BUTLER-VOLMER CURRENT EQUATION AND FRACTAL NATURE CORRECTION IN ELECTROCHEMICAL ENERGY

by

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The Global Energy Crisis necessitated improving research into new, renewable and alternative energy sources. Due to that, our focus is on the area of some phenomena and applications where different synthetic methods and micro-structure property optimization achieved significant improvement in the electro physical properties of output materials and components. This is especially important for higher energy efficiency and electricity production (batteries and battery systems, fuel cells, and hydrogen energy).The improvement of energy storage tank capacity is one of the most important development issues in the energy sphere too. It is because of this very promising research and application area that we are expanding the knowledge on these phenomena through fractal nature analysis. So, the results obtained in the field of electrochemical energy sources, especially in electrolyte development, are taken into account the analysis of fractal nature optimization. Based on the research field of fractal material science, particularly electronic materials, we conducted research in micro-structure fractal influence in the area of electrochemistry. We investigated the consolidation parameters of Fe_2O_3 *redox processes. The influence of activation energy, fundamental thermodynamic parameters, and also the fractal correction of electrode surface area through complex fractal dimension with recognized grains and pores, and the Brownian motion of particles is introduced. Finally, the electrochemical Butler-Volmer equation fractalization is obtained. These results practically open new frontiers in electrochemical energy processes performed through the Arrhenius equation within electrolyte bulk and electrode relations and more complete and precise energy generation.*

Keywords: *electrochemistry, Arrhenius equation, Butler-Volmer equation, thermodynamic parameters, fractals, fractal dimension*

Introduction

Our entire civilization is confronted with high energy deficit today. Researchers are looking for new energy solutions worldwide. Many phenomena and parameters in the field of

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energy have been of minor interest to researchers. Nowadays, when we have a growing energy crisis, there are new and alternative studies in energy sources so the above-mentioned phenomena are becoming increasingly important in terms of scientific and technological development and exploitation. The situation has changed. Many new energy source development projects are based on some findings of earlier research, even though they were marginalized all along. In the struggle for new energy sources, it has become evident that the research fields in this area are actually very rich and full of challenges [1-4].

Regarding the subject, we will give a short review of the main knowledge points in electrochemistry. Electrochemistry, as the branch of physical chemistry that studies chemical reactions taking place at the electrode interface (solid metal or semiconductor) and the electrolyte, *i.e*. anionic conductor involved as electrical charge between the electrodes and the electrolyte motion which also happens to be the point of interest of our research, fig. 1 [1]. Electrochemistry examines the interaction between electrical energy and chemical changes. Catalysis and electrocatalysis, as a part of electrochemistry, are related to the increase in the rate of chemical reaction processes with one or more reactants, involving the presence of an additional substance [5]. This includes all the electrochemical reactions such as the reactions at the surface of an insertion electrode and at the surface of permeation cells. Mixed-ionic-electronic conducting (MIEC) oxides have an increasingly important role in the electrocatalysis. The MIEC are solid semiconductors and metals that conduct both ionic and electronic defects [6, 7]. For example, we can mention the oxygen permeation cell, fig. 2.

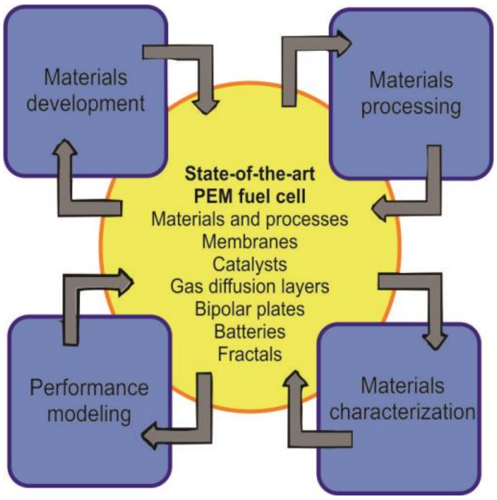

Figure 1. New trends, phenomena, and applications of electrochemical energy sources

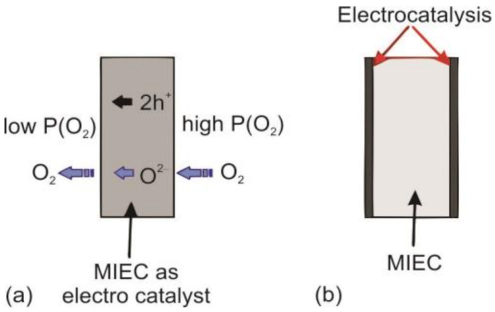

Figure 2. Principle scheme of oxygen processes

The driving force is an oxygen partial pressure difference on the two separate sides of the membrane. The membrane is a MIEC, which allows the oxygen permeation in the form of ions O^{2-} being accompanied by an electronic (electron/hole) current for maintaining charge neutrality, either the MIEC which also catalyses the cathodic and anodic reactions, fig. 2(a), or thin layers that are added on top of the MIEC in order to catalyze these reactions, fig. 2(b). As these layers must be permeable, they are either also MIEC or porous.

In our previous research [8-10] we have already developed and defined the complex fractal correction which includes the influence of grain-and-pore surfaces and also Brownian motion on particles that was already applied to intergranular capacity and dielectric and ferroelectric properties through the Curie-Weiss law and the Clausius-Mossotti equation [11].

We take into consideration the Arrhenius and the Butler-Volmer (describes the electrical current, related to the electrodes and the electrolyte bulk) equations, which define the generation of electrochemistry current and characterize many of mentioned processes as the activation energy, *Ea*, absolute temperature, *T*, the Gibbs free energy, ΔG, and the contact surface area, *A*, [8, 11, 12]. We would like to report on some newest findings from our experimental and theoretical research in the area of micro-structure and the electro physical (electrochemical) properties. This is significant for the electrolyte bulk and for the electrode processes too [8].

Short intro to fractals

Most of the physical, chemical, and mechanical behaviours of practical engineering components and structures can be analysed taking into account the Euclidean geometric dimensions. However, unlike the orderly unit cells, particles, and particle cluster motion as well as the atomic scale and the Euclidean surfaces at macro-scale, micro-nano surface structures, are characterized by randomness and are difficult to characterize quantitatively. In order to analyse these micro-, nano- and super micro-structures, we introduce a new fractal approach. The notable trend in the recent literature is that a wide range of disordered systems, *e.g.*, linear and branched polymers, biopolymers, epoxy resins, and percolation clusters can be characterized by fractal nature over a microscopic correlation length. It is favourable to the fact that energy transformations are permitted on a small scale. Fractals are geometric objects which have broken, fragmented, wrinkled, or amorphous form or are highly irregular in some other way. The term *fractal*, first used by Mandelbrot [13, 14] as a neologism derived from the Latin adjective *fractus*, meaning *fragmented* or *irregular*. What is specific for fractals is some irregularity which cannot be described properly using the concepts of traditional geometry. Fractals reveal a fine-detailed structure on several levels of magnification or scale. On some of these scales self-similarity is sometimes present. This may be the case only approximately or in a random sense. Standard Euclidean geometry fails to describe such objects so they are subjects of fractal geometry.

The classic Cantor *non-middle-third* set, can be constructed using the so-called iterated function system (IFS) with two transformations $w_1(x) = x/3,\ \ w_2(x) = x/3 + 2/3$, joined into one single set operator $W = w_1 \cup w_2$. Starting with the unit interval $X = [0, 1]$:

$$W\big([0,1]\big) = w_1\big([0,1]\big) \bigcup w_2\big([0,1]\big) = \left[0, \frac{1}{3}\right] \bigcup \left[\frac{2}{3}, 1\right] \tag{1}$$

Then, by iterating:

$$\begin{aligned} W^2\big([0,1]\big) &= W\left(\left[0, \frac{1}{3}\right] \cup \left[\frac{2}{3}, 1\right]\right) = w_1\left(\left[0, \frac{1}{3}\right] \cup \left[\frac{2}{3}, 1\right]\right) \bigcup w_2\left(\left[0, \frac{1}{3}\right] \cup \left[\frac{2}{3}, 1\right]\right) = \\ &== \left[0, \frac{1}{9}\right] \cup \left[\frac{2}{9}, \frac{1}{3}\right] \cup \left[\frac{2}{3}, \frac{7}{9}\right] \cup \left[\frac{8}{9}, 1\right] \end{aligned} \tag{2}$$

$$W^3\big([0,1]\big) = \left[0, \frac{1}{27}\right] \cup \left[\frac{2}{27}, \frac{1}{9}\right] \cup \left[\frac{2}{9}, \frac{7}{27}\right] \cup \left[\frac{8}{27}, \frac{1}{3}\right] \cup \left[\frac{2}{3}, \frac{19}{27}\right] \cup \left[\frac{20}{97}, \frac{7}{9}\right] \cup \left[\frac{8}{9}, \frac{25}{27}\right] \cup \left[\frac{26}{27}, 1\right] \tag{3}$$

and so on, fig. 3.

The Cantor set C is the fixed point (invariant) of the operator W, *i.e.* W(C) = C.

Bearing this in mind, the fractal set A could be defined as a subset of the complete metric space, which is invariant in relation to the union W of contraction mappings, *i.e.* W(A) = A.

Figure 3. Cantor set generation using IFS

The main property of a fractal is its fractal dimension DH which is typically non-integer in contrast to the traditional topological dimension DT. For instance, the fractal dimension of the Cantor set on the real line is 0.63, while its topological dimension is 0. The topological dimension of the Koch snowflake is equal to 1, while its fractal dimension is 1.26. Similarly, the topological dimension of the Menger sponge is 2, but its fractal dimension is 2.73. The concept of a dimension and of a fractal dimension in particular is not trivial.

The Hausdorff dimension of the bounded set $A \subset R^n$ is defined as a (unique) real number:

$$\dim_H A = \sup\{d : S_d(A) = \infty\} = \inf\{d : S_d(A) = 0\} \tag{4}$$

where

$$S_d(A) = \lim_{\varepsilon \to 0} \inf \sum_i [\text{diam}(B_i)]^d \tag{5}$$

and the infimum in the last equality is taken over all collections of open balls $\{B_i\}$ in R^n with diameters not greater than ε whose union covers A. It is hard to use this definition directly for numerical computations. That is why other concepts and specific computational methods where proposed.

If a bounded set A is a subset of R^n, then the box dimension is defined as a limit:

$$\dim_B A = \lim_{\varepsilon \to 0} \frac{\ln N(\varepsilon)}{-\ln \varepsilon} \tag{6}$$

where $N(\varepsilon)$ is the smallest number of sets of the diameter ε which can cover A.

It can be shown that:

$$0 \le \dim_H A \le \dim_B A \le n \tag{7}$$

Experimental

For better understanding and demonstration of fractal nature analysis within the electro-chemical processes, we performed a redox experimental procedure, related recombination's and other chemical reactions on the Fe_2O_3 system. To simplify and to make more evident all of this for better understanding, for the moment, we explain the system using one electrode and the electrolyte bulk, while the other electrode and related bulk is neglected.

The Butler-Volmer equation describes how the electrical current on an electrode depends on the electrode potential, considering the fact that both a cathodic and an anodic reaction occur on the same electrode. It accounts for simultaneous anodic (oxidation) reaction and cathodic (reduction) reaction on the same electrode surface, fig. 4.

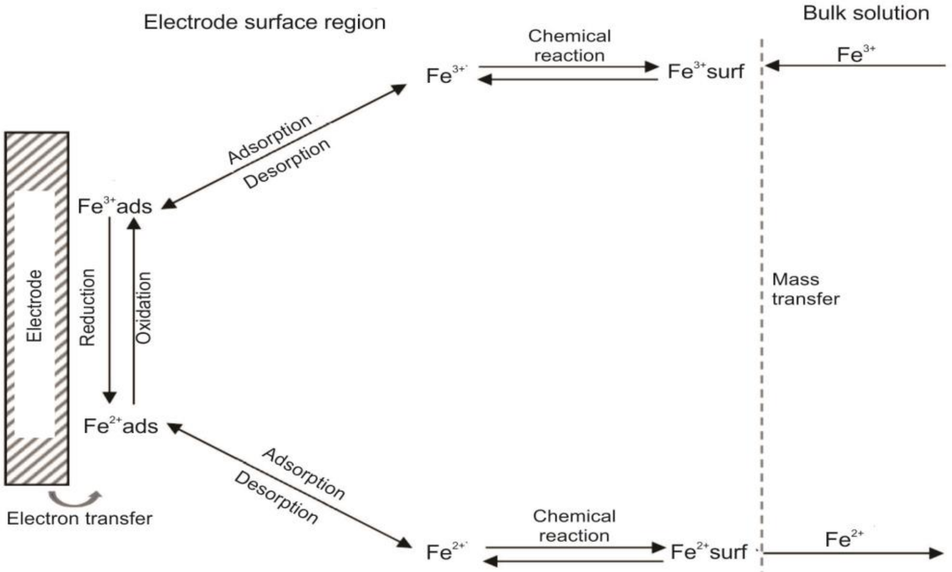

Figure 4. Principal simultaneous redox processes on electrode and electrolyte bulk

Theoretical experiment

To provide better, concrete, and clear insight, we demonstrate the collision processes between ions (cations and anions) and electron clusters within the area of electrolyte bulk. Here, we basically understand the relations of the extremely different masses of ions and electron clusters which are listed and explained below:

Mass of electron = 5.486×10^{-4} amu
Mass of Fe^{3+} ion = 55.93333 amu
Mass of Fe^{2+} ion = 55.9338 amu
amu = 1.6605×10^{-24} g

The ionic radius of Fe^{2+} is 0.6 nm and that of Fe^{3+} is 0.9 nm [15]. However, in aqueous solutions, these ions do not appear individually but hydrate (co-ordinated) with 6 molecules of water. Thus, their formula is $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$ so that their real radii are about three times larger, or about 1.8 nm and 2.7 nm, respectively. So, it is evident, when the Fe^{2+} ion loses one electron and transforms itself into Fe^{3+}, with amu which is, in comparison with Fe^{2+} amu, reduced by one electron mass. However, on the other side, we have six associated molecules of water amounting to extremely high Fe^{3+} amu. All this reflects on the collision process between the electron cluster and the Fe^{3+} ion with these six molecules of water by an order of magnitude of 105, which is demonstrated on fig. 5:

For the moment we are neglecting and not taking into consideration electrostatic processes as those will be the subject of another scientific paper.

Regarding the contact processes of ions and electron clusters on the electrode surface, we simulated and demonstrated those on fig. 6.

Using this simulation, we made visible the grains and their polyhedral surface morphology only but without the insight into the porosity which will all reflect on our physical-mathematical discussion and fractal corrections later on.

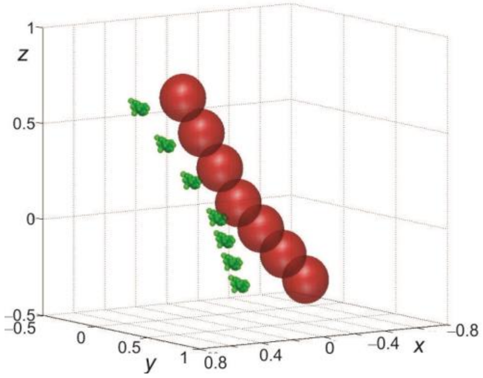

Figure 5. Simulation of collision process between hydrated Fe^{3+} ion (red) electron (green)

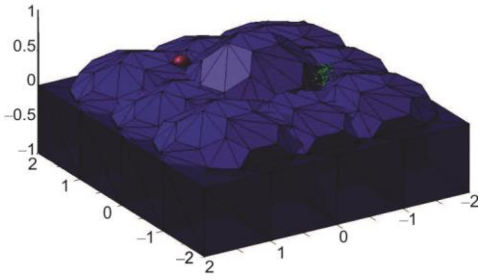

Figure 6. Model of electrons (green) and and ions (red) interacting with polyhedral fractal surface grain shapes

Results and discussion

In all electrochemical processes, which are important for the electrochemical renewable energy sources, we will consider numerous new approaches. The fractal nature of the contacts and collisions of cations, anions, electron clusters, and also the electrode surface effects is recognized. On the other hand, in the contact, collision, and electrostatic recombination of particles with electrode surfaces, we recognize that Brownian motion can also be described using fractal nature.

Regarding the ultimate goal of achieving the most precise electrical current based on the aforementioned electrochemical process, we consider the Butler-Valmer equation. This equation is based on the rate constant that is related to temperature and performed as the Arrhenius equation. In both cases, we have different experimental constants whose values can vary in accordance with different redox processes, and also some physical parameters like the process temperature, T, (absolute temperature), activation energy, E_a, correspondent with specified reaction as well as the Gibbs energy of activation. We can see from the Butler-Valmer equation and the surface area parameter, A, that the micro-structure geometry and morphology exhibit characteristics of fractal nature. In modern microelectronic miniaturization, there is a challenge to describe and analyse many electrochemical processes by fractal nature. So, we will correct all the aforementioned parameters in domain surface, temperature, and energy using fractal corrections.

The driving force for a reaction is an increase in entropy which may be considered a degree of system disorder. In a closed system, a process will occur spontaneously if the entropy of the system increases. The thermodynamic function which is the quantitative measure of the net driving force (at constant temperature and pressure), the Gibbs energy change, ΔG:

$$\Delta G = \Delta H - T\Delta S \tag{8}$$

where ΔH is the enthalpy change of the system (the approximate entropy changes in surroundings) and ΔS is the entropy change of the system. This is the Gibbs-Helmholtz equation. The process that results in a decrease in Gibbs free energy ($\Delta G < 0$) is one which causes a net increase in the entropy of the system plus surroundings and is, therefore, able to occur spontaneously if such a mechanism is available.

In this scientific paper, we are not analysing fractal nature related to entropy because our previous results regarding this question are the subject of an already published paper [11].

Consider a simple reaction A→B occurring in a closed system. Let Γ be the mass action ratio equal to [B]/[A]. If the mixture of a reactant and a product happens to be at equilibrium, the mass action ratio of these equilibrium concentrations is the equilibrium constant K. When G is plotted as a function of the logarithm of Γ/K, a parabola is obtained.

The Gibbs free energy change ΔG is as follows:

$$\Delta G = \mathrm{R}T\ln\frac{\Gamma}{K} = -\mathrm{R}T\ln K + \mathrm{R}T\ln\Gamma \tag{9}$$

where R is the gas constant 8.3144598 $\mathrm{Jmol^{-1}K^{-1}}$ and T – the absolute temperature.

The values of $-\mathrm{R}T\ \ln K$ (at equilibrium concentrations) can be derived for standard conditions. It is the standard Gibbs free energy change ΔG^0, thus:

$$\Delta G = \Delta G^0 + \mathrm{R}T\ln\Gamma \tag{10}$$

where ΔG defines the capacity for the useful work, w:

$$w = -\Delta G \tag{11}$$

Redox reaction

Redox reaction occurs at the electrode surface and can be written:

$$Ox + \mathrm{ne}^- \underset{k_b}{\overset{k_f}{\Leftrightarrow}} \mathrm{Red} \tag{12}$$

and, for the $\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+}$ system, as:

$$\mathrm{Fe}^{3+} + \mathrm{e}^- \underset{k_b}{\overset{k_f}{\Leftrightarrow}} \mathrm{Fe}^{2+} \tag{13}$$

The electrical work, w, done by the redox couple, in which n electrons participate:

$$w = nFE \tag{14}$$

where F is the Faraday constant (96485 C/mol) and E – the Redox potential, yields: $-\Delta G = nFE$, similarly $-\Delta G^0 = nFE^0$, E^0 is the standard redox potential.

From eq.10 this follows:

$$-nFE = -nFE^0 + \mathrm{R}T\ln\frac{[\text{reduced}]}{[\text{oxidized}]} \tag{15}$$

Which can be reduced to:

$$E = E^0 + \frac{\mathrm{R}T}{nF}\ln\frac{[\text{oxidized}]}{[\text{reduced}]} \tag{16}$$

When current is passed, some electrochemical change occurs at the electrode (the dependence of current on potential). The reaction has forward and backward paths. The forward component proceeds at a rate of v_f that must be proportional to the surface concentration of Ox. We express the concentration at the distance d from the surface and at the time, t, as $C_{Ox}(d, t)$. Hence, the surface concentration is $C_{Ox}(0, t)$. The constant of proportionality linking the forward reaction rate to $C_{Ox}(0, t)$ is the rate constant k_f. Since the forward reaction is a reduction, there is the cathodic current i_c, proportional to v_f:

$$v_f = k_f C_{Ox}\left(0,t\right) = \frac{i_c}{nFA} \tag{17}$$

where A is the surface area of the electrode

Likewise, for the backward reaction, we have:

$$v_b = k_b C_{\mathrm{Red}}\left(0,t\right) = \frac{i_a}{nFA} \tag{18}$$

where i_a is the anodic component to the total current. Thus, the net reaction rate is:

$$v_{\mathrm{net}} = v_f - v_b = k_f C_{O_x}\left(0,t\right) - k_b C_{\mathrm{Red}}\left(0,t\right) = \frac{i_c - i_a}{nFA} \tag{19}$$

Then, the net current can be written:

$$i = nFA\left[k_f C_{O_x}\left(0,t\right) - k_b C_{\mathrm{Red}}\left(0,t\right)\right] \tag{20}$$

- Both k_f and k_b are potential-dependent functions.
- The forward reaction (a reduction) is an electron accepting process – the rate increases as the electrode potential becomes more negative; this is because the electrode can give away electrons more easily.
- The opposite trend is observed for the backward (oxidation) reaction – the rate increases as the electrode potential becomes more positive.

It is possible to adjust the electrode potential and *Ox* and Red concentrations to make the net reaction rate zero. At this point:

$$i_c = i_a; \quad k_f C_{Ox}\left(0,t\right) = k_b C_{\mathrm{Red}}\left(0,t\right) \tag{21}$$

This yields:

$$\frac{C_{Ox}\left(0,t\right)}{C_{\mathrm{Red}}\left(0,t\right)} = \frac{k_b}{k_f} \tag{22}$$

$$\ln k_b - \ln k_f = \ln\frac{C_{Ox}\left(0,t\right)}{C_{\mathrm{Red}}\left(0,t\right)} \tag{23}$$

From eq. 16:

$$\ln\frac{[\mathrm{oxidized}]}{[\mathrm{reduced}]} = \frac{nF}{\mathrm{R}T}(E - E^0) \tag{24}$$

Obviously:

$$\frac{\mathrm{R}T}{nF}\left(\ln k_b + \ln\frac{1}{k_f}\right) = E - E^0 \tag{25}$$

By differentiation with respect to E:

$$\frac{\mathrm{R}T}{nF}\left[\frac{\mathrm{d}}{\mathrm{d}E}(\ln k_b) + \frac{\mathrm{d}}{\mathrm{d}E}\left(\ln\frac{1}{k_f}\right)\right] = 1 \tag{26}$$

Let 1-α be the first addend and α the second one:

$$\frac{\mathrm{R}T}{nF}\frac{\mathrm{d}}{\mathrm{d}E}\left(\ln\frac{1}{k_f}\right) = \alpha, \quad \frac{\mathrm{R}T}{nF}\frac{\mathrm{d}}{\mathrm{d}E}(\ln k_b) = 1 - \alpha \tag{27}$$

where α is the transfer coefficient.

By the integration of:

$$\mathrm{d}\left(\ln\frac{1}{k_f}\right)=\frac{\alpha nF}{\mathrm{R}T}\mathrm{d}E,\quad \mathrm{d}(\ln k_b)=\frac{(1-\alpha)nF}{\mathrm{R}T}\mathrm{d}E \tag{28}$$

we get:

$$k_f=k_f{}^0\mathrm{e}^{-\frac{\alpha nF}{\mathrm{R}T}\left(E-E^0\right)},\quad k_b=k_b{}^0\mathrm{e}^{\frac{(1-\alpha)\mathrm{n}F}{\mathrm{R}T}\left(E-E^0\right)} \tag{29}$$

where k_f^0,k_b^0 are the standard rate constants for $E = E^0$.

If the concentrations of *Ox* and *Red* are equal and the potential is maintained at E^0 to prevent current flow from, eq. 21:

$$k_f{}^0=k_b{}^0=k^0 \tag{30}$$

$$k_f=k^0\mathrm{e}^{-\frac{\alpha F}{\mathrm{R}T}\left(E-E^0\right)},\quad k_b=k^0\mathrm{e}^{\frac{(1-\alpha)F}{\mathrm{R}T}\left(E-E^0\right)} \tag{31}$$

finally, the Butler-Volmer equation is:

$$\begin{aligned} i &= nFA[k_f C_{Ox}(0,t)-k_b C_{Red}(0,t)]= \\ &= nFAk^0\left[C_{Ox}(0,t)\mathrm{e}^{-\frac{\alpha nF}{\mathrm{R}T}\left(E-E^0\right)}-C_{Red}(0,t)\mathrm{e}^{\frac{(1-\alpha)\mathrm{n}F}{\mathrm{R}T}\left(E-E^0\right)}\right]\end{aligned} \tag{32}$$

Rate constant

It is an experimental fact that most rate constants of solution-phase reactions vary with temperature in a common fashion: nearly always, log(k) is linear with $1/T$. Arrhenius was the first one to recognize the generality of this behaviour, and he proposed that rate constants be expressed in the form of:

$$k=A\mathrm{e}^{-\frac{E_a}{\mathrm{R}T}} \tag{33}$$

where A is the pre-exponential factor (a constant for each chemical reaction), E_a – the activation energy for the reaction, R – the gas constant 8.3144598 $\mathrm{Jmol^{-1}K^{-1}}$, and T – the absolute temperature.

The pre-exponential factor is considered the probability of surmounting the energy barrier of the height, E_a (the activation energy) by using thermal energy. While the exponential expresses the probability of surmounting the barrier, A must be related to the frequency of attempts; thus, A is considered the frequency factor. According to collision theory, the frequency factor is given by:

$$A=\left(\frac{\sigma_1+\sigma_2}{2}\right)^2\pi\sqrt{\frac{8k_BT}{\pi}\left(\frac{1}{m_1}+\frac{1}{m_2}\right)} \tag{34}$$

where m_i is the mass of particle i (I = 1,2), σ_i – the diameter of particle i (I = 1,2), and k_B – the Boltzmann constant.

According to transition state theory, the reactants are first transformed into intermediate transition state (also known as *activated complex*). The activation energy is the additional energy which should be supplied to the reactants in order to form the activated complex or to reach the peak of the energy barrier as shown in fig. 7.

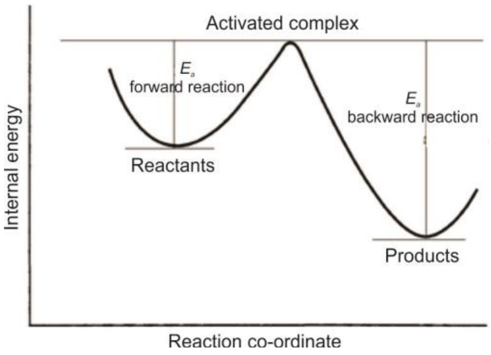

Figure 7. Internal energy surface as function of reaction co-ordinate

One zone of this surface corresponds to the state we call *reactants*, and the other corresponds to the state of the *products*. Both occupy minima on the internal energy surface because they are the only states possessing a significant lifetime. As the reaction takes place, the co-ordinates are changed from those of the reactants to those of the products and *vice versa*. The height of the maximum above the minima is identified with the activation energy, for the forward or the backward reaction, respectively.

We might designate the activation energy E_a as the standard internal energy of the activation $\Delta E^{\neq}$. Then, the standard enthalpy of activation $\Delta H^{\neq}$ would be $\Delta E^{\neq} + \Delta(PV)^{\neq}$ but $\Delta(PV)^{\neq}$ is usually negligible in a condensed-phase reaction so that $\Delta E^{\neq} \approx \Delta H^{\neq}$. Thus, the Arrhenius equation could be recast as:

$$k = A\mathrm{e}^{-\frac{\Delta H^{\neq}}{\mathrm{R}T}} \tag{35}$$

The enthalpy of activation $\Delta H^{\neq}$ could be expressed as $\Delta G^{\neq} + T\Delta S^{\neq}$ with $\Delta G^{\neq}$ the standard Gibbs free energy of activation and $\Delta S^{\neq}$ the standard entropy of activation. This yields:

$$k = A\mathrm{e}^{-\frac{\Delta S^{\neq}}{\mathrm{R}}}\mathrm{e}^{-\frac{\Delta G^{\neq}}{\mathrm{R}T}} \tag{36}$$

or

$$k = A_r\mathrm{e}^{-\frac{\Delta G^{\neq}}{\mathrm{R}T}} \tag{37}$$

Where

$$A_r = A\mathrm{e}^{-\frac{\Delta S^{\neq}}{\mathrm{R}}} \tag{38}$$

If we take this form of the standard rate constant k_0, the Butler-Volmer equation is:

$$i = nFA\left(\frac{\sigma_1+\sigma_2}{2}\right)^2 \pi\sqrt{\frac{8k_BT}{\pi}\left(\frac{1}{m_1}+\frac{1}{m_2}\right)}\mathrm{e}^{-\frac{\Delta G^{\neq}}{\mathrm{R}T}}\left[C_{Ox}(0,t)\mathrm{e}^{-\frac{\alpha nF}{\mathrm{R}T}\left(E-E^0\right)} - C_{Red}(0,t)\mathrm{e}^{\frac{(1-\alpha)\mathrm{n}F}{\mathrm{R}T}\left(E-E^0\right)}\right] \tag{39}$$

Regarding the reaction rate which is proportional to the absolute temperature, our hypothesis is that the Brownian motion of particles in the electrolyte bulk and the absolute temperature influence the reaction rate. Let the fractal dimension of the Brownian motion of particles be $\alpha_M > 1$ so we propose the following correction of the absolute temperature factor T^1:

$$T_f \approx \left(\frac{T}{T_0}\right)^{\frac{1}{\alpha_M}} T_0 \tag{40}$$

$$T_f \approx \left(\frac{T}{T_0}\right)^{\alpha_M} T_0 \tag{41}$$

where T_0 is the unit temperature.

If we consider the case of $T_f \sim (\cdot)^{\alpha_M}$, we can understand that Brownian motion as a physical representation of chaotic motion in particles system within the framework of general thermodynamic rules, practically causes the temperature rise in the local particle system. In the case of $T_f \sim (\cdot)^{\frac{1}{\alpha_M}}$, because of the decrease in exponential value we have a slight temperature decrease in the local particle system due to the spread of frequently colliding particles in high volume extended area which brings about the energy depletion in small particle systems. So, we take the second approach to be more realistic. Thus, in this paper we will use this approach.

Regarding the electric current on the electrode which is proportional to the electrode surface area *A*, the following correction is proposed. Supposing that the nature of the electrode surface is fractal, we consider the relation between the surface area *A* and its volume *V*:

$$A \approx \left(\frac{V}{V_0}\right)^{\frac{2}{3}} A_0 \tag{42}$$

where A_0 and V_0 are the unit surface area and the unit volume, respectively.

Similarly, as 2 is the topological dimension of a surface, the previous factor could obviously be generalized for the fractal surface *A* with the fractal dimension $\alpha_s > 2$, as:

$$A_f \approx \left(\frac{V}{V_0}\right)^{\frac{\alpha_s}{3}} A_0 \tag{43}$$

In case of a non-fractal, *i.e.* smooth surface $\alpha_s = 2$, the previous relation is reduced to an ordinary one.

As far as the physical-mathematical grain micro-surface and the overall electrode surface analysis is concerned, we have identified the presence of fractal nature in this morphology which is confirmed by reconstructing many micro-structure fractals.

Finally:

$$\begin{aligned} i = knF\left(\frac{V}{V_0}\right)^{\frac{\alpha_s}{3}} A_0\left(\frac{\sigma_1+\sigma_2}{2}\right)^2 \pi\sqrt{\frac{8k_B\left(\frac{T}{T_0}\right)^{1/\alpha_M} T_0}{\pi}\left(\frac{1}{m_1}+\frac{1}{m_2}\right)}\,\mathrm{e}^{-\frac{\Delta G^{\neq}}{\mathrm{R}T}} \cdot \\ \cdot\left[C_{Ox}(0,t)\,\mathrm{e}^{-\frac{\alpha nF}{\mathrm{R}T}\left(E-E^0\right)} - C_{Red}(0,t)\,\mathrm{e}^{\frac{(1-\alpha)\mathrm{n}F}{\mathrm{R}T}\left(E-E^0\right)}\right] \end{aligned} \tag{44}$$

where *k* is constant.

If we summarize our findings, we can complete our analysis and comprehensive overview by physical-mathematical redesigning of the Arrhenius and the Butler-Volmer equations. After many changes and the completion of these equations in past decades, which mostly treated some physical-chemical constants and parameters, now we have additional corrections based on fractal nature which are giving significant contribution to more realistic and precise understanding of the processes on thin and super-micro levels.

Conclusion

Today, we are definitely faced with an increasing demand for energy. The diversity of research and development in new and alternative energy sources contributes to energy growth and the establishment of a more efficient equilibrium between the demand for energy and the lack of it. Many new phenomena in the area of electrochemical sources open quite new possibilities to get more energy, provide efficient storage and, in general, more flexible electrochemical energy sources according to the variety of applications.

In this paper, we applied the fractal nature analysis to the electrolyte bulk and the electrode processes so we could provide a more precise control of the real chemical-physical substance in the whole closed electro-chemical system. So, we practically introduced quite a new approach and illuminated different aspects of thermodynamic parameters (the Gibbs free energy, the absolute temperature), the contact surfaces between electrodes, and the electrolyte bulk. We have new shape and structure of the Butler-Volmer current equation which includes the insight into the fractal nature of these energy source systems. In this scientific field, we have undertaken a pioneering endeavour and there is a possibility of its application in current photovoltaic systems. The scope of the application along with the limitations of the proposed model could be the subject of some future research.

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