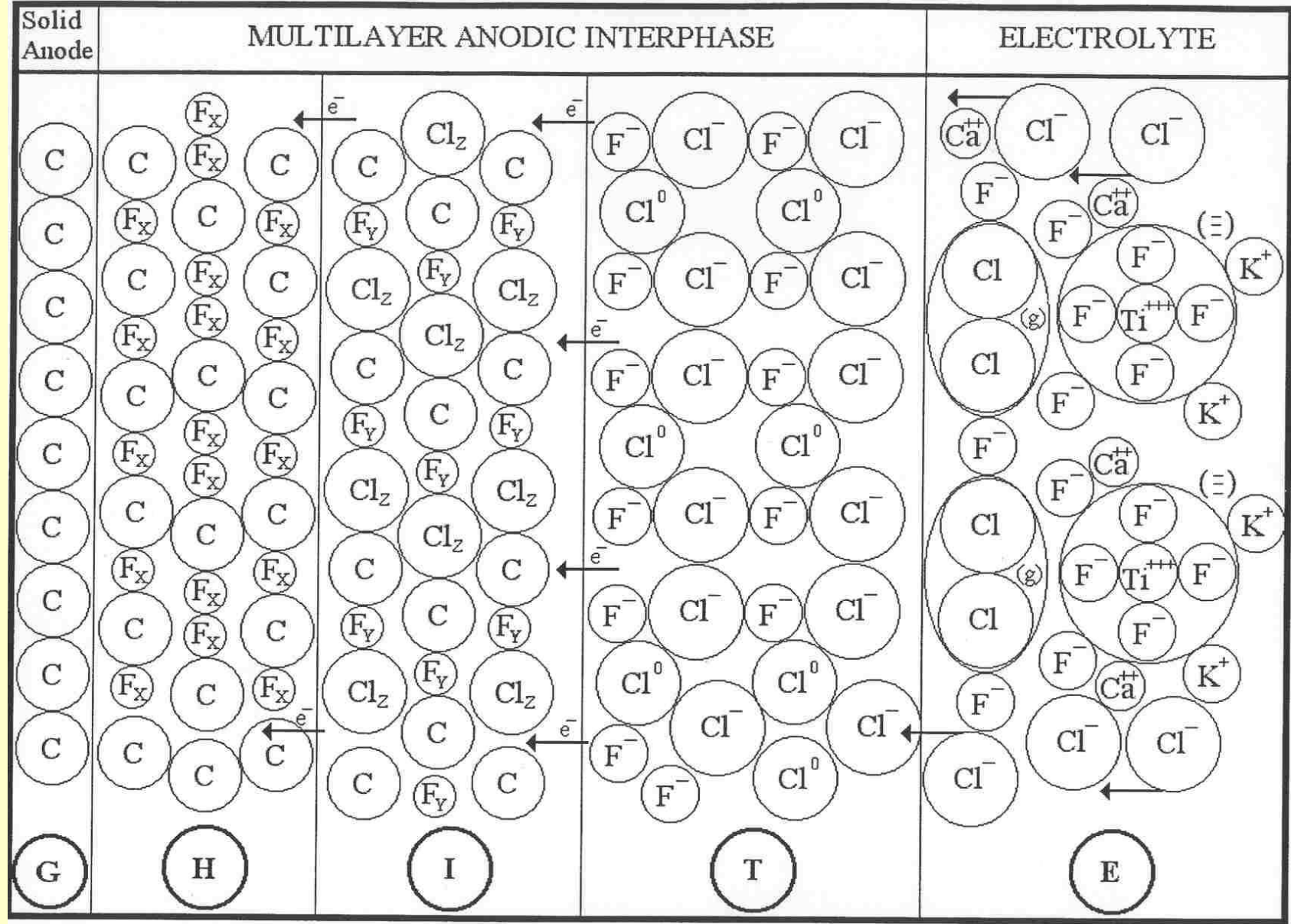
Now we have arrived to describe the most beautiful concept of electrochemistry: the phenomenon of the **exchange current density**.

Consequently a clearer physical meaning as to why the electrochemical reactions are not restricted by the Carnot limitation.

**In the electrodic Interphase there are at all times high energy species reacting at high rates.**

The **mechanism** occurring **within the cathodic Interphase in molten salt** may be this:

Coming from the electrolyte the Ti containing complex enters layer B where under the influence of the electric field its configuration becomes distorted, rearranging into a **dimer**  $\text{Ti}_2\text{F}_8$  and moving into layer S, where the local electrochemical potential makes it loose a  $\text{F}^-$  and becomes a **cation**  $(\text{Ti}_2\text{F}_7)^+$ , which is accelerated towards the electron transfer to become first  $(\text{Ti}_2\text{F}_5)^+$  loosing other  $\text{F}^-$  and then becoming **free**  $\text{Ti}^{++}$  moving into layer R where it becomes  $\text{Ti}^0$  in layer Q.



**Fig. 6: Multilayer Anodic Interphase.**



# CONCLUSION

We would like very much to set up a team to **develop the formalism** for the mechanism of the **five-region Interphase model** as illustrated.

A dynamic model that is meant to **represent a live steady-state electrochemical reduction process** in operation at **current densities** of industrial interest.