PENOMENOLOGICAL CONSIDERATIONS RELY ON THE DOUBLE MIXED ELECTRIC LAYER MODEL AT THE ELECTRODE-ELECTROLYTE INTERFACE

Gheorghe Semenescu
Faculty of Science, University of Pitesti, Romania

Constantin Cioaca, Gabriela Gughea, Bogdan Iorga
Department of Physics, Faculty of Chemistry, University of Bucharest,
Regina Elisabeta Avenue, No. 4-12, Bucharest-70346, Romania

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Abstract

The “tension surface” defined by Gibbs in treating the interface area is structurally specified by a “transition layer” made up by the outer Helmholtz plane and the one containing the surface active centres.

In the “double mixed electrode layer” model, considered to be one step taken towards the microscopic-level understanding of the electrolyte interface phenomena, the electrochemical sensors operations, as well as the electric phenomena at the membrane level are explained in a simple manner, and the cyclic polarisation potentio-dynamic diagrams can be more simply interpreted.

Introduction

The classical approach of the electrode–electrolyte interface supposes a thermodynamical characterization of this through observations (measurements of current, electric charge and potential) concerning the effect of the disturbances of the equilibrium state. In the theoretical thermodynamics tackled by Gibbs, for the study of the interface, it supposes mainly that all the properties of the transition layer are determined by the area and the curvature of an ideal geometric surface, so-called “tension surface”. The Gibbs’ model has the advantage to lead at results with a wide domain of practice, without being necessary to take into account the concrete structure of the transition layer. However, a such treatment does not permit the understanding in detail of the interfacial phenomena like those at electrode/electrolyte interface.

Experimental

The working mechanism of the electrochemical sensors that is based on the ionic exchange equilibrium between membrane and the studied solution is, sometimes, in contradiction with the experimental data.[1÷5] An interesting reason, which is in the detriment of this mechanism, can be expressed by a simple and reproducible experiment. One produces three liquid electrochemical sensors, as in Figure 1: the first is of the type R^+X^- and contains cethildimethilbenzilammonium perchlorate as active substance, the second is of the type R^-Y^+ and contains potassium tetraphenylboron and the third is of the type R^+R^- with cethildimethilbenzilammonium tetraphenylboron.

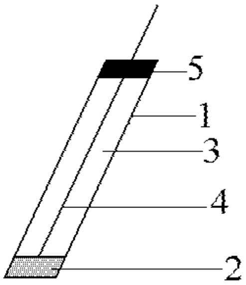

Figure 1. The constructive scheme of some liquid electrochemical sensors: (1)-isolated electrode body; (2)-inert conductive support (vegetal coal); (3)-nitrobenzene's solution of the active substance; (4)-conductor wire from stainless steel; (5)-tight lid

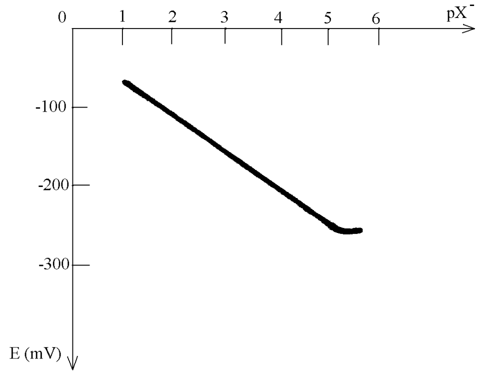

Figure 2. The calibration diagram of the first sensor with perchlorate of cetildimetilbenzilammonium (R^+X^-), selective for the anion ClO_4^-

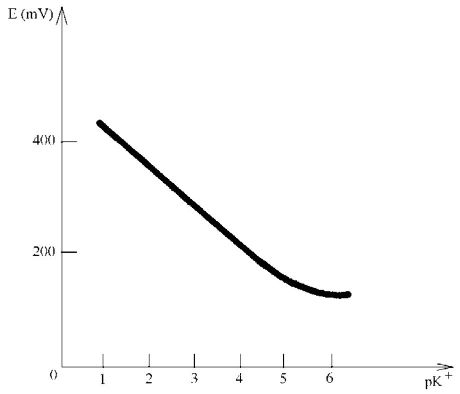

Figure 3. The calibration diagram of the second sensor with potassium tetraphenylboron (R^-Y^+), selective for the cation K^+

All three sensors were previously tested in corresponding aqueous solutions containing the ions of the active substances with which they were filled.

Using a millivoltmeter with very high impedance, we obtained the results shown in Figures from 2 to 6.

The dependence from Figure 2 presents a response of Nernst type that grows up in absolute value of the potential once with the rise of the anion ClO_4^- activity in the analysed solution.

In Figure 3, we have a linear dependence of the potential as a function of the variation of the cation activity K^+ from the tested solution.

Until now, one can consider that the principle of the ionic exchange equilibrium is valid. Thus, these two electrochemical sensors present reversibility for the macro-cations R^+ (cethilmethilbenzilammonium), in the first case, and for the macro-anions R^- (tetraphenylboron), in the second case.

The Figure 4 shows the response of the electrode for the tetraphenylboron macro-anion for the second electrochemical sensor.

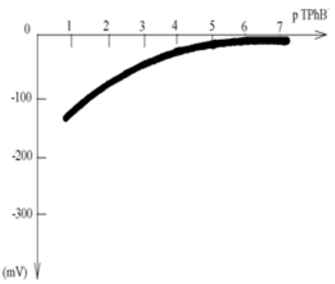

Figure 4. The calibration diagram of the second sensor with potassium tetraphenyl (R^-Y^+), selective for the tetraphenylboron macro-cation

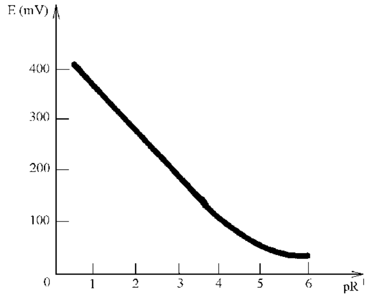

Figure 5. The calibration diagram of the third sensor with tetraphenylboron of cetildimetilbenzilammonium (R^+R^-), selective for the cetildimetilbenzilammonium macro-cation

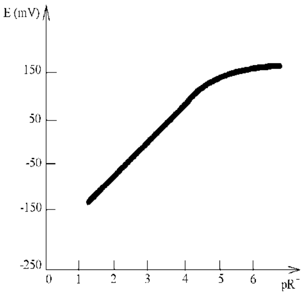

Figure 6. The calibration diagram of the third sensor with tetraphenylboron of cetildimetilbenzilammonium (R^+R^-), selective for the tetraphenylboron macro-anion

It is observed that, instead of an anionic response, increasing towards absolute values of the negative potential concomitantly with the increase of the activity of the tetraphenylboron macro-anion, the response is slowly cationic, especially for the high concentrations of the sodium tetraphenyl (in accordance with the selectivity constant of the selective electrode for K^+ in the presence of sodium ions).

We obtained the similar results in the case of a sensor with cethildimethilbenzilammonium perchlorate, tested in cethildimethilbenzilammonium chloride solutions.

The behaviour of such ion-selective electrodes would be justified either by the too small mobility of these macro-ions, or by the fact that such macro-ions suffer a process of fast extraction from the aqueous solution to the extracting solvent of the membrane.

These speculative reasons can be easily removed by using the third electrochemical sensor, with cethildimethilbenzilammonium tetraphenylboron (R^+R^-). This sensor has reversibility relative to the tetraphenylboron (R^-) and cethildimethilbenzilammonium macro-cation (R^+) too. The cationic and anionic nernstian responses of this sensor are shown in Figure 5, and Figure 6, respectively. These are linear, rapid and are not disturbed neither by the very slow mobility of the macro-ions in the study solution, nor their extraction in the organic phase. Finally, we ask ourselves, why the supposed macro-ionic exchange equilibrium are possible only in the case of the membranes achieved under of R^+R^- and they are not possible in the case of those achieved under R^+X^- or R^-Y^+? We suppose the processes that determine the variation of the electrode potential versus the activity of the ion in solution are not based on the ionic exchange equilibrium, but they are under the charge transfer equilibrium between the ions in solution and the active superficial centres (counter-ions), which have a donor or acceptor character, of the selective membrane. Thus, the ion-selective interfaces whose response is shown in Figures 2, 3, 5 and 6 can be simply represented in the Figures 7, 8, 9 and, respectively 10. As a support of this idea, we also obtained other experimental results.[11]

The working of the solid membranes is similarly to that of the liquid membranes. For instance, the membrane Ag_2S has $Ag^{\delta+}$ as a superficial active centre for S^{-2}, and $S^{\delta-}$ as a superficial active centre for Ag^+ in study solution. A silver rod, superficial protected with an oxide layer, is reversible and has a nernstian reply at the Ag^+ ion through superficial active centres $O^{\delta-}$ of the oxide film. In an open circuit, the potential of the system metal (silver) –oxide – electrolyte is a fundamental parameter which is used for the evaluation of the corrosion susceptibility of the metal by electrochemical tests.

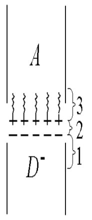

Figure 7. The ideal anion-selective interface

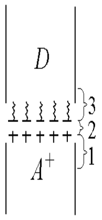

Figure 8. The ideal cation-selective interface

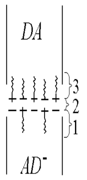

Figure 9. The mixed-selective interface with macro-cationic selectivity

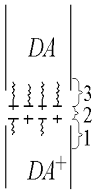

Figure 10. The mixed-selective interface with macro-anionic selectivity

Similar to the case of the ion-selective membranes, this potential, so-called the corrosion-potential, is the one mixed of electrode and it is determined by the equilibrium of electrons interfacial transfer. From the other similar experiments, it results the possibility to have a unitary approach of the phenomena that takes place at the interface with the electrolyte.

Results and Discussion

For the understanding of the phenomena at the metal–electrolyte interface, it is necessary to present the structure of the "tension surface" introduced by Gibbs, at the level of the double electric layer. We tackle the metal–electrolyte interface, in fact the oxide–electrolyte interface, from a phenomenological point of view.

In Figure 11, we show a simplified image of the interface. The oxide layer, heterogeneous from the chemical viewpoint contains in IHP (the Inner Helmholtz Plane) both anions and cations adsorbed among the water molecules. It is necessary to take into account a double mixed electrode layer model. This would lead to the understanding of the phenomena, which take place at solid/electrolyte or liquid/electrolyte interface, of the polarisation diagrams and of the electrochemical parameters used in order to estimate the susceptibility to corrosion of the metals.

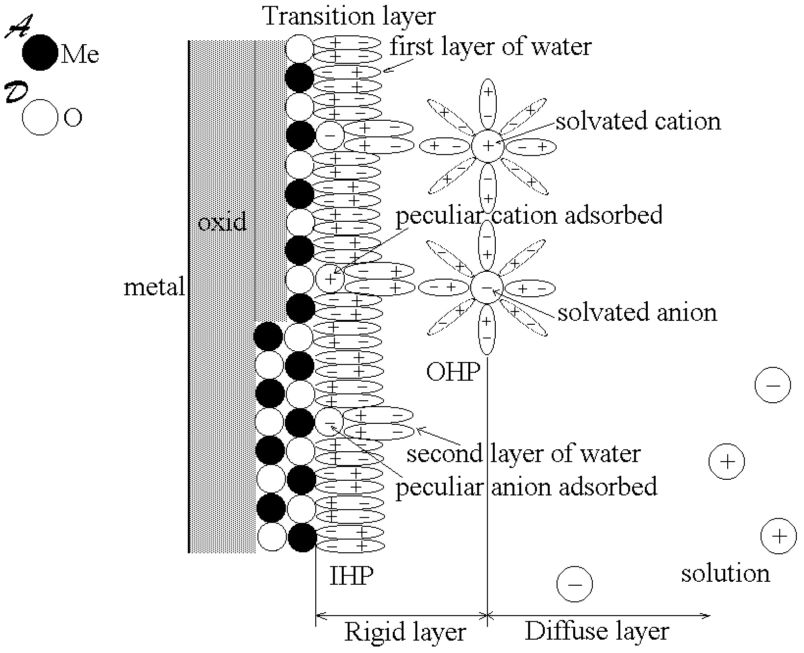

Figure 11. The “double mixed electrode layer” model at metal/oxide–electrolyte

A qualitative image of the phenomena which appear during the anodic polarisation at the metal (stainless steel) – oxide – electrolyte (H_2SO_4) interface is shown in the polarisation diagram from Figure 12. In the cathodic domain, the neutralisation of the hydrogen ions takes place, accompanied by the emission of the molecular hydrogen. This process is catalysed by the active superficial centres of donor type ($O^{\delta-}$) at the oxide layer level.

In the active domain, the solubilization takes places by the “intramolecular” destruction of the oxide, because of the synergetic action of the anion SO_4^{2-} and the cation H^+ upon metal-oxide bond (M-O); the simplified mechanism of this process is shown in Figure 13. This process is purely chemical and does not justify the increase of the current that corresponds to I_{critic}. The physical significance of I_{critic} (anodic current) can be found in the oxidation process of the metal that is uncovered with the oxide layer due to the water molecules from the level of the double electric layer. This process is encouraged by a potential, significant as value, like that which corresponds to the active domain of the polarisation diagram (see Figure 12).

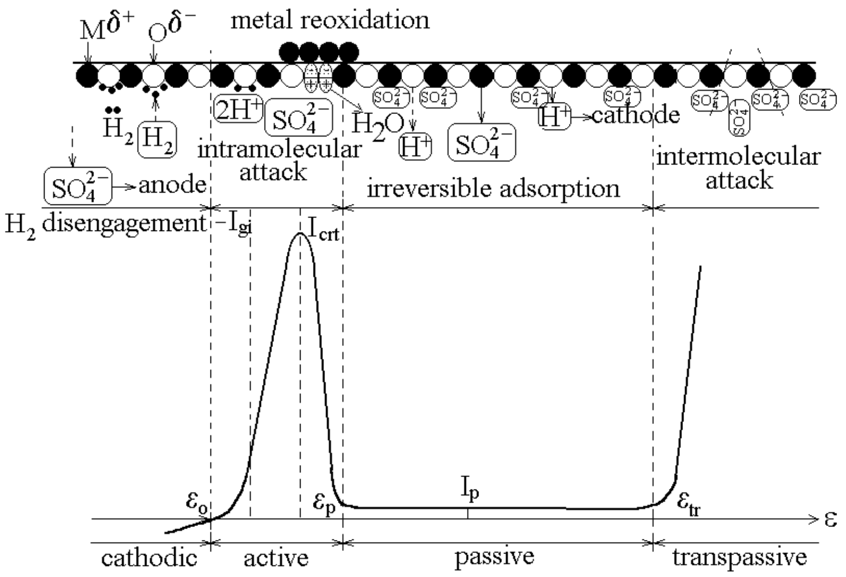

Figure 12. The intuitive explanation of phenomenon that takes place at stainless steel/electrolyte (H_2SO_4) interface during the anodic polarisation (top). The polarisation diagram (bottom).

In the pre-passive domain of the polarization diagram (see Figure 12), it appears and then increases the depletion tendency of the transition layer in the species H^+, due to the anodic polarisation, that prefers to be neutralised at the cathode.

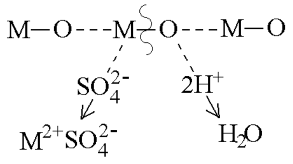

Figure 13. The destruction of “intramolecular” type of the oxide layer in the active domain of the polarisation diagram of the metallic electrode (stainless steel)

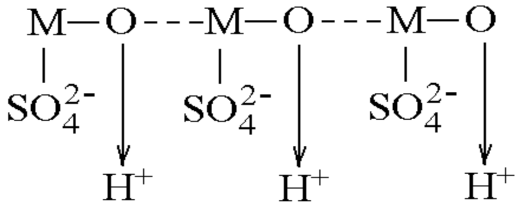

Figure 14. The passivation of the metallic electrode (stainless steel) through irreversible adsorption of the anions SO_4^{2-} on the metallic oxide surface

Beginning with the passivation potential value ε_P, the chemical dissolving of the oxide cannot take place only through the action of the adsorbed SO_4^{2-}, like in the scheme presented in the Figure 13. The oxide film becomes insoluble as a result of the deposition on the metal of a layer of SO_4^{2-} irreversibly adsorbed. The anodic current rapidly decreases up to the passivation current value, because the metal becomes protected and there are no electrochemical processes of re-oxidation and reconstruction of a passive layer (see Figure 14).

Because the desorption of the species H^+ is characterised by a threshold value of the potential in the case of the pure metals, a sudden decrease of the current should be emphasised in the passivation domain. For the steels, this fact is not possible because of the different desorption thresholds determined by the elements of alloy. In other situations (electrodes from iron, nickel doped with sulphur or from nitrate steels), in the pre-passive domain from Figure 12, oscillating phenomena take place for the electric current or potential, and which are qualitative represented in Figure 15.[9] These phenomena are determined by the existence of the resonating state initiated by the tendency of the potentiostat to maintain the pre-established potential and the tendency of the electrode to modify the value of the mixed potential.

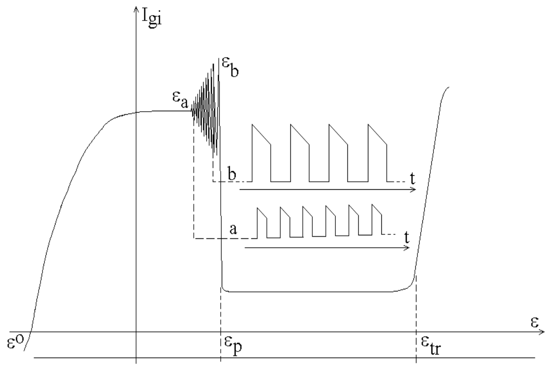

Figure 15. The oscillating phenomena characteristic to the pre-passive domain of the polarisation diagrams

This is an effect of the fact that the cations H^+ leave from the “transition layer”. Finally, the increase of the potential towards high values after the exceed of the trans-passive jump can lead to the phenomena of neutralisation and emission of the oxygen or/and the oxidation at higher valences of some elements such as chromium, molybdenum,… (see Figure 12). In addition to these processes we have the increase of the superficial stress as a result of the interaction of the adsorbed anions[1] and it can determine a destabilisation of “intra-molecular” type of the oxide layer, as seen in the scheme from Figure 16.

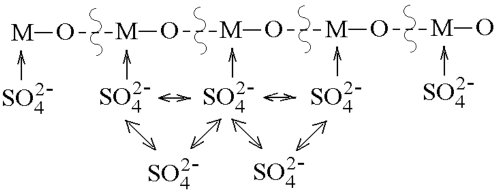

Figure 16. The destabilisation of “intra-molecular“ type of the oxide layer in the trans-passive domain of the polarisation diagram

So, one can explain the current jump and the simultaneous apparition of superficial fissures of the electrodes in the case of the anodic polarisation whenever one exceed the potential characteristic of the trans-passive jump.

Conclusions

In the “double mixed electrode layer” model, the origin of the potential of electrode is sought at the level of some equilibrium with interfacial charge transfer of electrons, but one cannot exclude the existence of the equilibrium of ions change with their implications. The two phenomena can superpose more or less. In case of the electrochemical sensors, the ionic change between membrane and the solution in study can lead to an instability of the electrode potential. With this model, we made some remarks about some electrochemical domains of general interest.

The domain of the electrochemical sensors. On the basis of the donor–acceptor character of the active superficial centres (A and D), one can couch the following scheme of an electrochemical general system for the electrochemical sensors:

The aqueous solution of ions for analysis. PHASE I	The interphasic transition layer formed in the superficial actived positions donor (D) and/or acceptor (A) with a fixed concentration and the ions from solution. PHASE II	The conductive inert background solution. PHASE III

The nernstian domain of response is depending on the concrete structure of the interface and is determined by the limiting value of the concentration of the ion for analysis and that is characteristic to a saturation value of the surface.[1÷4]

The reply time of the electrochemical sensors is determined by the transport stage of the ions from the electrolyte’s inner to the zone OHP (the Outer Helmholtz Plane) of the electrode, stage which is determined by the scanning rate and not by the migration of the ions through membrane. The selectivity of the electrochemical sensors is associated with the chemical activity of the ions in electrolyte for the counter-ionic active positions at the level of transition layer (A and D), and not with their chemical activity for the “membranar phase” in its ensemble.[1,3,4,5]

Depending on the structure of the interface at the level of double mixed electrode layer, one can make a general classification of the electrochemical sensors in: anion– (Figure 7), cation– (Figure 8), and mixed–selectives (Figures 9 and 10).

On the basis of this model, the construction of the i–selective electrochemical sensor does not imply the presence of the ion i in the two phases in contact, which is necessary for the achievement of the equilibrium of ionic change, but implies the presence of the superficial active donor positions D and/or acceptor A, with a counter sign that of the ion i, implied in equilibrium of electrons change.[1,3,4,5]

In the case of the potentiometrical titration at mixed–selective electrochemical sensors, the equivalence point corresponds to the potential jump associated to the passing of the electrode from the cationic reply to that anionic or inverse, with some corrections connected with the sensitivities for anions and cations. The ideal electrochemical sensors cation–selectives or anion–selectives have the asymmetrical titration curves, without potential jump at the equivalence point.[10]

The extent of the detection limit of the mixed–selective electrochemical sensors, in the characteristic area of the potential jump from the anionic reply to that cationic or inverse is an error and consists of the trend of over-appreciation of the electrodes performances (10^{-14} ion g $l^{-1}H^{+}$ for glass electrodes or less than 10^{-20} ion g l^{-1} S^{2-} for those ones of Ag_2S). In fact, the pH–selective glass electrode is a mixed–selective electrode with sensitivities approximately equal for H^+ and OH^-.

The domain of the membranes. After Prigogine, the energy flux in a liquid medium that contains different chemical compounds, leads to a spontaneous increase of the internal structuring. In such systems, by the anisotropic concentration of the products it forms a system made of interconnected elements which define a dissipative state.

If we put inversely the problem (for an already structured system), by analogy with the model of working of the liquid electrochemical sensors (see Figures 7, 8, 9, and 10), we suggest the model from Figure 17-a for the rest state of the membrane of the nervous cell and the model from Figure 17-b for its excited state, under the action of the perturbation of the exciting E.

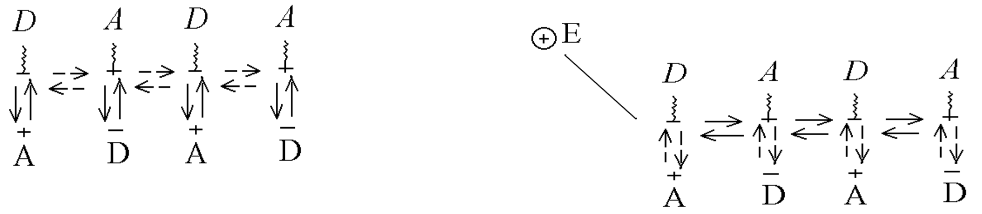

Figure 17 (a)

Figure 17 (b)

Figure 17. The charge transfer phenomena in a biostructured isolated fragment (a) and in the presence of an exciting E (b)

The play of the bounds D–A and A–D, during the excitation, above certain threshold values, makes possible the release of the species A^+ and D^-, which can freely diffuse just through the membrane. In this case, the "sodium pump" would not be only the effect and not the cause of the transmission of the signal along the axon. The shown phenomenon does not have any connection with the transport through the membrane of the ions and the macro-ions, but it does not exclude it and that we do not discuss here.

The domain of the electrochemical methods. In this area of investigation of metal corrosion, we can do an explanation for the polarisation diagrams with the assignment of some concrete significance for the activation and re-activation maxima, for the trans-passive and passive domains.

The active domain of the polarisation diagram signifies, on one hand, reactions of chemical pure dissolving of the oxide layer, and on the other hand, electrochemical reactions of reconstruction of the oxide layer. The latest are responsible of the appearance of the anodic current of which maximum is I_{critic}.[5,8] Therefore, the destruction of the oxide layer takes place by the breaking of the metal-oxygen (M-O) bound, the re-activation maximum having the same significance with that of the activation.

The pre-passive domain is sometimes dominated by the oscillating phenomena in current or potential, in which H^+ plays an essential role, at the level of the transition layer.

The passive domain of the polarisation diagram is determined by the irreversible adsorption of the species X^-, after the total desorption of Y^+, that is responsible for the catodic hysteresis obtained at reverse scanning.

The trans-passive domain corresponds to the oxygen neutralisation, the oxidation of some elements (Cr, Mo) or to the elastic deformation up to the potential that is accordingly for the mechanical destruction of the oxygen layer. One can demonstrate experimentally that, only in the trans-passive domain, a deposition that is strongly stressed of chromium on steel-carbon can be cracked.

In conclusion, if the "tension surface" structure is described in detail, defined by Gibbs, and taking into account a double mixed electrode layer model at interface electrode (metal)/electrolyte some phenomenological aspects of these interfaces can be explained much simpler.

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Povzetek

"Površinsko napetost", kot jo je definiral Gibbs pri obravnavi mejnih plasti strukturno obravnavamo kot "prehodno plast", sestavljeno iz Helmholtzove ravnine in plast z aktivnimi centri.

V modelu "dvojen mešane elektrodne plasti" na enostaven način razlagamo fenomene na stičišču faz, kot tudi električne fenomene na nivoju membrane.