A NEW PHENOMENOLOGICAL MODEL DESCRIBING CONDUCTION IN ELECTROLYTE SOLUTIONS

G. Semenescu[1], C. Cioaca[2], B. Iorga[2]

[1] *Faculty of Science, University of Pitesti, Romania;*
[2] *Department of Physics, Faculty of Chemistry, University of Bucharest,*
Regina Elisabeta Blvd. No.4-12, 70346 Bucharest, Romania,
e-mail: ibogdan@math.math.unibuc.ro

Abstract

A mechanism for electronic conduction in electrolyte solutions is presented. The structure of the electrode-electrolyte interface and the molecules in the ion solvation layer are the important element in this mechanism. The electrolyte chooses between one structure with a minimum electrical resistance and another one with a high electrical resistance as a function of the scanning rate value of the potential. The minimum resistance in the electronic conduction of electrolyte solutions is achieved basing on the multiwire-insulated conductor.

Introduction

This work presents a phenomenological model for electronic conduction in the electrolyte solutions. Some aspects regarding the role of the solvent and the adsorption to minimize the electrical resistance of the electrolyte solution become clear. The idea of the electronic conduction in electrolyte solutions is novel because it shows that the differences between the conductors of the first and the second order are minimized.

Experimental

The measurements have been made with the "Princeton Applied Research" electrochemical system (a potentiostat 273A model and an acquisition system). We used the cyclic voltammetry technique. A Tacussel minicell (50ml) with a platinum electrode ($1cm^2$) and a saturated calomel reference electrode (PAR) were used. The working electrodes ($1cm^2$) were polished at cold. It worked with the nickel electrodes and the

stainless steel electrodes in 1N H_2SO_4 or 1N KOH solution, and in 1N H_2SO_4 solutions, respectively. The temperature of stagnant and aerated solutions was 25^oC. Two experiments were achieved for 1N KOH solutions. In the first one, the potential was varied with a constant rate from –1370mV to +50mV, and in the second one, the potential was varied with different rates in the same range. Similar tests have been made in 0,1M sodium tetraphenil borate in dimetilformamide solution with two platinum electrodes and a silver wire as reference, and in other electrode-electrolyte systems (stainless steel — 1N H_2SO_4, Fe — 1N H_2SO_4).

Results

In the first experiment the cyclic voltammogram for the freshly polished nickel sample at 10mV/s scanning rate and following the electrolysis (voltage: –1300mV, electrolysis time: 600s) is shown in Figure 1. The cyclic voltammogram for the unpolished nickel sample, at 4mV/s scanning rate and not subjected to electrolysis is shown in Figure 2. In the first voltammogram (see Figure 1), the intensities of the electrical currents are of the order of amperes and in the second one (see Figure 2), the electrical currents are of the order of milliamperes.

In the second experiment unpolished nickel sample in KOH 1N solution without previous electrolysis was used. The cyclic voltammograms are classified in the next table:

Classification table

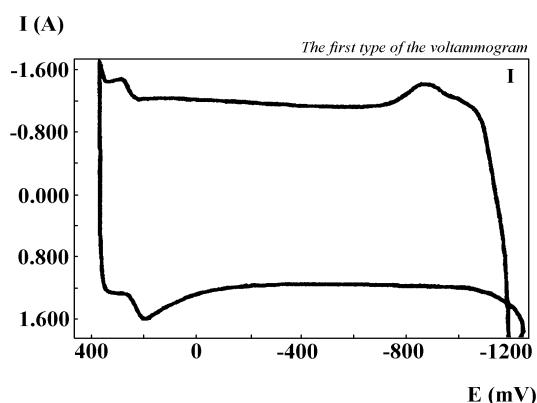| Determination numbers	1	2	3	4	5	6	7	8	9	10	11	12
Scanning rate [mV/s]	10	5	7	9	12	11	12	13	11	10	9	12
Classification	I	II	II	II	I	II	I	I	I	II	II	I

Figure 1. The cyclic voltammogram for the fresh polished nickel sample at 10mV/s scanning rate in 1N KOH solution at 25°C.
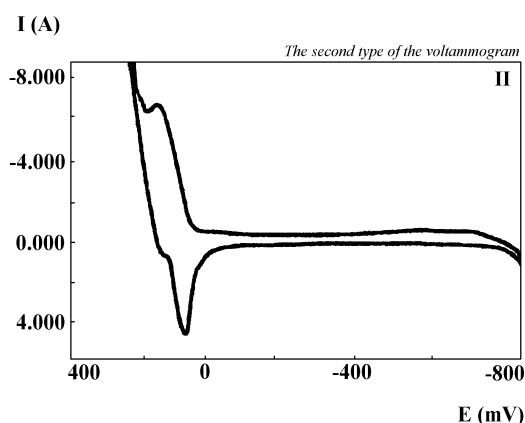
Figure 2. The cyclic voltammogram for the unpolished nickel sample at 4mV/s scanning rate in 1N KOH solution at 25°C.

The reduced electrical resistance of the circuit and the high currents in the first type of the voltammograms is explained by polishing the oxide layer or by cathodic reduction [1]. But, in the second experiment, the existence of the potential scanning rate for which the system can choose the first or the second variant, does not have any connection with sample polishing and cathodic reduction by electrolysis. It emphasized a critical scanning rate for which the system enters into a branch and can choose between a minimum electrical resistance structure (high currents) and one with a high electrical resistance (low currents) [2]. The scanning rate can be synchronized with the structural phenomenon of the electrolyte in the electric field between the nickel electrodes [3]. It is possible that the oxide electrical resistance will not be a determinative factor in the system choice at branch. The solution electrical resistance should be dependent on an energetic threshold masked by a threshold-value of the potential scanning rate. This rate can be correlated with some physical phenomena, which involve relative low energies such as ion-dipole interactions of the specific hydration and dehydration processes in the electrolyte structuring. The increase of the scanning rate can contribute to reach the energetic threshold necessary for adsorption. The sudden application of the overpotential will have the same effect, because this equates with an infinite scanning rate. Direct junctions between ions and substrate in adsorption may be achieved in metal dehydration, ion partial dehydration, and ion-substrate direct interaction.

Discussion

The water molecule, contributing to the stabilization of some opposite sign ionic pairs, becomes a mediator in the interionic charge transfer [4]. The non-participant oxygen electrons of the water molecule should be involved in energetic transitions together with the available electrons of the anions. In this way, the interionic charge transfer and the formation of the common conduction band are favored. Two or more water molecules in the *a* layer are able to do the dipolar stabilization of the ionic pairs, as shown in Figure 3 [1,4].

The unpolarized metal-oxide/electrolyte interface (M-O/E) contains acceptor centers ($M^{\delta+}$) and donor centers ($O^{\delta-}$) localized in the superficial oxide positions. The insulator/electrolyte system is not interesting from the electrochemical point of view. The oxide electrical resistance is considered negligible. The electrolyte solution is considered of X^-Y^+ type [5,6].
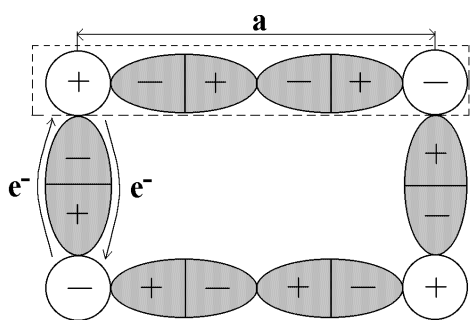

Figure 3. The dipolar stabilization of the water bimolecular interionic layer.

In open circuit, adsorption at the interface may exist or not. In the affirmative case, two possibilities exist: a) The X^- anions and the Y^+ cations are adsorbed. They lead to decrease the strength of the metal-oxide bond and to dissolve the oxide [6]; b) Only one of the two ions (for example, the X^- anion) is specifically adsorbed on the oxide surface. In this case, the oxide disolvation phenomenon is stopped by anionic blockade and the system is found in the natural passivity state (spontaneous state) [7,6].

In closed circuit, the specific adsorption of the anions and the cations can be activated by adequate overpotential application. If only the cation was adsorbed, through anodic polarization, then the anion can be activated by adsorption, the metal becomes active, and it can dissolve. If the X^- and Y^+ ions were adsorbed, through anodic polarization, appears the artificial passivity phenomenon by Y^+ desorption and by maintaining the X^- species in adsorbed state. In this passive domain, the current continues to be constant despite of potential increase [8,6].

The active domain and the beginning of the passive domain of the polarization diagram represent a sensitive zone, which offers to the system two possible ways of evolution: either electrolyte structuring with a low electrical resistance (α-conduction associated with the first diagram type) or another one with a high electrical resistance (β-conduction associated with the second diagram type). Hydration ion structuring which involves an energetical stabilization by ion-ion, ion-dipole and dipole-dipole association, should justify the β conduction mechanism. The dielectric constant of water does not vary much and it is impossible to realize directly the interanionic and intercationic junctions (see Figure 4). Partial hydration ion structuring encourages the realization of the previous junctions after overcoming the energetic threshold necessary for the electronic transfer ($X^- \rightarrow X^*$) as a α conduction mechanism support [3]. This energetic threshold can be overcome by a potential scanning rate increase.

In the low scanning rate case, the interaction between the adsorbed anion (X^-) and the cation pair (Y^-) decreases. The consequence should be an increase of the interaction between this cation and the donor active center of the metal. This quadrupolar stabilization between two superficial active centers and two oppositely charged ions in the solution is possible just in the heterogene solide-electrolyte interface case, in an electrical double layer. The anion-cation pair arrives at the interface through diffusion.
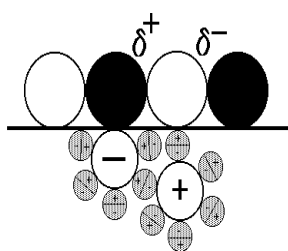

Figure 4. The ionic pair arrangement for low scanning rate situated under interionic charge transfer threshold.

The orientation in the superficial field is like in the ionic crystal. Thus, it achieves a very stabile structure from the thermodynamic point of view. The structural process is preferentially started in the points where the adsorption achieves in the most quickly way and goes on very fast, unidirectional to the other electrode for closing the electric circuit.

Thus, it achieves a β conduction mechanism as shown in Figure 5. In the electric field, the electrolyte structuring is very fast at the n-n' mobile interface level. At the same time with the potential increasing, the electrical solution resistance increases through a tridimensional structure forming as in the ionic crystal (see Figure 5).

May be, the structural stabilization is possible through the intermediate of the polarized water molecule.

In the high scanning rate case, the condition of the energetic threshold overcoming can take place, which is necessary for the interionic interactions, $X^- \rightarrow X^*$.
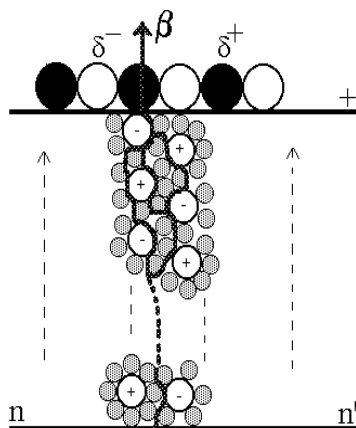

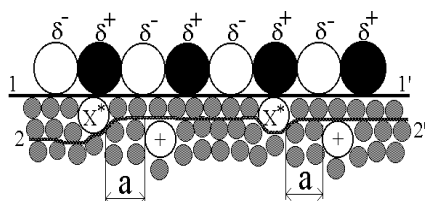**Figure 5.** The β electronic conduction mechanism.

Figure 6. The ionic pairs arrangement for high scanning rate situated over interionic charge transfer threshold.

The adsorbed anion is strongly polarized and it becomes an acceptor from a donor of electron through the intermediate of some activated species in transition. It is possible that X^* will displace an electron into the metal conduction band and will set free an orbital [9]. The mobile interface will move with one monolayer to solution, from 1-1' to 2-2', as shown in Figure 6.

The formation of the common conduction band after anion-metal direct junction has as consequence the decreasing interaction between that anion and its associate cation, which develops a complete hydration cover. Thus, there appears a concentric insulated layer of *a* thickness built from two stabilized dipoles of water between ex-associate ions.

After the mobile interface advancement, the created vacancy on the new superficial active center (X^*) will be occupied through an electronic transfer from another solution donor (X^-). Thus, the conditions will be created for the monowire interionic charge transfer by α conduction mechanism with a low electrical solution resistance. The electrolyte structuring devolves very fast and unidirectional at mobile interface level, which displaces successively in 1-1' → 2-2' → … → n-n' positions, as shown in Figure 7. The necessary energy of the $X^- \rightarrow X^*$ charge transfer exceeds the energetic threshold necessary for ion partial dehydration at the mobile interface level. The junction at the mobile interface level, corresponding to the cathodic and anodic zones, is made in the

median zone of the space between the electrodes, where the charge interionic transfer can be mediated by the water molecule as shown in Figure 8.
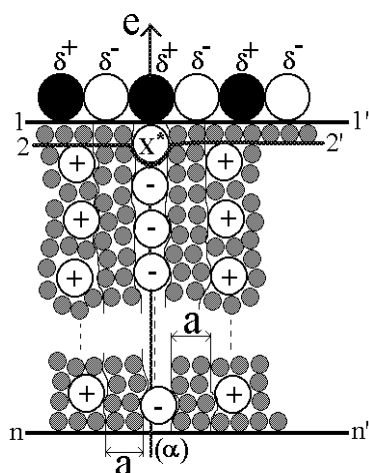

Figure 7. The α electronic conduction mechanism.

Caption of figures:

$\delta\bigcirc$ = acceptor centers localized in the superficial oxides positions

$\delta\bullet$ = donor centers localized in the superficial oxides positions

$\bigcirc$, $\ominus$ = anions (X^-)

$\bullet$, $\oplus$ = cations (Y^+)

$\circ$ = water molecules

First, an optimization of the conductive ways number takes place between electrodes as a function of solution concentration. Then, an optimization of the contacts takes place at the mobile interface level in the median
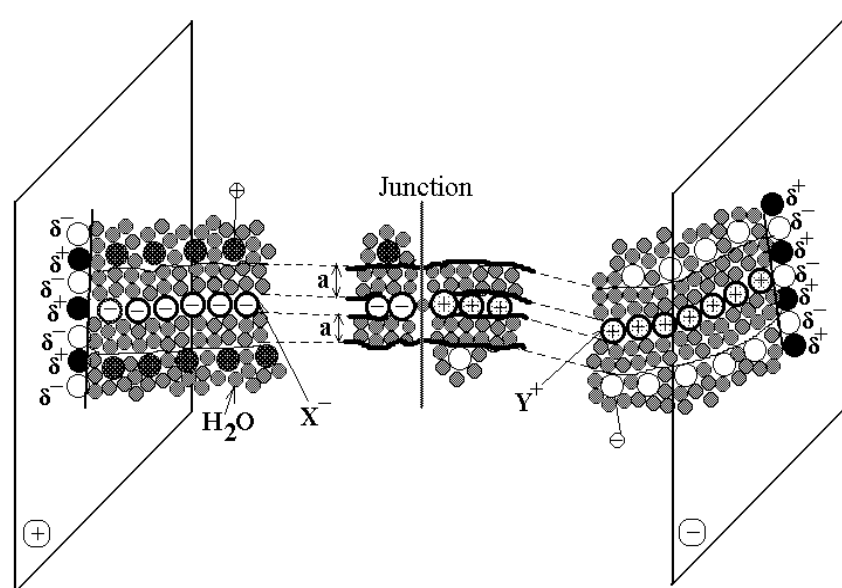

Figure 8. The structural arrangement for the α electronic conduction (monowire conductor type).

zone of the solution by short time activation of the counterions of the adjacent layers, prohibiting increase of the electrical resistance of the electrolyte. Therefore, in the passive domain of the polarization diagram, the electrical current is practically constant. The destabilization of the *a* layer and the tridimensional dynamic reorganization will begin in the electrode zone. An interruption of the circuit in the structural variant

associated with β conduction finds the system near a minimal energy level from the thermodynamic point of view, because this structure does not differ very much from the state of the electrolyte found in open circuit (see Figure 5). An interruption of the circuit in the structural variant associated with α conduction finds the system in instability thermodynamic state, but with a hasty possibility of stabilization by reorientation in limited spaces of the ionic pairs (see Figure 7). In fact, the electrolyte structure forming and the electrolyte structure destroying mechanism at the inverse scanning of the potential is more complex and depends on working conditions, potential scanning rate, temperature, pH, concentration of the solution.

Conclusions

This mechanism is a dynamic model, which starts with a normal distribution of the ions in solution. Electrolyte structuring in the two variants of α and β conduction depends only on overcoming the potential threshold necessary for the interionic charge transfer. The electrolyte structure forming in the field is very fast due to the ionic pair displacement in limited spaces and to high mobility in the energetic transition periods.

In conclusion, as a function of the potential value applied to the electrode and the potential scanning rate, there exists the possibility that the system enters into a branch and it can choose between a minimum electrical resistance variant (α conduction mechanism) or one with a high electrical resistance (β conduction mechanism) where the interionic mixed charge transfer takes place. For the α conduction mechanism in electrolyte solutions, the suggested image is that of an insulated multiwire conductor.

References

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Povzetek

Opisan je mehanizem prevajanja električnega toka v raztopinah elektrolitov. Pomembna elementa tega mehanizma sta struktura medfazne površine elektroda-elektrolit in pa orientacija molekul v solvatni oblogi iona. Elektrolit na osnovi velikosti potenciala izbira med dvema strukturama, eno z minimalno električno upornostjo in drugo z visoko električno upornostjo. Minimalno električno upornost je moč ponazoriti z modelom "večžičnega izoliranega upornika".