The Fractal Nature Materials Microstructure Influence on Electrochemical Energy Sources

V.V. Mitić$^{1,2}$, Lj. Kocić$^1$, V. Paunović$^1$, F. Bastić$^{1*)}$, D. Sirmić$^1$

$^1$University of Niš, Faculty of Electronic Engineering, Aleksandra Medvedeva 14, 18000 Niš, Serbia
$^2$Institute of Technical Sciences of SASA, Knez Mihailova 35, 11000 Belgrade, Serbia

Abstract: With increasing of the world energy crisis, research for new, renewable and alternative energy sources are in growth. The focus is on research areas, sometimes of minor importance and applications, where the different synthesis methods and microstructure properties optimization, performed significant improvement of output materials' and components’ electro-physical properties, which is important for higher energy efficiency and in the electricity production (batteries and battery systems, fuel cells and hydrogen energy) contribution. Also, the storage tanks capacity improvement, for the energy produced on such way, which is one of the most important development issues in the energy sphere, represents a very promising research and application area. Having in mind, the results achieved in the electrochemical energy sources field, especially electrolyte development, these energy sources, materials fractal nature optimization analysis contribution, have been investigated. Based on materials fractal structure research field, particularly electronic materials, we have performed microstructure influence parameters research in electrochemistry area. We have investigated the Ho$_2$O$_3$ concentration influence (from 0.01wt% to 1wt%) and sintering temperature (from 1320°C to 1380°C), as consolidation parameters, and thus, also open the electrochemical function fractalization door and in the basic thermodynamic parameters the fractal correction introduced. The fractal dimension dependence on additive concentration is also investigated.

Keywords: Electrochemistry, Battery systems, Microstructure, Thermodynamic parameters, Fractals, Fractal dimension.

1. Introduction

Today, we confront with our entire civilization future development high energy deficit, a good reason the worldwide scientific research are looking for new energy solutions. Many, new and alternative energy sources studies, which have been done in a previous couple of centuries, and the scientific and technological development have less importance in exploitation, up today. Nowadays, just opposite, many new energy sources development projects are focused just on some results and phenomena which have been a subject of previous investigations, as it was mentioned above, and while the time have been, somehow “aside”. So the research fields in energy area are actually very rich and full of challenges [1,
Fig. 1. Global new energy sources R&D circle design of PEM (Proton Exchange Membrane) fuel cell materials and processes.

Because of this scientific paper subject, we will give short electrochemistry main points knowledge review. Electrochemistry, as the chemical reactions studies science, which takes place at the interface of the electrode (solid metal or semiconductor) and the electrolyte, i.e. an ionic conductors, involved as electrical charge between the electrodes and the electrolyte movement is the area of our interest in research, too (Fig.1) [3]. It means, practically examines the interaction between electrical energy and chemical changes. The catalysis, or especially electrocatalysis, as a part of electrochemistry, practically considering the chemical reaction rate increasing processes with one or more reactants with the additional substances presence, known as the catalyst [4]. It is also including, all of the electrochemical reaction, such as reactions at the surface of an insertion electrode and at the surface of permeation cells. Mixed-ionic-electronic conducting oxides have an increasing role in the electrocatalyst [5]. Typical examples are the electrodes in solid oxide fuel cells, SOFC, and the membrane that separates oxygen from the air. Mixed Ionic Electronic Conductor, MIEC, are solid semiconductors and metals that conduct both ionic and electronic defects [6]. Also, we can mention as example a cell for oxygen permeation (Fig. 2). The driving force is an oxygen partial pressure difference on the two separation membrane sides; 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. It is, either, the MIEC which also catalyses the cathodic and anodic reactions (Fig. 2a), or, thin layers that are added on top of the MIEC, in order to catalyze these reactions, (Fig. 2b). As these layers must be permeable, they are either also MIECs or porous.

Fig. 2. a) Oxygen MIEC permeation membrane that is also the electro-catalyst, b) oxygen MIEC permeation membrane with two thin MIEC electro-catalysts coating (also MIECs).
In that sense, we will take in consideration some of equations, which are electrophysically characterize, many of previous mentioned processes, as the Gibbs free energy equation, the Gibbs free energy ($\Delta G$), the cell potential ($E^{\circ}_{\text{cell}}$) and the equilibrium constants ($K$) connection equation and the Butler-Volmer equation (describes the electrical current, related to electrodes, potential dependence).

Also, we would like to reminded on some newest results from our experimental and theoretical research in the area of microstructure fractalization and the electro-physical properties, which have been resulted based on that. This is very significant for electrolyte bulk, too.

2. Experimental procedure

The samples of $\text{Ho}_2\text{O}_3$ doped $\text{BaTiO}_3$ were prepared by conventional solid state reaction. Reagent grade $\text{BaTiO}_3$ powder (Murata) with Ba and Ti ratio of 1,005 and $\text{Ho}_2\text{O}_3$ powders (Fluka chemika) were used as starting materials. The content of additive oxides ranged from 0.01wt% to 1wt% $\text{Ho}_2\text{O}_3$. Starting powders were balls, milled in ethyl alcohol for 24 hours using polypropylene bottle and zirconia balls. After drying at 200°C for several hours, the powders were pressed into 7mm disk diameter and 3mm thickness under 120 MPa. The compacts were sintered from 1320°C to 1380°C in air for four hours. Sintered samples were further exposed to the standard preparation procedure, such as cleaning of refractory sand, then partly silvering using silver-palladium paste, to which the solder is performed for further samples measurement, testing and characterization, and further electrophysical testing on the lifecycle and moist heat with appropriate equipment and chambers.

The electron microscope further analysis these previously tested samples, have been also applied; the necessary preparation procedures were completed, the samples were covered with a gold thin layer, using the sputter process. Thus prepared samples were exposed to analysis in the electron microscope (JEOL JSM-5300), where the microstructure analysis were performed under different magnifications [7, 8]. SEM micrographs of $\text{Ho}_2\text{O}_3$ doped $\text{BaTiO}_3$ with diferent dopant concentration and different sintering temperatures are shown in Fig. 3.

![SEM micrographs of $\text{Ho}_2\text{O}_3$ doped $\text{BaTiO}_3$ sintered at 1320°C with a) 0.01wt% $\text{Ho}_2\text{O}_3$, b) 0.1wt% $\text{Ho}_2\text{O}_3$, c) 1wt% $\text{Ho}_2\text{O}_3$ and sintered at 1380°C with d) 0.01wt% $\text{Ho}_2\text{O}_3$, e) 0.1wt% $\text{Ho}_2\text{O}_3$, f) 1wt% $\text{Ho}_2\text{O}_3$.](image-url)
3. Results and Discussion

Based on SEM analysed samples, we noticed, for 0.1wt% of Ho$_2$O$_3$/BaTiO$_3$, the size of the grains was up to 50µm, but by increasing the dopant concentration to 1wt% the average grain size was from 4µm to 10µm. Also, the spiral concentric grain growth, for the samples sintered with 0.1wt% of Ho$_2$O$_3$, disappeared when the concentration increased up to 1wt% of dopant.

For Ho$_2$O$_3$ doped BaTiO$_3$-ceramics, sintered at 1320ºC, density varies from 80% of theoretical density (TD) for high doped samples (1.0wt% of dopant), to 93% TD for samples doped with 0.01wt% Ho$_2$O$_3$ [9].

In previous papers [8, 11, 12, 19, 20] the stress was set on fractal nature of perovskite ceramics structure. It was interesting here to estimate fractal dimensions D$_f$ of BaTiO$_3$-ceramics specimens with different Ho$_2$O$_3$ percentage (0.01wt% - 1wt%) and compare obtained results. Fig. 4 (middle) shows the surface reconstruction of the SEM (a) from Fig. 3, and its Fourier transform indicating pretty high fractal dimension of such a reconstructed surface. Three sets of BaTiO$_3$-ceramics specimens were prepared with 0.01wt%, 0.1wt% and 1wt% Ho$_2$O$_3$ and shot on SEM with magnifications of 3500, 5000, 7500, 10000 and 15000 each. The box-counting algorithm then applied to reveal fractal dimension of such SEM photos. The results are given in Tab. I.

Tab. I. Fractal dimension (by box-counting) of BaTiO$_3$-ceramics with different additive concentrations and different magnifications

<table>
<thead>
<tr>
<th>Additive</th>
<th>Fractal dimension calculated by box-counting technique</th>
</tr>
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<tbody>
<tr>
<td>0.01wt%</td>
<td>1.7549 1.7697 1.8102 1.7282 1.8076</td>
</tr>
<tr>
<td>0.1wt%</td>
<td>1.7890 1.7570 1.7633 1.7534 1.8228</td>
</tr>
<tr>
<td>1wt%</td>
<td>1.7903 1.7694 1.7894 1.8264 1.8515</td>
</tr>
</tbody>
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The data of each set then are approximated by a cubic spline function which are represented by Fig. 5.

Fig. 4. Left: The square sample of the SEM (a) from Fig. 3. Middle: Surface reconstruction based on gray levels distribution. Right: Fourier transform of the surface data.

The latest materials fractal nature and structure research, which involves the necessary fractal correction to the corresponding basic thermodynamic parameters and associated physical-mathematical apparatus, can introduce significant new results within the research which rebuilt the thermodynamic fundamental process principles in the material world. Above all, it is bringin, in functional connectivity, Hausdorff fractal dimension, which enables the order recognition, reconstruction and prognosing the materials microstructural constituents shape and bringing them out of the chaotic and asymmetric shapes in a controlled and regulated, on the one hand, with the thermodynamic system fractalized entropy, on the other hand.
Because the intergranular contacts inside the BaTiO$_3$-ceramics materials, we may understand, now, the intergranular capacities real nature, and use it as a phenomena explanation of capacities fair high amount realized with barium-titanate ceramics and ceramics based on the other perovskite materials. This phenomena are stressed in a set of recent papers [10-18], in the form of a correction factor $r_\varepsilon$ that we added as a multiplicative constant for relative permittivity $\varepsilon_r$ of the ceramics material under consideration. In this manner, instead of $\varepsilon_r$ in all formulas we set $\alpha r_\varepsilon$, with a hypotheses that the real number $\alpha$ compensates increasing capacity that comes from the intergranular contacts fractal nature. One way is to estimate the value of $\alpha$ to lead it out from the outline fractal dimension or the ceramics grains surface. In the meantime this idea was more elaborated to get its final form.

Since the fractal dimension $D_H$ of a typical grain's surface is just slightly above surface’s topological dimension, $D_T = 2$, the difference $D_H - D_T = D_H - 2$, is thereby supposed to be responsible for affection to a part of ferroelectric phenomena in barium-titanate ceramics that can not be explain by purely grain surfaces Euclidean geometry [19]. But, since the measured fractal dimension differs throughout the ceramics material, it is suitable to introduce a normalized surface fractality parameter $\alpha_s$:

$$\alpha_s = \frac{1}{\max\{D_H\} - \min\{D_H\}} \left( D_H - \min\{D_H\} \right),$$

which ensures the unit range $0 < \alpha_s < 1$.

But, BaTiO$_3$-ceramics is also a porous material that corresponds to a lacunar fractal models. It brings in a new phenomenon. Namely, solidification of porous and “spongy” materials increases overall fractal dimension from (theoretically) 2 to full solid 3. In other words, fractal dimension $D_H$ of a porous material ranges $2 < D_H < 3$. It causes another correction factor, “$\alpha$-pores”,

$$\alpha_p = D_T - D_H,$$
where \( D_T \) is dimension of the space and \( DH_p \) is corresponding fractal dimension of a porous configuration. Therefore, \( 0 < \alpha_p < 1 \). Due to their geometric root, the dimensionless quantities \( \alpha_s \) and \( \alpha_p \) will be called geometric fractality factors.

Further, we are aware of the existence of the third (dimensionless) factor \( \alpha_M \) carrying over the influence of disorder movement of ferroelectric particles that is factor of fractal movements.

As it is known, there is a moving “cloud” of moving particles in semiconductors (and metals as well) consists of electrons in atoms with large atomic numbers, nucleons in heavy atomic nuclei, and gases consisting of quasi particles with half-integral spin. This is called Fermi gas and obeys Fermi-Dirac statistics. The classic theory of Fermi gas assumes that (i) the interactions between the electrons are irrelevant and can be ignored; (ii) the electrons move in a constant potential and we can ignore everything about the structure of the material; (iii) The crystal comprises a fixed background of \( N \) identical positively charge nuclei and \( N \) electrons, which can move freely inside the crystal without seeing any of the nuclei (monovalent case); and (vi) Coulomb interactions are negligible because the system is neutral overall.

Now, real Fermi gas dynamics impose necessity of fractal movements factor \( \alpha_M \) inclusion, that makes third factor, next to geometric ones \( \alpha_s \) and \( \alpha_p \). Since Fermi gas particles have dynamics similar to 3D Brownian one, \( \alpha_M \) should be derivate of Hausdorff fractal dimension \( DH_M \) of a Brownian 3D space-filling curve. It is obvious that \( 1 \leq DH_M \leq 3 \). The lower limit, \( \min_{DH_M} = 1 \), is imposed by continuity of trajectory of a particle. The upper limit \( \max_{DH_M} = 3 \), in turn is the maximum of trajectory complexity in 3D space. It is reasonable to normalize quantity \( \alpha_M \), by taking

\[
\alpha_M = \frac{1}{\max \{DH_M\} - \min \{DH_M\}} \left( DH_M - \min \{DH_M\} \right),
\]

which ensures \( 0 < \alpha_M < 1 \).

In this way, three independent dimensionless fractality factors \( \alpha_s \), \( \alpha_p \) and \( \alpha_M \) are introduced. These are real numbers from the open interval \((0, 1)\).

Now, our hypothesis is that working temperature of \( \text{BaTiO}_3 \)-ceramics must be influenced by these three fractality factors, making correction of „theoretic” temperature \( T \), to get the new “real” temperature \( T_r \), which is temperature actually lower than \( T \) which is affected by the material inner fractality, and thereby \( T_r = T - \Delta T \). Obviously, \( T_r \leq T \) with equality if no fractal structure of \( S \), \( P \) or \( M \) type is present. Now, by setting \( \alpha = \frac{T_r}{T} = 1 - \frac{\Delta T}{T} \), one has \( T_r = \alpha T \), where \( \alpha \) is depends on all three alpha-components \( \alpha_s \), \( \alpha_p \) and \( \alpha_M \) given by (1), (2) and (3), so,

\[
\alpha = \Phi \left( \alpha_s, \alpha_p, \alpha_M \right). \tag{4}
\]

Now by the Curie-Weiss law, the relative permittivity will be given by

\[
\varepsilon_r = \frac{C_c}{T_r - T_C} = \frac{C_c}{\alpha T - T_C} = \frac{C_c}{\Phi \left( \alpha_s, \alpha_p, \alpha_M \right) \left( T - T_C \right)},
\]

where \( C_c \) is the Curie constant \( C_c = 1.7 \times 10^6 \text{K} \). This is the natural way to show how the dielectric constant incorporates the influence of fractal nature of the ceramics materials.
this way, capacity is slightly bigger than it will be if the fractal nature of BaTiO$_3$-ceramics is neglected [20].

We underline that the function $\Phi$ is unknown by now, but a good approximation would be a linear combination of $\alpha_s, \alpha_p$, and $\alpha_M$, 
\begin{equation}
\alpha = \Phi(\alpha_s, \alpha_p, \alpha_M) = \omega_1\alpha_s + \omega_2\alpha_p + \omega_3\alpha_M,
\end{equation}
where $\omega_1, \omega_2, \omega_3 \geq 0, \omega_1 + \omega_2 + \omega_3 = 1$, are so called barycentric coefficients. The identity (5) ensures boundedness of the function $\Phi$ (and so of $\alpha$ as well), i.e.,
\begin{equation}
\min(\alpha_s, \alpha_p, \alpha_M) \leq \Phi(\alpha_s, \alpha_p, \alpha_M) \leq \max(\alpha_s, \alpha_p, \alpha_M).
\end{equation}

After the fractal correction, the Gibbs free energy equation, the Gibbs free energy, the cell potential and the equilibrium constants connection equation and the Butler-Volmer equation will have the following form:

**Gibbs free energy equation:**
\begin{equation}
G(p, T) = U + pV - TS
\end{equation}
or
\begin{equation}
G(p, T) = H - TS
\end{equation}

$\Delta G$, $E^{\circ}_{\text{cell}}$ and $K$ connection equation:
\begin{equation}
\Delta G^\circ = -RT \ln K = -nFE^{\circ}_{\text{cell}}
\end{equation}

**Butler-Volmer equation:**
\begin{equation}
I = A \cdot j_0 \cdot \left\{ \exp \left[ \frac{\alpha n F}{RT} \left( E - E_{\text{eq}} \right) \right] - \exp \left[ -\frac{\alpha n F}{RT} \left( E - E_{\text{eq}} \right) \right] \right\} \tag{6}
\end{equation}
or
\begin{equation}
j = j_0 \cdot \left\{ \exp \left[ \frac{\alpha n F \eta}{RT} \right] - \exp \left[ -\frac{\alpha n F \eta}{RT} \right] \right\} \tag{7}
\end{equation}

where is:
\begin{itemize}
  \item $T_r$ – real temperature, and it holds $T_r = \alpha T$,
  \item $\alpha$ - correction function;
  \item $\alpha_s$ - a normalized surface fractality correction factor;
  \item $\alpha_p$ – porosity correction factor;
  \item $\alpha_M$ - factor reflecting fractal dynamics.
\end{itemize}

In this way, global phenomenological parameters, processes and equations, as a results at the science development level, transformed into modern thermodynamics, physicochemical and mathematical apparatus, that provides new scientific research area in the direction of more precise control of particles and processes within the deeper nanoscale microstructure level, which opens the further components and integrated systems miniaturization frontiers, especially in the electrochemistry energy sources area. This extension towards the electrochemistry field, practically continuing to justify opening the new research and scientific areas nominated by terminology “Fractal Microelectronics”.

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4. Conclusions

On the base of the batteries, fuel cells and hydrogen usage area analysis results, it is evidently that the civilization in energy field facing with different challenges.

Our experimental-research and theoretical work is a part of extended investigations in the materials structures analysis area, in the fractal nature domain, what is important for more precise contact surface in energy storage area and in materials consolidation for battery systems.

BaTiO$_3$-ceramics with Ho$_2$O$_3$ additive, has larger importance in new energy sources and technologies application field. Our results confirm microstructure constituents shapes, grains and pores, reconstruction possibilities as also Brownian motion particles application, as a particular part of the fractal nature, by long term scientific results and knowledge on the electronic materials fractal analysis. The Tab. 1 and Fig.s 4 give plenty of information about fractal nature of dopped BaTiO$_3$ ceramics. Especially illustrative is Fig. 5, showing that addition of Ho$_2$O$_3$ increses fractal dimension, as it is expected and it was also mentioned in some earlier papers [15, 16, 17]. Also, higher magnification reveals more complex structure caused by additives, so the dimension increses with magnification.

These investigations have original contribution in the basic thermodynamic parameters area (by introducing the $\alpha$ fractal correction function, having as the arguments three correction parameters $\alpha_S$ (representing grains’ surface fractality), $\alpha_p$ (fractality of pores) and $\alpha_M$ (Brownian motion), as electrochemistry area functions, especially from the energy storage aspects and creating new approach towards intergranular capacity. This is very capital for the new and alternative energy sources, as the new frontiers establishing towards electronic components and systems miniaturization and also higher level integration area, what is in the new experimental-theoretical approach frame and in direction to new theoretical model [Mitić-Kocić], which could consider as a future fractal electronics, and specifically in this paper in electrochemistry area.

Acknowledgements

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5. References

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Садржај: Са порастом енергетске кризе у свету, развијена су истраживања за нове, обновљиве и альтернативне изворе енергије. Фокус је на истраживању у областима, некада мањег значаја и примене, где се различитим методама синтезе, као и оптимизацијом микроструктурних својстава, врши значајно побољшање излазних електрофизичких својстава материјала и компонената, од значаја за већу енергетску ефикасност и принос у производњи електричне енергије (батерије и батеријски системи, гориве ћелије, као и хидрогенски извори). Такође, побољшање капацитета резервоара за складиштење тако произведене енергије, који је један од најзначајнијих развојних проблема у енергетској сфери, представља изузетно подручје за перспективна истраживања и примене. Имајући у виду постигнуте резултате у области електрохемијских извора енергије, посебно развоја електролита, истраживали смо допринос анализе фракталне природе материјала у оптимизацији ових енергетских извора. На бази истраживања из области фракталне структуре материјала, посебно електроинских материјала, извели смо истраживања утицајних параметара микроструктуре у области електрохемије. Испитивали смо утицај концентрације Ho₂O₃ (од 0.01wt% до 1wt%) и температуре синтеровања (од 1320°C до 1380°C), као консолидационих параметара и тиме отворили врата фрактализацији електрохемијских функција и увели фракталну корекцију код основних термодинамичких параметара. Испитивана је зависност фракталне димензије узора из концепције адитиве.

Кључне речи: електрохемија, батеријски системи, микроструктура, термодинамички параметри, фрактали, фрактальна димензија.