

SMART NANOCOMPOSITES

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NATURAL POLYSACCHARIDES AS SELECTIVE SORPTION COMPONENTS IN COMPOSITE SYSTEMS BASED ON POROUS POLYETHYLENE FILMS

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ABSTRACT

Novel composite systems containing layers of natural polysaccharides, i.e., chitosan and chitin nanofibres and their mixtures, deposited on a porous polyethylene film (matrix) have been suggested. Sorption and mechanical properties of the film composites obtained are studied. It is shown that the composites fully preserve the sorption-selective properties of active components (chitosan and chitin), and the porous polyethylene support provides a proper elasticity and mechanical strength to the system.

Keywords: natural polysaccharides, chitin nanofibers, chitosan, polyethylene porous films, Nanocomposites

INTRODUCTION

Owing to a wide set of functional properties, natural polymers chitin and chitosan not only find application in different areas of industry and medicine but also attract attention of researchers as promising objects for modification of the polymer properties and elaboration of novel composite systems on their basis [1]. The interest to preparation and investigation of the film materials containing chitin and chitosan has recently grown [2, 3]. The biocompatibility with living tissues, biodestruction, the absence of toxicity, ability to selectively sorb different substances including heavy metals and organic solvents make such films attractive for biomedicine and development of optical waveguides and chemosensitive sensor coatings [3]. An important real advantage of chitosan is its film formation ability. However, as it is well known, the films obtained from a pure nonmodified chitosan are characterized, along with a rather high strength, by a rather low elasticity (the elongation at break is 1.2 – 2.5%). Film coatings based on modified chitosan with satisfactory mechanical

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properties have been reported in the literature [2]. At the same time, such systems have a number of disadvantages, such as a low content of chitosan in the composite (1-6 mass %), the presence of toxic substances, and a long preparation process (it includes many stages). The basic drawback of the nonmodified chitin for applications is its poor solubility. To prepare films and fibres, derivatives of chitin which are soluble not only in the water medium but also in organic solvents are often used.

One of appropriate ways to prepare film materials containing polysaccharides as active components is to form layers of these polymers on the surface and in the bulk of a chemically inert polymer matrix with a high mechanical strength. It is reasonable to use for this purpose a polyethylene (PE) porous film [4] as a strengthening elastic support (a matrix of the film composites with polysaccharides). It has been shown [5 - 7] that the films obtained by the method based on the polyethylene melt extrusion contain through pores and have a strongly developed surface relief. It has been found that these specific features of the films provide a sufficiently good adhesion between the constituents of the composite, even if the hydrophilic-hydrophobic natures of the matrixes and active components introduced into them are different. If porous PE supports are used to prepare film composites with polysaccharides, the chemical inertness of the matrix prevents its interaction with the active component and at the same time allows it to preserve the properties of the initial chitin and chitosan, thus providing a mechanical integrity of the composite.

Porous Polyethylene Supports

To prepare porous films, a linear high-density PE of commercial grade HDPE 276 ("Stavropolpolymer," Russia) with molecular mass $M_w = 170000$, molecular mass distribution $M_w/M_n = 4\div 5$, and $T_m = 132^\circ\text{C}$ was used. The porous PE samples prepared by the method described in [4] had a pronounced surface relief with a scale of 600-800 nm, specific surface of 40-45 m^2/g , overall porosity of 40-50%, and thickness of 12-15 μm . The samples contained through channels with an average size of 200 nm and maximum size of 520 nm [4, 6].

Natural Polysaccharides and Composites

As active components of the composite systems, chitosan of the commercial grade (Aldrich, medium molecular weight) and a concentrated water suspension of chitin nanofibres (chiNF) which were rods 5-70 nm thick and 150-800 nm in length (MaviSud S.r.l., Italy) were used. The following systems were prepared: (1) a chitosan film formed from a 2-% solution of chitosan in a 2% acetic acid; (2) PE-chitosan composites; (3) PE-chiNF composites, and (4) PE-chitosan/chiNF mixture composites (the mixture of these polysaccharides was prepared by mixing a solution of chitosan and suspension of chiNF in the volume ratio 1:1). All the composite samples were prepared by casting a corresponding solution on a PE porous support. The samples were dried in a thermostat at 30°C . The sample thickness depended on the composite composition, it was 35, 50, and 95 μm for PE-chitosan, PE-chiNF and PE-chitosan/chiNF mixture (from here on PE-mixture), respectively. The content of the active component in the composite ranged from 50 to 80%. The adhesion

of the polysaccharide layer to the support was rather high for all the composites, no exfoliation of the surface layer from the PE support occurred at sample deformation up to the composite breakdown.

As electron microscopic photographs showed [7], the layers of natural polymers were formed as homogeneous coatings on the PE porous matrix and almost fully masked the surface relief of the support. However, the layers in the PE-chiNF composite systems were found to have some defects which were seen on the micrographs at large magnifications. This fact was supported by the data on gas permeability measured by passing nitrogen under pressure through this film. No gas flow through the film was observed for other composites even under a pressure of 7-8 atm, which indicated that a dense defect-free layer was formed at the support surface.

Sorption-Selective Properties of the Composites

Sorption of solvent vapors was performed in a hermetically closed vessel at $22\pm 2^\circ\text{C}$. The amount of sorbed vapors was determined by the gravimetric method by weighing the initial and swollen films. The process of swelling of the composite systems in vapors of water and of a number of organic solvents, such as alkanes (heptane), aromatic hydrocarbons (toluene) and monoatomic alcohols, were studied. It is known [8] that chitosan is able to absorb a large amount of water due to formation of hydrogen bonds, which is accompanied by a considerable increase in the volume. As one can see from Figure 1, the composite PE-chitosan system has the highest degree of swelling (S) in water vapors among the samples studied and that there is no saturation of the swelling curve during the experiment. Curves 2 and 3 show that the presence of chitin nanofibres in the composite (a more hydrophobic component than chitosan) leads to an appreciable decrease in the swelling degrees of the PE-chiNF and PE-mixture composites in water vapors as compared with the PE-chitosan samples.

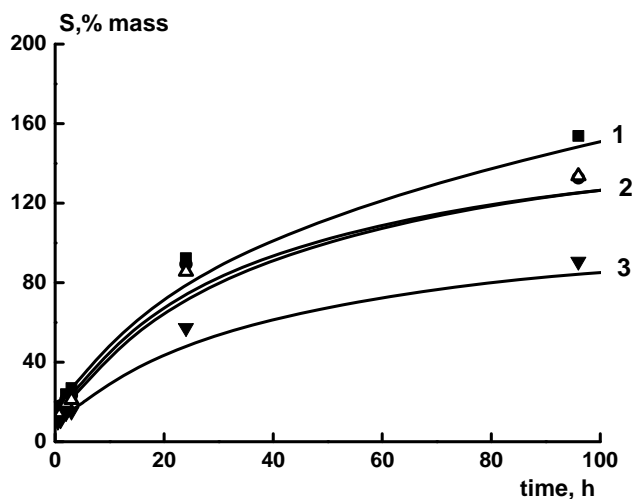


Figure 1. Kinetics of film swelling in water vapors at room temperature:
1 - PE-chitosan; 2 - PE-chiNF; 3 - PE-mixture.

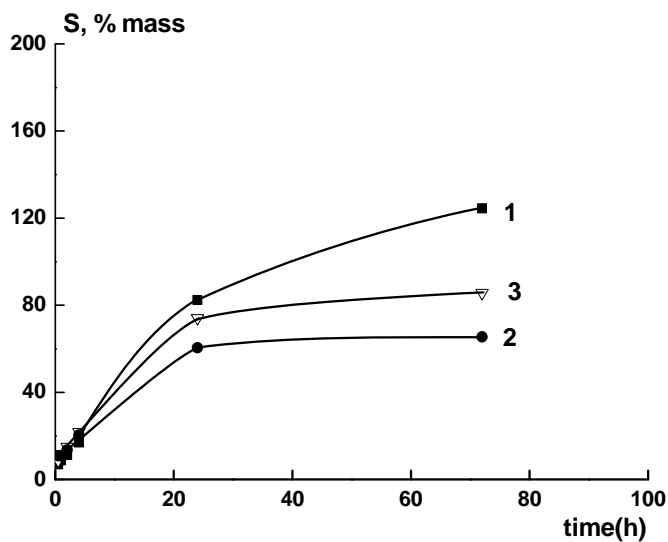


Figure 2. Kinetics of film swelling in methanol vapors at room temperature:
1 - PE-chitosan; 2 – PE-chiNF; 3 – PE-mixture.

According to the literature data [9], chitosans swell to exceptionally high degrees in methanol due to an active influence of methanol on the chitosan structure during sorption. A similar result was obtained for composite PE-chitosan systems (Figure 2) which demonstrated high degrees of swelling in methanol, and no tendency of saturation of chitosan with this alcohol was observed. At the same time, the PE-chiNF and PE-mixture samples had considerably lower degrees of swelling, and the sorption curves saturated.

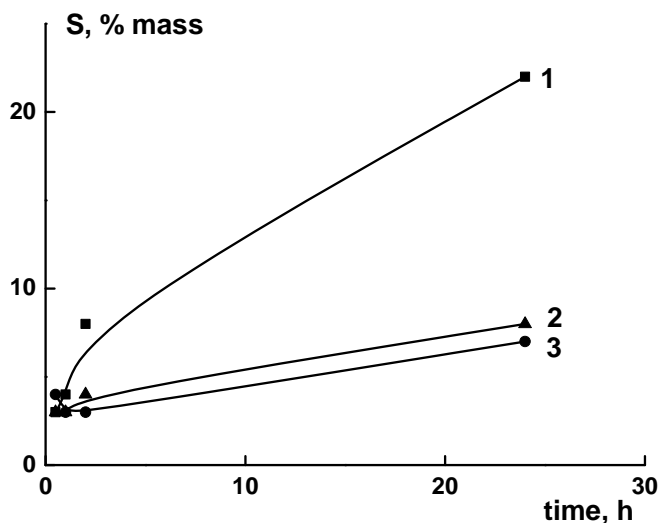


Figure 3. Kinetics of film swelling in toluene vapors at room temperature:
1 - PE-chitosan; 2 – PE-chiNF; 3 – PE-mixture.

Aromatic hydrocarbons, and, in particular, toluene, are rather strongly held by hydrophilic chitosan due to a specific interaction of the aromatic nucleus with polar groups of the polysaccharide (PE-chitosan composite, Figure 3, curve 1). An increase in the hydrophobicity of the composite due to the introduction of chiNF resulted in a sharp decrease in the sorption of toluene vapors by the PE-chiNF and PE-mixture samples (Figure 3, curve 2 and 3).

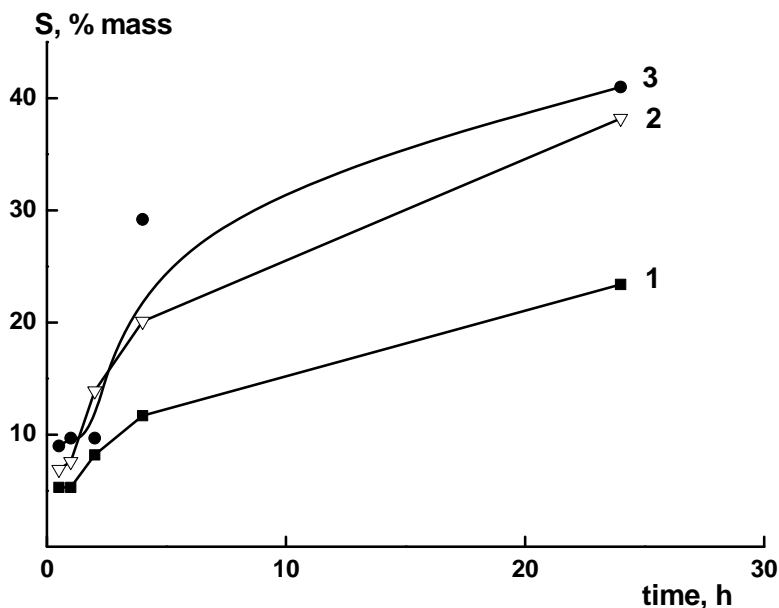


Figure 4. Kinetics of film swelling in n-heptane vapors at room temperature:
1 - PE-chitosan; 2 – PE-chiNF; 3 – PE-mixture.

Chitosans have a weak affinity for n-alkanes, and, in particular, to n-heptane, which is the reason for a low degree of swelling of the PE-chitosan system in vapors of this solvent (Figure 4, curve 1). Organic substances are most efficiently absorbed by hydrophobic materials, and therefore an increase in the degree of hydrophobicity in the PE-chiNF and PE-mixture samples leads to a more intense sorption of n-heptane vapors by these composites (Figure 4, curve 2 and 3) as compared with the PE-chitosan samples.

Mechanical Properties of the Composites

Mechanical characteristics of the films were measured at a 2166 P-5 test machine (Ivanovo, Russia) during uniaxial extension of the samples with a rate of 100 %/min. Table 1 lists breaking strength (σ), elastic modulus (E) and elongation at break (ϵ) of the samples in the dry and swollen state. As one can see, the composites in the dry state are characterized by a much lower breaking strength than the initial PE film, which can be explained by the presence of defects in the layer of the rigid-chain polysaccharide at the support surface. The number and size of the defects increase when the sample is deformed. At the same time, the elongation for the PE-chitosan and PE-chiNF samples is similar to that for the PE support.

Like the decrease in the strength, this can be explained by the fact that the sample extension gives rise to either cracking of the surface layer (PE-chitosan) or its exfoliation from the support (PE-chiNF), and the elongation at break of the composite is determined by the PE support alone. The modulus of elasticity of the composites is much higher than that of the PE film because of the presence of the rigid-chain polymer in the system. Changes in the mechanical characteristics of the samples in the swollen state are due to the fact that the polysaccharide surface layer becomes more elastic at swelling, which leads to a sharp decrease in the elastic modulus, while the elongation at break remains the same and even somewhat increases.

Table 1. Mechanical properties of initial components and composite systems in the dry/swollen state

Sample characteristics	PE porous support	Chitosan film	PE / Chitosan	PE / chiNF	PE / mixture Chitosan - Chitin
σ , MPa	115	70/-	90/40	65/45	50/60
E, MPa	700	3000/-	1800/300	1300/400	1700/500
ε , %	110	3/-	110/110	100/130	70/130
Thickness, mkm	16	20	35	50	95

It should be noted that the chitosan film obtained from nonmodified uncrosslinked chitosan fully loses its mechanical integrity at swelling in vapors of solvents, while all the composite systems we studied, including PE-chitosan, preserve their strength and elasticity in the entire range of swelling degrees.

CONCLUSION

Novel sorption-selective composite systems containing layers of natural polysaccharides deposited on porous film PE have been prepared. All the composites were characterized by a good adhesion of the polysaccharide layer to the support even at a high content of the active rigid-chain component. Investigations of sorption characteristics of the systems obtained showed that the PE-chitosan sample exhibited the swelling degree in vapors of solvents equal to that of the chitosan film, but, in contrast to the chitosan film, it preserved high mechanical characteristics in the entire range of the swelling degrees studied. The introduction of chitin nanofibres into the sample that increased the hydrophobicity of the composite system led to a considerable reduction in the degree of swelling in water vapors and also in vapors of methanol and toluene. In all the experiments on swelling in vapors of solvents the PE-chiNF and PE-mixture samples exhibited similar behaviors. However, since the chitosan/chiNF mixture formed a dense defect-free layer characterized by a better adhesion to the PE support, the composite PE-mixture system was found to be most attractive for applications.

ACKNOWLEDGMENTS

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WATER TREATMENT SYSTEMS WITH THE USE OF MAGNETRON-SPUTTERED NANOSTRUCTURED COATINGS Ti-Ru-O

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ABSTRACT

The feasibility of making a dimensionally stable anode (DSA) with an active coating Ti-Ru-O prepared by reactive magnetron sputtering was demonstrated through the present work. In addition, a utilization efficiency of water treatment systems, the main element of which is the developed anode.

Keywords: dimensionally stable anodes, magnetron sputtering, nanostructured coating, water treatment

INTRODUCTION

Recently, the use of dimensionally stable anodes (DSAs) has become technologically and economically preferred for many electrolytic processes. Previously used as anodes graphite, iron, lead had satisfactory characteristics, however, corrosion and mechanical wear occurred during operation led to contamination of the electrolyte, reduction of the geometric dimensions of the anode and its subsequent replacement. The success of the dimensionally stable anodes is caused by their very low wear rate. Thus the wear is limited by electroactive surface layer which can be easily restored [1, 2].

DSAs consist of an electrochemically active coating applied on the base metal, usually titanium. The coating presents a mixture of oxides, one of which is an electrical conductor and another is inert. DSAs with mixture of 30% mol. RuO₂ and 70% mol. TiO₂ has obtained the greatest amount of researches and widespread use [1, 3, 4].

For preparation of DSAs a number of chemical, electrochemical or physical methods are used. Among chemical methods coating deposition by thermal decomposition of the metal salts [5] takes a special place, because it is traditionally used in industrial production. It is also

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possible to prepare the anodes by sol-gel method [6-8]. The electrochemical methods involve electrodeposition using a precursor of hydrogen peroxide [9-11]. Developments in the field of physical methods of anodes preparing are currently in the initial stages and concentrated on deposition of active coatings by magnetron sputtering [12, 13].

In this work, we describe the technology of magnetron sputtering of Ti-Ru-O coating on anodes and show the possibility of their using in water treatment systems.

EXPERIMENTAL

A coating of ruthenium and titanium oxides was deposited using the magnetron sputtering. Prior to deposition the titanium substrate was sandblasted and annealed at 400 °C for 20 min to remove the impurities and to activate the surface. The deposition was carried out with two cathodes, which were running simultaneously. One of the cathodes was made of titanium VT1-0 (98,61-99,7% Ti, <0,18% Fe, <0,07% C, <0,1% Si, <0,04% N, <0,12% O, <0,01% H), the second was a composite and it consisted of a titanium disc and inserted therein a pressed powder ruthenium disc. The size of ruthenium disc corresponded to the spray area. The disk was produced from ruthenium powder by pressing and high temperature annealing up to 750 °C to obtain density level 0,78-0,84 of monolithic ruthenium.

The pressure of the sputtering chamber MIR-1 was pumped down to $2 \cdot 10^{-3}$ Pa, then the plasma-supporting gas Ar was delivered to $3 \cdot 10^{-1}$ Pa, a glow discharge emerged and required operating currents was set. With the set current density on the titanium cathode 250 mA/cm² the currents on the cathode with ruthenium insert was settled. After 20 s oxygen was fed at a partial pressure $5-6 \cdot 10^{-2}$ Pa and the coating with titanium and ruthenium oxides was deposited on titanium substrate. The active coating Ti-Ru-O of 5 μm thickness was obtained.

The scanning electron microscopy (SEM) analysis of the surface morphology of Ti-Ru-O coating was performed using a Tescan VEGA microscope equipped with energy-dispersive X-ray spectrometer.

The electrochemical application test was conducted in a NaCl solution (300 g/l) using an IPC-Pro potentiostat. Platinum wire was employed as a counter electrode, Ag/AgCl electrode was a reference electrode.

The hardness of the coating were determined by scanning nanohardness tester NanoScan.

A test batch of anodes coated with ruthenium-titanium oxides was produced. Its performance test was carried out in water treatment system "Kaskad" and water analysis was conducted before and after water treatment.

RESULTS AND DISCUSSION

The morphology of the coating surface is shown in Figure 1, a. For comparison, Figure 1,b demonstrates an image of the coating surface obtained by thermal decomposition of ruthenium and titanium salts. As the coating formation by magnetron sputtering occur uniformly the coating surface has a featureless and smooth surface (Figure 1,a). In contrast, the thermally decomposed Ti-Ru-O coating has a rough surface with cracks and exfoliation.

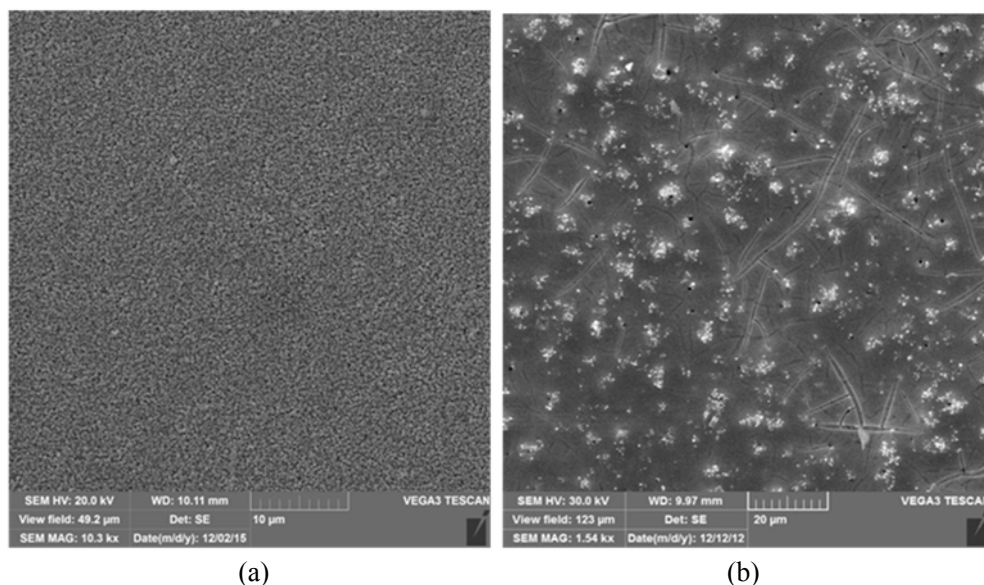


Figure 1. SEM images of the surfaces of Ti-Ru-O coatings prepared by (a) thermal decomposition and (b) magnetron sputtering.

As a result of selection of the deposition current density at the cathode with ruthenium insert it has been found that in case of value of 90 mA/cm^2 the coating has a composition close to optimal. Table 1 shows the results of the analysis.

Table 1. The chemical composition of the coating

Elements content, mol.%			
Ti	Ru	Fe	Co
68.1	34.8	0.98	0.97

The peeling of the coating was not noticed during bending around the cylindrical rod. The preliminary tests showed that the samples obtained by magnetron sputtering have higher mechanical properties in comparison with the samples prepared by thermal decomposition of metal salts. For the magnetron sputtered Ti-Ru-O coating the hardness is 12 MPa, respectively, while for thermally decomposed it is 8 MPa.

Information on the achieved catalytic activity was found in the polarization curves (Figure 2), which describe the simultaneous flow of all anodic reactions. Ti-Ru-O anode has slightly less rates of taking place processes on it than the platinum anode. However, at lower potentials polarization curves are close to each other, while at higher potentials the difference in the magnitude of the current density does not exceed 30 mA/cm^2 .

According to the developed technology of magnetron deposition of Ti-Ru-O coating a test batch of anodes was obtained. As a result of complex research mutually realized with consortium “ElectroEcoTechnologies” a water treatment system “Kaskad” was created, the main element of which is the anode with an electroactive coating Ti-Ru-O. The system is a column with two electrodes and a polarizable particulate filler between them. An absence of necessity of replacement cartridges applying is a feature of this water purification equipment

based on the method of electrosorption. These water purification systems using the anode with the active nanostructured coating Ti-Ru-O can perform a complete treatment of water containing different types of organic and inorganic microparticles such as protozoa, bacteria, viruses and their waste products, mineral particles, indecomposable petroleum products, as well as soften and purge water of such toxic mineral and organic contaminations as the ions of heavy metals and manganese, phosphates, nitrites, sulfides, cyanides, mercaptans, phenols and others while preserving an important for human body the ions of calcium and natrium. Table 2 shows the results of water analysis before and after water treatment. There is a significant improvement of water quality upon all indications according to the analysis. Purification equipment provides an effective treatment of water according to sanitary regulations and standards on the maximum permissible concentration of impurities.

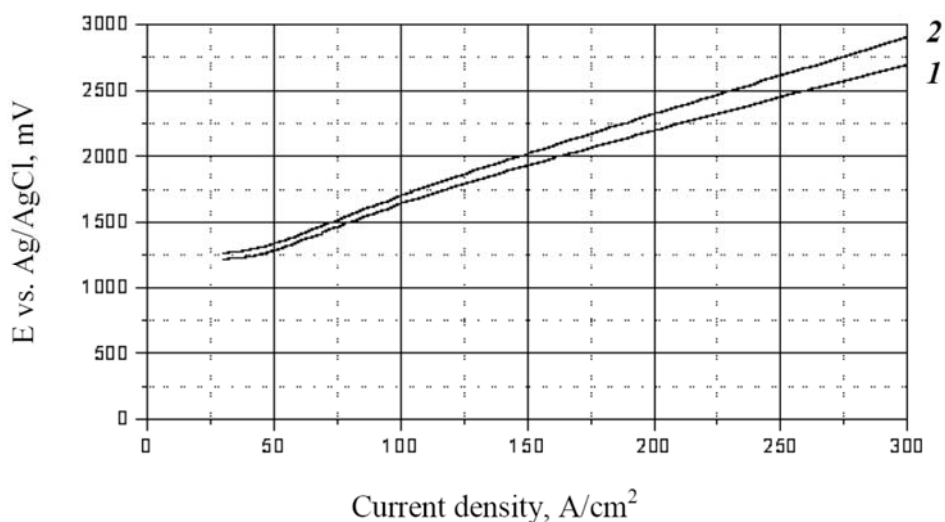


Figure 2. Polarization curves of (1) Ti-Ru-O and (2) platinum anodes.

Table 2. The results of water analysis

№	Indicators	Units of	The results	The results	The	Specification
1	pH	Point	8,2	8,0	6-9	ISO 10523
2	Odor	Point	2	0	2,0	GOST 3351-74
3	Taste	Point	3	0	2,0	GOST 3351-74
4	Turbidity	mg/dm ³	43	0,28	1,5	GOST 3351-74
5	Colour	degree	39	2,3	20,0	GOST 3351-74
6	Iron	mg/dm ³	1,2	<0,05	0,3	GOST 4011-72
7	Permanganate	mgO ₂ /dm ³	8,9	1,7	5,0	ISO 8467
8	Active chlorine	mg/dm ³	0,50	<0,15	0,8-1,2	GOST 18826-
9	Aluminum	mg/dm ³	0,33	<0,04	0,5	PNDF
10	Ammonia	mg/dm ³	1,0	0,5	2,0	GOST 4192-72
11	Water	mmol/dm ³	1,3	0,95	7,0	GOST 4151-72
12	Chloroform	mg/dm ³	0,03	<0,001	0,2	MUK 4.1.646-

CONCLUSION

The technology of magnetron sputtering of the active Ti-Ru-O coating with predetermined chemical composition was developed.

The tests showed that Ti-Ru-O coating has no cracks, which indicates its high adhesion. The comparative analysis of the electrode processes on platinum and magnetron sputtered Ti-Ru-O coating found that they possess comparable electrochemical characteristics and the study results confirmed the possibility of forming DSA electrode by magnetron sputtering for industry applications.

The comprehensive test of Ti-Ru-O anodes was performed in the water treatment system «Kaskad». The results of analysis of water showed a significant improvement of water quality upon all the indications. The developed water treatment system “Kaskad,” the main element of which is the anode with an active coating Ti-Ru-O, can be used in domestic buildings, hospitals, hotels and cottage complexes, remote settlements, as well as it is possible to create mobile water treatment systems for using in places with the lacking of pure water such as scientific stations, expeditions, field hospitals. In addition, the utilization of these systems is effective for wastewater treatment (including wastewaters of heavy industry).

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DEVELOPMENTS IN THE AREA OF ENZYMATIC BIOFUEL CELLS

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ABSTRACT

This review aims to survey the current status of enzymatic bio-fuel cells (EBFCs). The continuous increase in the search for alternative energy sources worldwide is pushing the demand for “fresh” and efficient energy production processes. Enzyme based bio-fuel cells are attracting attention rapidly due to the promising advances in the area of its research. Bio-fuel cells (BFCs) have been the target of many research groups worldwide. This device is an alternative to the fuel cells employing metal catalysts that is capable of formation of electricity, with the advantage of using biological molecules as catalysts. Recent studies have demonstrated promising characteristics of these devices; however, despite the several advances in this area, some challenges are still to be faced. This review is focused on to provide an overview of the enzymatic bio-fuel cells by discussing the latest papers in this field and presenting an outlook for future research in this area.

INTRODUCTION

The term bio-fuel cell has been known for almost one century since the first enzymatic bio-fuel cell was reported in 1964 using glucose oxidase (GOx) as the anodic catalyst and glucose as the “fuel” [1]. Fuel cell research focuses on the search for the catalyst that are not prone as platinum to deactivation through surface poisoning on minimizing catalyst loading to reduce costs and on electrolyte properties to prevent fuel–oxidant crossover between half cells [2, 3].

No doubt, bio–fuel cells are electric generators, which have recently attracted considerable attention. The term “bio–fuel cell” refers to a type of fuel cells in which biocatalysts (enzyme, micro–organism) are used to convert chemical energy to electrical energy [4], due to their unique advantages over the conventional fuel cells [5]. Energy conversion processes are completed in three steps. First, bio-fuel cells generate electric power using catalysts such as microorganisms and enzymes, which can be very cost–effective

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compared to the conventional noble metal (Pt, Au, Pd) catalysts. These metals are expensive, scarcely available and exhaustible. Second, fuel substances can be selected from a wide range of reactions that can be catalyzed by properly selected enzymes. Third, bio-fuel cells can be operated under mild temperatures and neutral pH. Therefore, bio-fuel cells can be an attractive candidate.

Generally, BFCs are considered for various types of applications. According to the type of the biocatalyst there are two types of BFCs. Microbial BFCs use living cells such as bacteria [6, 7] to catalyze the electrode reactions of the fuel and the oxidant, and enzymatic bio-fuel cells use enzymes [4, 8] depending on the nature of the catalyst to perform redox reaction at the electrodes. Microbial BFCs typically have high coulombic efficiencies, can completely oxidize bio-fuels and can have long lifetimes (up to 5 years) [9–11]. In contrast, enzymatic BFCs typically have high current and power densities due to higher volumetric catalytic activity and improved mass transport, which results in partial oxidation of the fuels and have limited lifetimes owing to the fragile nature of the enzymes [12].

EBFCs have attracted great interest because they allow the use of renewable and inexpensive fuels with high energy density and safety. In this device, the biocatalysts are directly involved in the reaction generating electricity. In bio-fuel cell, the fuel is enzymatically oxidized at the anode side, producing protons and electrons. At the cathode side, the O₂ reacts with the protons and electrons, generating water.

In the last five years, many different EBFCs relying on enzymatic reactions at both electrodes numerous reviews and continuous progresses made in this field have been published. The most common enzyme system employed in enzymatic biofuel cells is glucose oxidase (Gox) [13–22]. Glucose oxidase oxidizes glucose to gluconolactone; thereby, generating 2 electrons for each molecule of glucose. Complete oxidation of glucose to carbon dioxide occurs. The enzymes like laccase [23–26] or bilirubin oxidase are used at cathode. Some publications employing enzymes from hydrogen, ethanol, methanol and krebs cycle metabolism also exist in the literature: Hydrogenase [27–30], alcohol dehydrogenase [31, 32], cytochrome [33], cellobiose dehydrogenase [21, 34], D-fructose dehydrogenase [35, 36], glucose dehydrogenase [37–45], lactate dehydrogenase [46], malate dehydrogenase [47], urease or thehalase [48, 49] as catalysts respectively oxidizing dihydrogen alcohols, cellobiose, fructose, glucose, lactate, malate, ureas or trehalase at the anode and poly phenol oxidase [50, 51] or tyrosinase [17] reducing oxygen at the cathode.

Enzymatic bio-fuel cells (EBFCs) have become a hot topic of research and have great potential in certain niche market. These types of fuel cells could be used in a number of applications including environmental sensors to monitor some specific pollutants [52–54], portable electronic devices such as laptops, cell phones [55–58], auto-mobile batteries [59, 60] and mp3 (MPEG-1 Audio Layer 3) players. These are new areas to use enzymatic biofuel cells [61–63]. Sony Company has developed a bio-fuel cell using glucose as the fuel and enzymes as catalysts to power a walkman [64]. EBFCs show potential application in various areas which have almost exclusively been targeted towards biomedical applications—powering implantable devices [3, 65, 66].

The performance of enzymes and their properties with respect to bio-fuel cell applications have been recently studied by Andrade et al. [67] and Lojou et al. [68]. A summary of their own work has been made by Opallo et al. [69], Leech et al. [70], Young et al. [71] and Falk et al. [72]. Several reviews published during the last five years (Table1)

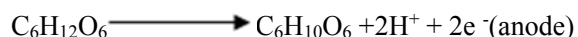
covering the latest developments and the different challenges being faced by bio-fuel cells are worth considering. Regarding this field, important publications are made by Andrade et al. [67], Lojou et al. [68], and Leech et al. [70].

Our research group has started work on bio-fuel cells in 2009. Inamuddin et al. [74] reported the glassy carbon electrode immobilized with the conducting polymer polypyrrole (Ppy) as electron transfer enhancer. After a long time gap (at least 5 years) this research topic is now restarted. In early 2014, a glassy carbon (GC)/Graphene/Ferritin/Glucose oxidase (Gox) was developed by using graphene ferritin biocomposite as an electron enhancer and mediator, respectively [73].

In this review, the main focus will be given to the enzymatic bio-fuel cells with the aim to provide the overview of this enzymatic device, their developments, recent outcomes, advantages and disadvantages. The latest paper in this field, reports on enzyme immobilization at nanostructured interfaces. Finally, for future research in this area major challenges are further addressed in this review.

THE OPERATING PRINCIPLES OF ENZYMATICAL BIO-FUEL CELLS

The nature of employed catalysts in enzymatic fuel cells allows the utilization of numerous fuels, including a variety of sugars and lower aliphatic alcohols. The most common and intuitive fuel for enzymatic bio-fuel cells is glucose due to its high abundance in nature and essential role in human metabolism. Glucose is an important metabolic intermediate and a source of energy for a variety of living organisms. In general, bio-fuel cells employ isolated enzymes or microbes which contain enzymes to catalyze. Electrochemical processes generate electricity and operate at room temperature. At the anode of a glucose consuming BFC, the oxidation of glucose with the help of enzymes such as glucose oxidase gives rise to two protons. The bio-catalytic half reaction at the anode can be represented as:



The electrons produced in the anodic reaction are transferred to the electrode and protons flow through a proton exchange membrane to the cathode. In order to increase the electron transfer efficiency, an electron transfer mediator is necessary in the anode chamber.

At the cathode, oxygen molecules dissociate into atoms, which combine with the electrons and the migrating protons to form water. The cathodic reaction is catalyzed by another kind of enzyme, such as laccase. Similarly, another electron transfer mediator is needed in the cathode side.

The half reaction at the cathode can be represented as:



The whole reaction is thus



Both the reactions occur in the solution. Therefore, electrons produced in the anode chamber must pass through enzyme to mediator, then to the electrode, and finally, to the cathode through an external circuit. The electron transfer in the cathode chamber cannot be achieved without mediator and enzyme.

Basically microbial BFCs operate the same way as enzymatic BFCs. The only difference is that microbes are used as biocatalysts in microbial BFCs.

ELECTRONIC CHARGE TRANSFER

According to several reports BFCs have been classified as direct electron transfer (DET) and mediated electron transfer (MET). There are two types of electric connections between enzymes and electrodes to realize bioelectrocatalysis. One is the mediated electron transfer (MET) type, in which the mediator shuttles the electrons between the enzyme and the electrode to reduce the kinetic hindrance in the interfacial electron transfer (ET). The other is the direct electron transfer (DET) type, in which the enzyme can directly transfer the electrons to or from the electrode. Although, the number of redox enzymes capable of directly communicating with electrodes is limited, many researchers pay attention to the DET-type enzymatic bio-fuel cell (Table 2), since it has several advantages over the MET-type. The majority of enzymes are not capable to transfer electrons directly [75, 76].

Enzyme-based fuel cells have remained popular for research due to the high turnover rates associated with enzymes that lead to a high biocatalysis rate. One problem associated with bio-fuel cells is that the electrons produced by biological moieties cannot be exploited unless they can be transferred to the electrode. Researchers are developing two types of enzymatic bio-fuel cells.

- Product type: In this type of fuel cells, enzymes are not involved in direct energy generation.
- Direct energy production type: In this type of bio-fuel cells, enzymes are directly involved in the bioreactions for energy production.

Since, we are studying the applications of bio-fuel cells in implantable medical devices; we are going to focus on the type that is relevant for these applications—the direct energy production. Most enzymatic fuel cells are of this type [8]. One of the main challenges for this type of fuel cells is to establish efficient electron transfer between enzymes and the electrode supports. Researchers have increasingly targeted DET, although this process often leads to lower power as compared to mediated systems.

PROBLEMS: SHORT LIFE TIME AND LOW POWER DENSITY

The two critical problems in enzyme based systems are the short life time and low power density. A great deal of research has focused on improving the life time and power densities. There are four principal enzyme electrode requirements for achieving high power density: (a) a high mass transfer rate of reactants and products to and from the enzyme active sites, (b) a

high density of enzymes on the electrode surface, (c) a high enzyme activity, and (e) a high electron transfer rate between the active site of the enzyme and the conductive electrode surface. The short lifetime (a few hours) is an inherent characteristic of enzymes even in their natural environment, but the lifetime may be increased for a few days by immobilization.

The issues to consider include short active lifetimes, low power densities and low efficiency. There are a number of strategies for solving these problems, but our group is focused on strategies for immobilization and stabilization of the enzymes, electron transport between the enzyme and the current collector.

Table 1. Important review papers appeared in the literature during 2009–2014

S.No.	Year	Topic	Research group	References
1	2009	Recent advances in material science for developing enzyme electrodes	Minteer et al.	A. K. Sarma, P. Vatsyayan, P. Goswami, S. D. Minteer, <i>Biosensors and Bioelectronics</i> 24 (2009) 2313–2322.
2	2010	Recent advances in enzymatic fuel cells: experiments and modeling	Ivanov et al.	I. Ivanov, T. Vidaković-Koch, K. Sundmacher, <i>Energies</i> , 3 (2010) 803-846.
3	2011	Recent progress and continuing challenges in bio-fuel cells. Part I: enzymatic cells	Osman et al.	M.H. Osman, A.A. Shah, F.C. Walsh, <i>Biosensors and Bioelectronics</i> 26 (2011) 3087–3102
4.	2011	Recent developments of nanostructured electrodes for bioelectrocatalysis of dioxygen reduction	Opallo et al.	M.Opallo, R. Bilewicz, <i>Advances in Physical Chemistry</i> , Volume 2011, Article ID 947637, 21 pages doi:10.1155/2011/947637
5.	2012	Enzymatic fuel cells: recent progress	Leech et al.	D. Leech, P. Kavangh, W. Schuhmann, <i>Electrochimica Acta</i> , 84 (2012) 223-234.
6.	2012	Immobilization technology: a sustainable solution for biofuel cell design	Yang et al.	X-Y. Yang, G. Tian, N. Jiang, B-L. Su, <i>Energy Environ. Sci.</i> , 5 (2012) 5540–5563
7.	2012	Direct electron transfer based enzymatic fuel cells	Falk et al.	M. Falk, Z. Blum, S. Shleev, <i>Electrochimica Acta</i> , 82 (2012) 191–202
8.	2013	New energy sources: the enzymatic biofuel cell	Andrade et al.	S.A. Neto, A.R. De Andrade, J. <i>Braz. Chem. Soc.</i> , 24 (2013) 1891–1912.
9.	2013	Nanomaterials for bio-functionalized electrode: recent trends	Walcarious et al.	A. Walcarious, S.D. Minteer, J. Wang, Y. Lin, A. Merkoci, <i>Journal of materials chemistry B</i> , 1 (2013) 4878–4908.
10.	2014	New trends in enzyme immobilization at nanostructured interfaces for efficient electrocatalysis in biofuel cells	Poulpiquet et al.	A.D. Poulpiquet, A. Ciaccafava, E. Lojou, <i>Electrochimica Acta</i> , 126 (2014) 104–114.

Table 2. Summary of enzymatic biofuel cells

S. No.	Fuel	Enzyme	Electrode	Electron transfer	OCV (V)	Current density ($\mu\text{A cm}^{-2}$)	References
1.	Glucose/O ₂	GDH/PDMS	Pt	DET	0.80	11000	Sakai et al. (2009)
2.	Glucose/O ₂	GOx/laccase	Silicon/SWNTs	DET	N/A	30	Wang et al. (2009)
3.	Glucose/O ₂	GOx/laccase	Au/SWNTs	DET	0.46	960	Lee et al. (2010)
4.	Glucose/O ₂	PQQGDH/BOD	Au/MWNTs substrates	DET	0.60	200	Tanne et al. (2010)
5.	Glucose/O ₂	GDH/NB	Glass carbon/SWNTs	DET	0.35	100	Saleh et al. (2011)
6.	Glucose/O ₂	LAC/GOD	GCS/NCNTs	DET	0.2	21	Liu et al. (2012)
7.	H ₂ /O ₂	O ₂ -tolerant hydrogenase/BOD	Pyrolytic graphite electrode (PG)	DET	0.6	300	Lojou et al. (2012)
8.	Fructose/O ₂	(FDH)/BOD	CNTs-decorated carbon fiber fabrics	DET	0.64	1.21	Miyake et al. (2013)
9.	Glucose/O ₂	GOD/Laccase	GO/Co(OH) ₂ /chitosan	DET	0.46	3.3	Kim et al. (2013)
10.	Fructose/O ₂	(FDH)/BOD	Multi-copper oxidase	DET	0.46	2.6	Kano et al. (2014)
11.	Ethanol/O ₂	Laccase	Polyacrylonitrile/gold material	DET	0.75	1.6	Selloum et al. (2014)

OVERVIEW OF THE LITERATURE OF ENZYMATIC BIO-FUEL CELLS

A literature search conducted in the Chemical Abstract database using the term “Enzymatic bio-fuel cell” indicates that the number of publications in this area has increased over the last 5 years, thus demonstrating the growing interest in this new technology. The exponential interest in enzymatic bio-fuel cell allows us to present and discuss the very recent papers which contribute to the continued development of this topic.

Figure 1 shows that the progress in enzymatic bio-fuel cell research has often been reviewed in the literature. Minter and coworkers [77] who are very active in this field have summarized recent trends and accomplishments. Enzymatic bio-fuel cells are attracting increasing attention mainly due to promising advances from the research laboratories around the world.

Bio-fuel cell is a very developing subject, so many research groups worldwide are currently investigating several methods regarding bio-anode preparation and enzyme immobilization, also looking for high power output values and longer bio-fuel cell lifetime. In 2009, the main focus of the papers was the immobilization method; once a good anchoring condition is obtained, both power output and bio-anode lifetime can be enhanced.

Gao et al. [78] investigated the performance of different polymer backbones in 7.24 pH PBS, GOx from *Aspergillus niger*, containing 15 mM glucose and atmospheric O₂. The main purpose of this study was to investigate the effect of the enzyme purity. In 2009, Kuwahara et al. [79] proposed a bio-anode prepared with a conducting polymer film electrochemically copolymerized with 3-methylthiophene and thiophene-3-acetic acid into a film on a gold coated alumina plate. Subsequently, GOx and bilirubin oxidase (BOD) were covalently attached to the carboxyl groups of the polymer. Appropriate mediators were used in phosphate buffered saline (PBS) solutions (pH = 7.0) separated by a Nafion membrane. The analyte was saturated with nitrogen and contained 0.1 M glucose while the catholyte was saturated with O₂. The open circuit voltage (OCV) and maximum current density, both are higher with BOD/copolymer in comparison to Pt/C cathodes and were found to be 0.61 V and 0.15 mWcm⁻² at 0.35 V. With these polymers, the authors claimed that many functional groups can be introduced into the main chain by selection of appropriate monomers that facilitate access to the enzyme binding sites.

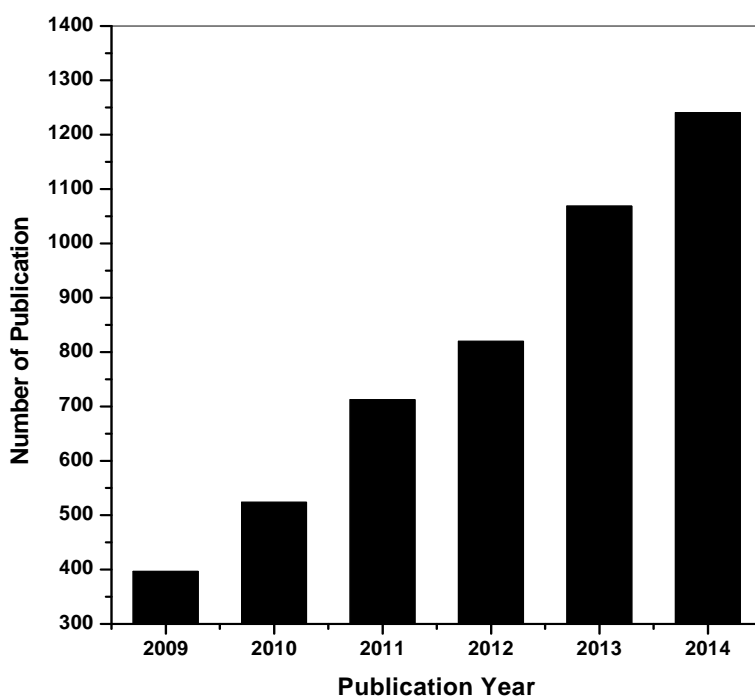


Figure 1. A literature search carried out in the Chemical Abstract database using the term “Enzymatic bio-fuel cell.” Sources: Sciencedirect.

Wu et al. have demonstrated a membraneless fructose/air biofuel cell by using D-fructose dehydrogenase and bilirubin oxidase and employing a cellulose-multiwalled carbon nanotubes matrix [80]. This kind of matrix provide a promising environment for the anchorage of enzymes, achieving high power density and lifetime. Since, the biofuel cells based on dehydrogenase enzymes require the use of mediators, mediatorless biofuel cells are currently the target of some research groups. Miyake et al. [81] demonstrated the use of glucose dehydrogenase and its cofactor on “ketjenblack” electrode with enough power

density values for some medical sensors. Polyaniline is one of the often used conducting polymers, and bioanode composite films made from polyaniline and carboxy dextran gold hybrid nanomaterials were reported by Lee et al. [82, 83]. The high electrocatalytic performance makes such material a good candidate for enzyme immobilization. Good results using pyrroloquinoline onto gold electrodes for lactate dehydrogenase immobilization and an electrochemical study using ultra-small silicon nanoparticles for glucose oxidation were also described [84, 85].

Lee et al. [86] attached nicotinamide adenine dinucleotide (NAD) dependent lactate dehydrogenase (LDH) to pyrroloquinoline quinone (PQQ) electron mediators, which were in turn attached to a gold electrode by a cystamine monolayer. The novelty of the method introduced was that the final step of covalent attachment of lactate dehydrogenase (LDH) was performed in the presence of the NAD as cofactor, lactate substrate, and Ca^{2+} , which helped to promote a favorable orientation of the LDH after immobilization. Lee et al. compared a fuel cell fabricated using GOx and laccase with a cell containing single-wall carbon nanotubes (SWCNT) and DNA-wrapped SWCNT. The use of single-standed DNA-wrapped SWCNT was found to increase the GOx loading to SWCNT/Flavin adenine dinucleotide (FAD)-GOx and cystamine/PQQ/FAD-GOx anodes wired through a mediator activated polymer, this system was operated at neutral pH, a condition that is not optimal for *Trametes versicolor* laccase activity.

The Minter group and collaborators, employed multi-enzyme cascades for full or partial oxidation of pyruvate [87–89], glycerol [90] and alcohol [12], in EBFC assemblies, besides power curves presented to support the contribution of CO_2 for each enzyme in the cascade to the overall enhanced current and power densities. Harper et al. [91] employed on many systems, a mediator, which is usually enzyme specific. For glucose oxidation by glucose oxidase, examples of mediators are ferrocene monocarboxylic acid, pyrroloquinoline (PQQ), methylene blue, ferrocenecarboxaldehyde and ferrocenemethanol. Lehar et al. [92] developed the method for improving the stability consists of anchoring the hydrogel to the electrode surface through covalently attached tether groups.

The mediator-free glucose/ O_2 biofuel cell designed with the help of 3-dimensional glucose oxidase/SWNT/polypyrrole and tyrosinase/carbon nanopowder (CNP)/polypyrrole composites as bioanode and biocathode respectively, was developed by Yoo et al. [17]. A biofuel cell anode is developed on the basis of multi-walled carbon nanotubes (MWCNTs). Recombinant pyrroloquinoline quinone (PQQ) dependent glucose dehydrogenase (GDH) is covalently attached to a PQQ-layer which is adsorbed onto thiol-modified MWCNTs at the gold electrode. The process is based on mediated electron transfer of the enzyme [93]. Novel nanographene platelets (NGPs)-based glucose/ O_2 biofuel cell (BFC) with glucose oxidase (GOD) as the anodic and laccase as the cathodic biocatalysts have been developed. Modified electrodes GOD/NGPs exhibited good catalytic activity towards glucose oxidation and the laccase/NGP modified electrode exhibited good catalytic activity towards O_2 electroreduction [50]. Most efficient GBFC was based on composite graphite discs containing glucose oxidase and ubiquinone at the anode, polyphenol oxidase (PPO) and quinone at the cathode. PPO reduces dioxygen into water, at pH 7 and in the presence of chloride ions and urates at physiological concentrations [94]. An enzyme-modified electrode was fabricated by sequential deposition of carbon, benzoquinone (BZQ), glucose oxidase (GOD) and poly(3,4-ethylenedioxythiophene) (PEDOT). The modified electrode works both as a glucose

biosensor in the oxygen-independent solution and the anode of the biofuel cell by adding either glucose solution or the human blood sample [95].

Zafar et al. [96] described a wide-range of mediator containing five different osmium-based redox polymers that efficiently connected the oxidoreductase pyranose dehydrogenase with graphite electrodes. The prepared polymers covered a potential range from -0.270 to $+0.160$ mV vs Ag/AgCl. The latter presents a key factor limiting the performances of glucose bio-fuel cells (GBFCs). In this context, implantation of GBFC based graphite electrodes in rats has been reported [97]. However, these electrodes delivered only 0.05 mWmm⁻², a value far from that is required to supply for implantable biomedical devices.

Based on these studies, it is anticipated that EBFCs can be employed as self-powered miniaturized implantable devices, providing power to remotely located and portable electronic devices. The insight into EBFC research may in addition leads to routes for improved biomimetics, mimicking the catalytic active site of enzymes, including mimetics of the structural flexibility provided by protein assembly surrounding the active site, to provide improved catalysts in fuel cell systems [98].

Andrade et al. [99] described the preparation of a bioanode to use in ethanol oxidation. The bioanode was obtained via immobilization of dehydrogenase enzymes (ADH or AldDH) with polyamidoamine (PAMAM) dendrimers onto carbon paper platforms, using the layer-by-layer technique. An enzyme cascade for complete oxidation of lactate was immobilized on a bioanode and employed in a lactate/air biofuel cell. This paper showed that complete oxidation of lactate increased power density in a similar trend as was observed for complete oxidation of pyruvate in an enzymatic biofuel cell. The authors described the development of a cathode that can undergo DET and a 3D anode that was based on NAD⁺ dependent enzymes [47, 100].

Gupta et al. [85] discussed a gas-diffusion electrode based on hydrophobized carbon black composite for enhanced enzymatic oxygen reduction for the possible application as a biocathode in enzymatic fuel cells. Immobilized bilirubin oxidase (BOD) from *Myrothecium verrucaria* reduces oxygen in a 4-electron mechanism, as shown by Tafel kinetics and shows evidence of direct electron transfer. Although, enzymes are highly specific and efficient catalysts, they have limited lifetime in solution. Hence, their use in bio-fuel cells requires a critical step: immobilizing the enzyme onto an electrode surface [101]. Minteer's research group successfully used this methodology to modify a Nafion membrane and then immobilize dehydrogenase enzymes onto carbon surfaces [83, 102, 103]. Rengaraj et al. [104] obtained a fully assembled membraneless bio-fuel cell at graphite electrodes. These authors used the layer-by-layer technique to achieve the anode and the cathode. They employed osmium complexes along with glucose oxidase and laccase to obtain the 3D electrocatalytic structures.

In 2011, Frasconi et al. [105] reported a self-assembled bioelectrode containing genetically engineered glucose oxidase and gold nanoparticles, to obtain multiple enzymatic layers. Neto et al. [106] employed the electrostatic layer-by-layer technique to prepare bioanodes for ethanol/O₂ bio-fuel cells. Dónal Leech's research group extensively reported the use of osmium based complexes [96, 107–111].

Rengaraj et al. prepared a complete enzymatic biofuel cell using glassy carbon and graphite electrodes modified with osmium redox polymers, crosslinked with poly (ethylene glycol) diglycidyl ether. Forti et al. [112] introduced the use of PAMAM dendrimers in an ethanol/O₂ biofuel cell, by immobilizing alcohol dehydrogenase, PAMAM dendrimers onto a

carbon cloth platform. Holland et al. [82] applied site-specific gold nanoparticle in a glucose/O₂ bio-fuel cell. They attached a genetically modified glucose oxidase enzyme containing a free thiol group near its active site to a maleimide-modified gold nanoparticle, to obtain direct electrical communication between the conjugated enzyme and an electrode surface. Flexer et al. [84] showed that PQQ-dependent glucose dehydrogenase from *Acinetobacter calcoaceticus* underwent DET at carbon cryogel electrodes.

Martinez-Ortiz et al. described 4-(2-aminoethyl) benzoic acid-functionalized graphite electrodes in which the benzoic acid moiety interacted with the laccase T1 site and induced a DET environment between the T1 site and the graphite electrode surface. The authors also prepared a semi-enzymatic fuel cell using a zinc anode and the functionalized graphite electrodes with a substrate-like molecule, to obtain high electron transfer rate and a power density of 1.1 mW cm⁻² at 0.41 V [81].

Opallo and Bilewicz [69] presented the latest aspects regarding the development of nanostructured bioelectrodes, also focusing on catalysis of the oxygen reduction reaction. In 2012, Yang et al. [113] reviewed aspects associated with the immobilization of enzymes onto electrode surfaces, whereas Falk et al. [72] presented a mini review that discussed DET processes in enzymatic devices. The longer electron transfer path and the mass transport problems around the electrodes impaired the energy conversion efficiency. Further, the xylose based enzymatic bio-fuel cells could be greatly limited by the cost of enzyme purification. Moreover, the road for the xylose based enzymatic biofuel cell is blocked by the poor stability of the purified xylose dehydrogenase (XDH) at ambient conditions of temperature and pH as well as the undesirable long-term durability [114, 115]. Consequently, an enzymatic biofuel cell that could achieve direct and efficient electricity production from xylose is much desirable.

EBFCs are best choice for implanted fuel cells which operate in vivo. Development of the EBFC has been shown due to the operational difficulties. The concept of implanting fuel cells in mammals was suggested long ago [65]. Therefore, considerable attention has recently been paid to the possibility of implantation of bio-fuel cells in the human body. Others demonstrated the possibility to harvest energy from bio-fuel cells implanted in rats [48], clams [116], snails [65] or lobsters [117]. However, the major obstacle for implantation within mammals lies in the weak power of bio-fuel cells.

Rasmussen et al. [48] implanted an enzymatic bio-fuel cell based on trehalose oxidation and oxygen reduction in a living insect. The authors designed the bioelectrodes on the basis of a bienzymatic trehalase/glucose oxidase in the anode side; the cathode material consisted of bilirubin oxidase grafted along with osmium complexes on thin carbon fibers. Halamkova et al. [65] employed PQQ-dependent glucose dehydrogenase and laccase as biocatalysts immobilized on a buckypaper. The cross-linking agent (1-pyrenebutanoic acid succinimidyl ester) connected the enzymes to the CNT via covalent binding with amine groups of lysine residues.

Carbon nanotubes (CNTs) have become a privileged electrode material in EBFCs, not only for their high specific surface and high conductivity but also for their Direct Electron Transfer (DET) properties towards many types of redox enzymes [118]. Sequential coating of MWCNTs and gold nanoparticles on to the gold electrode transducer was shown by Akter et al. [119] to further increase the area on which the antibody is immobilized and to amplify the amperometric detection of cancer biomarkers. Improvements of the biocathodes were also

obtained in connection with oxygen reducing laccase. For example, SWCNTs functionalized with amino ethyl residues, and activated and reacted with laccase, displayed high bioelectrocatalytic activity [86]. Mass-production method is chemical, thermal, or electrochemical reduction of graphite oxide (GO). It is also considered to be the most economical way to produce graphene. Most of the graphene used in electrochemistry is produced by GO reduction [120].

Graphene based enzyme biosensors have been reported in many publications which have been well documented in recent review articles [121–128]. For example, a graphene–Au nanocomposite hybrid was synthesized by *in-situ* growth of Au nanoparticles (AuNPs) on the surface of graphene nanosheets in the presence of poly(diallyldimethylammonium chloride) (PDDA), which improved the AuNPs dispersion and also stabilized cholinesterase with high activity and loading efficiency. Zhang et al. [121] reported a facile procedure to efficiently prepare graphene–Prussian blue (PB) hybrid nanocomposite by directly mixing Fe^{3+} and $[\text{Fe}(\text{CN})_6]^{3-}$ in the presence of graphene oxide in poly(ethylene imine) aqueous solution, resulting in a novel acetylcholinesterase (AChE) biosensor for detection of organophosphate (OP) pesticides.

Zhu et al. [129] presented a DNA electrochemical biosensor based on a thionine–graphene nanocomposite. The proposed biosensor exhibited high sensitivity and low detection limit for detecting complementary oligonucleotides. A “sandwich–type” detection strategy is employed in this electrochemical DNA biosensor, which exhibited a fast response, high sensitivity and selectivity, with a detection limit of 3.4 M. Lu et al. [130] introduced an electrochemical DNA sensor into a folding paper based on the AuNPs/graphene modified screen-printed working paper electrode (SPWPE). The combination of these two excellent conductive materials produced a synergy effect on the electroanalytical performance of the resulting electrode, which can improve the electronic transmission rate as well as increase the surface area.

Loo et al. [131] developed a label–free immunosensor based on reduced graphene oxide modified electrodes for the direct electrochemical detection of antigen–antibody binding reactions. Graphene based immunosensors showed enhanced sensitivity and exhibited great promise for detection of protein biomarkers. This new area of bioengineering opens a number of new ideas for bio–functionalized electrodes. They have been used with electrochemical biosensing by both Katz et al. and Hu et al. to develop gated and switchable bioelectronic sensors [132].

In a review Goswami et al. [133, 134] provided an overview on alcohol oxidases from different categories focusing research on these oxidases with their potential industrial applications. The other review, reported the various immunoassays and immunosensors developed so far for the detection of heart type fatty acid binding protein (HFABP) in the buffer, plasma or whole blood. The direct electrochemistry of a multimeric alcohol oxidase (AOx) physically immobilized by encapsulating with polyethylenimine in a multiwalled carbon nanotubes–Nafion matrix on the gold electrode surface was established for the first time. Direct electron transfer facilitated by the MWCNT between the AOx protein and the electrode was confirmed. The entrapped AOx possesses good bioactivity and electrocatalytic activity at room temperature and physiological pH [135].

Since the first successful cardiac pacemaker was implanted in 1960, a variety of implantable battery–powered devices has been developed for various indications, ranging

from neurological disorders to hearing loss. We describe the first implanted GBFC that is capable of generating sufficient power from a mammal's body fluid to act as the sole power source for electronic devices. This GBFC is based on carbon nanotube/enzyme electrodes, which utilize glucose oxidase for glucose oxidation and laccase for dioxygen reduction. The GBFC, implanted in the abdominal cavity of a rat, produces an average open-circuit voltage of 0.57 V. Sales et al. [136] prepared an implantable enzymatic fuel cell in a living rat. The authors conducted assays under physiological conditions using glucose from the rat blood as the anodic fuel and dissolved oxygen as the oxidizing agent in the cathode side.

MacVittie et al. [117] implanted biocatalytic electrodes into the hemolymph between the exoskeleton and the stomach of an American lobster; employing immobilized PQQ-dependent glucose dehydrogenase in the anode compartment and a laccase-based cathode in a buckypaper conductive support, the authors produced the desired energy. Southcott et al. [137] demonstrated an implantable bio-fuel cell operating under conditions that mimicked the human physiology for a continuously operating pacemaker. A buckypaper support was employed as electrode material to immobilize PQQ-dependent glucose dehydrogenase and laccase on the anode and cathode respectively, along with 1-pyrenebutanoic acid succinimidyl ester. The prepared pacemaker produced a profile of electrical impulses similar to those usually registered with a commercial device operating on the basis of standard lithium-based battery.

With the aim of developing implantable power sources in the human body, reported more recently two “Cyborg” lobsters connected in-series to power a watch [138]. Although these experiments were not performed with mammals, these studies demonstrated that GBFCs can produce electricity out of living organisms. It appears that an attractive mode of operation for bio-fuel cells consists in the energy accumulation through capacitors for the intermittent activation of model devices. This mode of GBFC function may be applied to the activation of some sensor devices for medical monitoring. In another interesting work, Miyake et al. [36] described a layered biofuel cell constructed by laminating enzyme-modified carbon fabric (CF) strips and hydrogel film containing electrolyte. A heavy-duty “double network (DN) hydrogel” was used to generate very flexible, thinner BFC. The premodification of CF with carbon nanotubes (CNTs) was effective to improve the performances of both bioanode and biocathode. The laminated stack of the improved bioelectrodes was practical for light-emitting diode (LED) lighting.

Wang et al. [139] demonstrated a simple and convenient pathway to fabricate graphene-supported ferric porphyrin as a peroxidase mimics for electrochemical deoxyribonucleic acid (DNA) biosensing. The biosensing method could discriminate target DNA from single-base or three-base mismatched oligonucleotides. Liu et al. [140] fabricated an electrochemical DNA biosensor based on graphene-three dimensional nanostructure gold nanocomposite modified glassy carbon electrode (G-3D Au/glassy carbon electrode (GCE)) for detection of surviving genes. However, research has focused on more elegant techniques for deposition, including electro polymerization directly on the electrode surface and the use of electrophoretic deposition of charged polymers. These allow for both better tailoring of the biotic-abiotic interface and more control of thickness and morphology [141].

Carbon nanoparticles KetjenBlack (KB) with a high sorption capacity and single walled carbon nanotubes (CNTs) were “glued” together by chitosan for the preparation of a composite. The main aim of this work was to prepare a cheap and scalable composite matrix

with the aid of renewable biopolymer chitosan to make a BFC in a green way, with the amount of CNTs kept at the lowest possible level, while ensuring an efficient performance of the BFC [142].

The unusual ability of oxygen-tolerant hydrogenases to produce electricity from a H₂-air mixture was investigated with the aim of establishing a strategy for raising volume, power density, the measure of importance for miniature devices. The results indicated the feasibility of membrane-less hydrogen-air fuel cells delivering volume power densities well in excess of 1 mW cm⁻³ [27]. A laminated stack of bio-fuel cells that is composed of bioanode fabrics for fructose oxidation, hydrogel sheets containing electrolyte and fuel (fructose), and O₂-diffusion biocathode fabrics has been reported. The anode and cathode fabrics were prepared by modifying fructose dehydrogenase and bilirubin oxidase respectively, on carbon nanotubes-decorated carbon fiber fabrics. [36].

Glucose/O₂ biofuel cells (BFCs) with an improved power density and stability were developed, using glucose oxidase (GOD) nanotubes with polypyrrole (PPy)-carbon nanotubes (CNTs)-GOD layers deposited on their surface as an anode and a PPy-laccase-2,20-azinobis (3-ethylbenzothiazoline-6-sulfonate) diammonium salt (ABTS) film type cathode. The GOD nanotubes were fabricated within the nanopores of an anodized aluminium oxide membrane using a template-assisted layer-by-layer deposition method. Increase in enzyme loading of GOD nanotubes has improved electrochemical properties of the PPy-CNTs-GOD layers [143].

Reuillard et al. [144] described the fabrication of a novel bioanode for glucose oxidation. Electrochemical investigations clearly show the advantages of using MET for glucose oxidation with naphthoquinone (NQ) as a redox mediator. Compared to DET, the bioanode achieved 7-fold increases in catalytic current densities, despite the increase in OCP of the bioanode from -0.45 V to -0.2 V. A glucose biosensor based on direct electron transfer of glucose oxidase (GOD) self-assembled on the surface of the electrochemically reduced carboxyl graphene (ERCGr) modified glassy carbon electrode has been reported. Moreover, it will be a useful method to fabricate other analogous enzyme electrode biosensors with direct electron transfer based on carboxyl graphene [145].

The enzyme *Trametes hirsuta* laccase (ThLC) undergoes direct electron transfer at unmodified nanoporous gold electrodes, displaying a current density of 28 μA/cm². The response indicates that ThLC was immobilized at the surface of the nanopores in a manner which promoted direct electron transfer, in contrast to the absence of response at unmodified polycrystalline gold electrodes. The bioelectrocatalytic activity of ThLc modified nanoporous gold electrodes was strongly dependent on the presence of halide ions [146]. Choi et al. [147] reported the effect of pretreatment on indium-tin oxide (ITO) electrodes although metal and carbon electrodes have been enormously used. The electrochemical and surface properties of ITO electrodes were investigated after 6 different pretreatments.

Janus Au-mesoporous silica nanoparticles were used as scaffolds to design an integrated electrochemical biorecognition-signaling system [148]. A proof of concept of this strategy, based on the face-selective functionalization of the anisotropic colloid, involves the covalent immobilization of horseradish peroxidase on the mesoporous silica face as enzymatic signaling element, as well as the modification of the Au face with streptavidin and polyethylenglycol chains as biorecognition and solubilizing agents, respectively.

Great improvement has been reported during the last five years so that, these enzymatic biofuel cells have been implanted in various living hosts. Three major key issues have been addressed that could account for these improvements: (a) crystal structure of the enzymes and the catalytic pathways for enzyme immobilization on an electrode for a direct and mediated electron transfer (b) covalent attachment of the enzyme on the electrode for stability enhancement and (c) use of 3D-architectures, for an enhancement in the amount of electrically connected enzymes, hence, an increase in the catalytic current. This last point has stimulated numerous works during the last few years in the field of enzymatic bio fuel cells.

Lojou et al. reported for the first time, a comprehensive study of herringbone carbon nanofiber mesoporous films as platforms for enhanced bio oxidation of hydrogen. The 3D network allows mediatorless hydrogen oxidation by the membrane-bound hydrogenase from the hyperthermophilic bacterium *Aquifex aeolicus*. The key physico-chemical parameters that enhance the catalytic efficiency, including the surface chemistry and hierarchical porosity of the biohybrid film have been examined [93].

Cosnier et al. described the non-covalent functionalization of MWCNTs by pyrene derivatives with boronic acid. The functionalization of MWCNT electrodes by HRP alone or by GOX and HRP (horseradish peroxidase) association was investigated for the catalytic reduction of H_2O_2 and O_2 , respectively [94]. Kano et al. [149] have a hypothesis that when the electrode is modified with the substrate of BOD (or related compounds), BOD will attractively interact with the modified compound in such an orientation that the electron-accepting T1 site faces the electrode surface. The orientation seems to be convenient for the DET-type bioelectrocatalysis. The fructose/dioxygen biofuel cell, one of the direct electron transfer (DET) -type bioelectrochemical devices, utilizes fructose dehydrogenase (FDH) on the anode and multi-copper oxidase such as bilirubin oxidase (BOD) on the cathode as catalysts.

Contrary, to reported ethanol BFCs based on commercial carbon fiber papers, Selloum et al. [96] have explored the ability of a three-dimensional polyacrylonitrile material prepared by electrospinning combined with sputtering as a new nanostructured material. This material offered a large surface area to provide high loadings of enzymes to enhance the electrochemical performances of enzyme electrodes in BFCs. Electrospinning is a unique process that effectively produces a mat of small fibers with controllable compositions and sizes in a matter of minutes from a variety of polymer precursors.

Recently, Goswami et al. reported a fluorescence quenching based non-enzymatic method for sensitive and reliable detection of free bilirubin in blood serum samples using human serum albumin (HSA) stabilized gold nanoclusters (HSA-AuNCs) as fluorescent probe [150]. An alcohol oxidase (AOx) based third generation bioanode for generating power from methanol substrate in a fuel cell setup using air breathed laccase biocathode has been fabricated [151]. Alcohol oxidase (AOx) with a two-fold increase in efficiency was achieved by physical entrapment of the activator ferrocene in the protein matrix through a simple microwave based partial unfolding technique. It was used to develop a third generation biosensor for improved detection of alcohol in liquid samples [152]. The alcohol oxidase (AOx) cDNA from *Aspergillus terreus* MTCC6324 [153], Fabricating a laccase based amperometric biosensor for detection of pyrocatechol. *Trametes versicolor* laccase was co-immobilized in a nanocomposite matrix comprising of osmium tetroxide on poly

4-vinylpyridine, multiwalled carbon nanotubes, Nafion and carbon black on glassy carbon electrode [154].

The malaria biomarker is an important detection technique for diagnosis of the malaria disease. Among the various biomarkers, plasmodial lactate dehydrogenase and histidine-rich protein II (HRP II) have received increasing attention for developing rapid and reliable detection techniques for malaria. This technique provides the current status of malaria biomarkers, along with their potential utilization for developing different malaria diagnostic techniques and advanced biosensors [155]. The cell-bound cholesterol oxidase isolated from the *Rhodococcus* sp. NCIM 2891 was found to be active in a wide pH range with the physiological pH at center of the range, stable at RT for several weeks and in many organic solvents commonly being used in biotransformation studies [156].

CONCLUSION

In this final section of the article, from the entire discussion, we are now able to reach on the conclusion that the selection of any process for the bioconversion of substrates, and the realization of the current research challenges to be faced in the production of bio-fuels, both needs critical evaluation. Over the last five decades, these biofuel cells have been poised as advanced power sources of the future, expanding their role in diverse applications from sources in miniature electronics, electrical energy storage systems, to pacemakers and implantable devices and aerospace. Nano materials will continue to play an increasingly significant role in the development of high performance bio-fuel cells. Rapid electron transfer between the enzyme and the electrode surface offers considerable promise for maximizing the power density of bio-fuel cells. In addition to medical applications, enzymatic bio-fuel cells can also use renewable fuels with high energy density and safety for microelectronics. The technology developed for enzyme electrode fabrication has also stimulated the advances in biosensor applications. The most significant issues include: long term stability of the enzyme electrodes, efficient electron transfer between enzymes and electrode surfaces, and improved enzyme bio-catalytic activity: for bio-fuel cells with increased power output. These are the main objectives for the next generation enzyme electrodes for bio fuel cells.

However, the realization of miniaturized fuel cells faces several challenges that must be overcome to find market applications. At this time, the amount of power supplied by fuel cells of this size is not adequate to satisfy realistic energy demands. This is primarily limited by the anodic surface area, and requires further research in device architecture and novel catalysts. Miniature bio fuel cells also struggle with long term and consistent power supply, which would require the addition of capacitors to store charge or further investigation of novel catalysts.

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MICROCRYSTALLINE CELLULOSE ADDITIVE FOR MODIFICATION OF PROPERTIES OF POLYMER FILMS

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ABSTRACT

Studying structure and properties of various coatings used in industry is very important nowadays, and in particular understanding the electromagnetic response to the microstructure and electrochemical response to the chemistry of the coating. Changes in the properties of coatings containing microcrystalline cellulose were studied by electrochemical impedance spectroscopy. It was shown that barrier properties of films change with time depending on the amount of microcrystalline cellulose. This result can be explained by morphological changes related to swelling in voids and channels due to water uptake. This study suggests a more scientifically justified approach to the formulation of composite coatings for medical and technical applications.

Keywords: coatings, electrochemical impedance spectroscopy, microcrystalline cellulose, polymethylmethacrylate, moisture uptake, thin films

INTRODUCTION

Microcrystalline cellulose (MC) as biocompatible material attract a lot of attention over recent decades [7]. Cellulose-based composites can be used in flexible polymer displays [8], biocompatible and biodegradable optical diodes [9]. Electro-optical properties of cellulose are investigated for application in sensors [10], such as nanocomposite with silver is studied for applications for plasmon-base sensors [11]. In the very recent past the special attention has been drawn to biocompatible nano-cellulose for using in wet nano-cellulose membranes, artificial blood containers, materials for reconstructing bone tissue and stent coatings [12,

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13,14]. Microcrystalline cellulose is a polymer with straightened polysaccharide chain suitable for all the mentioned applications.

In this paper moisture uptake to films containing MC was studied by electrochemical impedance spectroscopy (EIS).

EIS is a non-destructive method that can be employed in thin films characterization. Different porous structure can be analyzed by the changes in the electromagnetic propagation through the material. Impedance spectra elucidate valuable information regarding physical properties of polymer films. Decrypting this information is an important task which requires joined approach of modeling and carefully advanced physical experiment.

Impedance method is based on measuring frequency dependent impedance (both real and imaginary part) in a wide frequency range [1 - 3]. Bode and Nyquist plots, which are built on the basis of EIS data, can be fitted with equivalent schemes containing resistors, capacitors, Warburg element, along with other passive elements [4]. Cell resistance is responsible for solution resistance and the resistance of a film to ions flow (ρ), which, in turn, depends on each ions mobility (μ), concentration (n), and ions charge z .

$$\rho = n\mu z$$

Warburg element represents connected in series resistance and frequency dependent capacitance for steady-state diffusion. This element describes mass transfer processes, in particular, diffusion, which in time domain obeys Fick's second law:

$$\frac{\partial C}{\partial t} = D \cdot \left(\frac{\partial^2 C}{\partial x^2} \right) \quad (1)$$

where C – concentration and D – diffusion coefficient.

In frequency domain the expression for a relevant impedance, Z , can be written as:

$$Z_w(j\omega) = \lambda(j\omega)^{-1/2} = \lambda\omega^{-1/2}(1-j) \quad (2)$$

Impedance modulus decreases with increasing frequency according to Eq. (2). Here λ – is so-called Warburg coefficient.

At the other hand, the solution of equation (1) considering electrochemical parameters comes up to expression:

$$Z_w(j\omega) = \kappa_f(j\omega D_0)^{-1/2} = \kappa_f(\omega D_0)^{-1/2}(1-j)$$

Which allows establishing relationships between W and electrochemical parameters.

$$\lambda = \kappa_f D_0^{-1/2}$$

where: K_f - the rate of oxidation or reduction reaction taking place at electrode surface, D_0 - diffusion coefficient of the ion participating in the reaction [1, 2].

This paper describes study of the properties of films containing different MC amount in the contact with weak solution close by concentration to physiological. As barrier coating, Polymethylmethacrylate (PMMA) was chosen as barrier coating due to its relatively good mechanical properties. Also it was important to correlate changes of barrier properties in the presence of filler with moisture uptake properties.

This is known that the mechanism of thin film damage in aqueous solutions starts with diffusion of the solution through a film by different mechanisms: uniform diffusion (UD) and non-uniform diffusion (ND) [5]. UD takes place through intermolecular pores and is considered a slow process (by orders slower than ND). ND takes place through intermolecular pores, such as micro-cracks, microscopic nonuniformities, and inclusions. MC particles create barriers for ND through film resulting in, on one hand, in moisture uptake [6], on the other hand, in corrosion processes from metal side. The corrosion process results in the release of corrosion products in the space between film and electrode and permeating corrosive products into a film.

EXPERIMENTAL

Barrier PMMA coating was casted from 0.05% (wt.¹) acetone solution. The solution coated panels were left to dry at ambient temperature. The amount of dissolved polymer was chosen to obtain films of a desired thickness, which was controlled by micrometer.

For example, to obtain coating of 7 μm thickness, 1 cm³ 0.5% PMMA was casted at working area of 5 cm². To obtain coating of 7 μm thickness, 1 cm³ 0.01% PMMA and 1% MC casted at working area 5 cm². The resulting film contained app. 10% MC.

MC was obtained by hydrolysis of cotton linter by hydrochloric acid [15]. Dry MC flakes were pulverized in a mortar to medium particle size 1 – 3 μm . Average particle size was controlled by optical microscope.

Steel panels of 2 mm thickness were used for film casting.

Measurements were performed with Gamry PC3 built-in potentiostat in 5000 - 0.02 Hz range.

As a result of film casting, samples were obtained with a transparent or opaque coating, depending on MC content.

0.9% NaCl solution in distilled water (5) filled one-compartment three-electrode electrochemical cell (Figure 1) with Ag/Ag⁺ reference electrode (4) and platinized grid as counter electrode (3). Steel panels casted with studied film (2) served working electrode (1). The experiment was terminated when films lost their barrier properties, nearly after one month of the beginning of immersion.

Chemicals used for solution preparation were analytical purity grade.

¹ All percentages are weight-based.

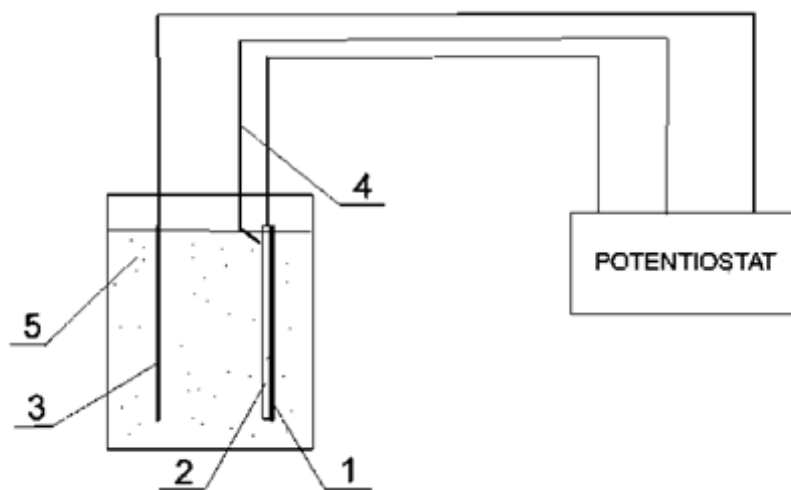


Figure 1. Schematic of electrochemical experiment.

RESULTS AND DISCUSSION

Nyquist plots indicate that it is clear that PMMA film possess permeability for electrolyte ions (Figure 2), which can be deduced from un-completeness of semicircle at low frequencies. The shift of Nyquist plots to the left as a consequence of increasing the exposure time is a sign of a coating degradation: swelling and disintegration. Simultaneously with swelling, the process of transfer of corrosively active chlorine ions to metallic panel takes place. This process is followed by corrosion products release at the film/panel gap, and transport of dissolved corrosion products through the film to solution.

This is typical to all samples either non-containing (Figures 2, 3) or containing (Figures 4, 5) MC to demonstrate initially lower impedance, probably due to lower film thickness before moisture uptake. Semicircle decay occurring at larger times of film immersion is a sign of films degradation due to their damage.

Opposite to control samples, showing diffusive properties simultaneously with the degradation of barrier coating, samples with MC demonstrate sharper semicircle, which is the sign of keeping the film its barrier properties until decomposition. For thicker film the shape of a semicircle is more pronounced. For different film thicknesses and exposure times plot shapes are similar. This is the evidence of corrosion products transport through the film rather than their storage inside film, which can be due to the presence of MC providing micro channels for draining of those products. Those micro-channels likely to remain unchanged during corrosion. Such behavior of samples containing MC suggests additional mechanism of changing in the media containing ions than for classical barrier coating without MC. The properties of a barrier coating seem to be modified by the presence of MC. After the initial period of moisture uptake followed by slight impedance increasing for both barrier and modified coatings, further process of films damage for modified coatings occurs at a lower rate and in more controlled manner, followed by keeping barrier properties longer, until decomposition.

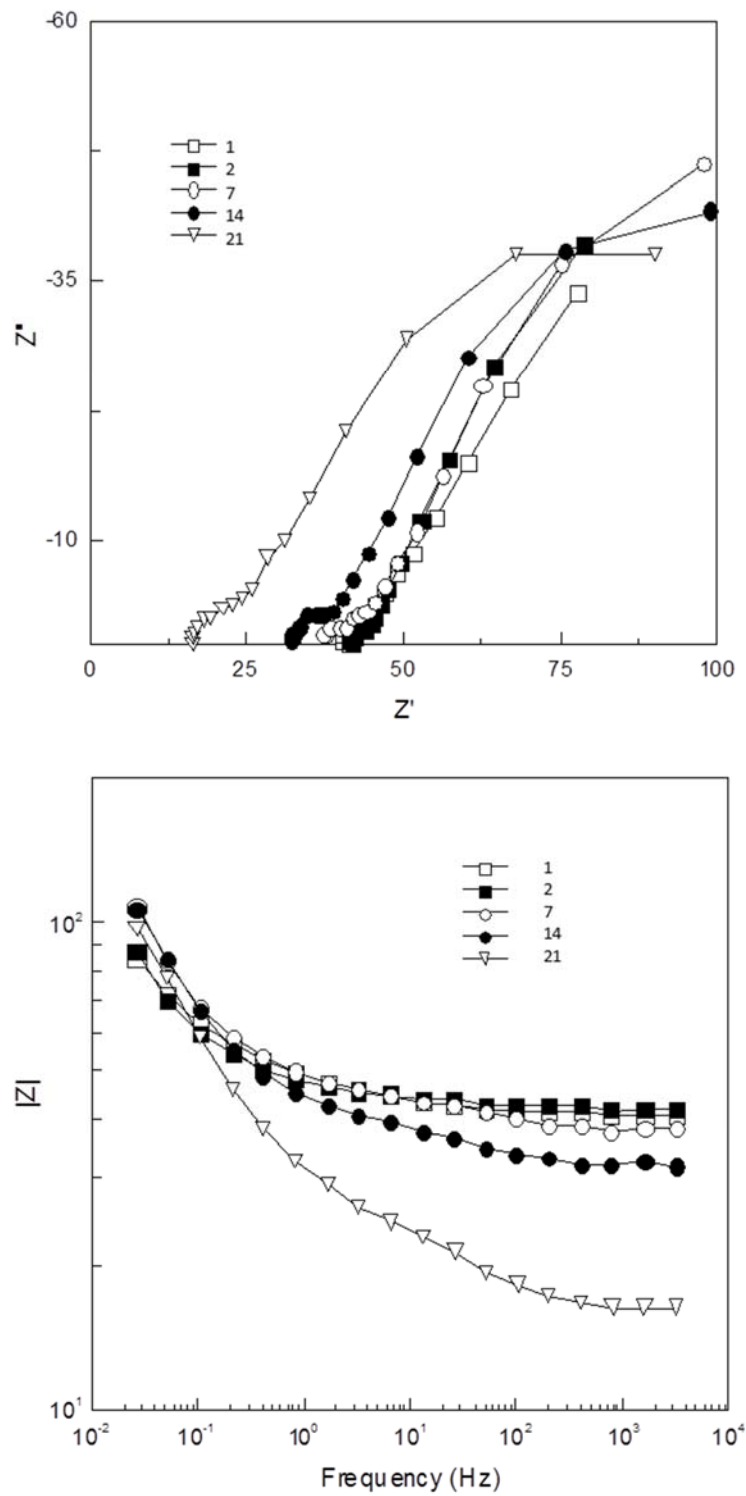
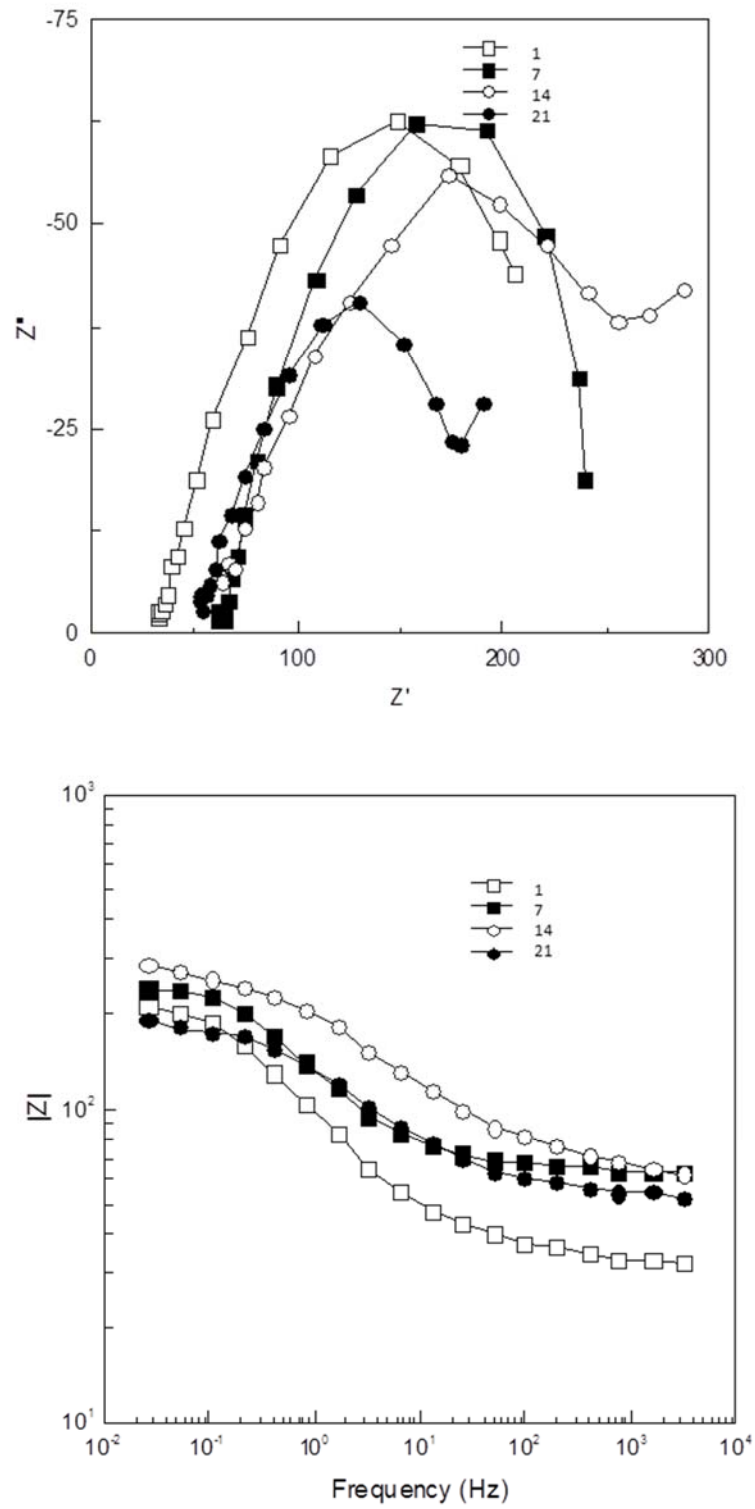


Figure 2. EIS data (Nyquist – top, Bode - bottom) for PMMA film 7 μm thickness. Numbers - days of measurement.

Figure 3. Nyquist and Bode plots for PMMA film 14 μm thickness.

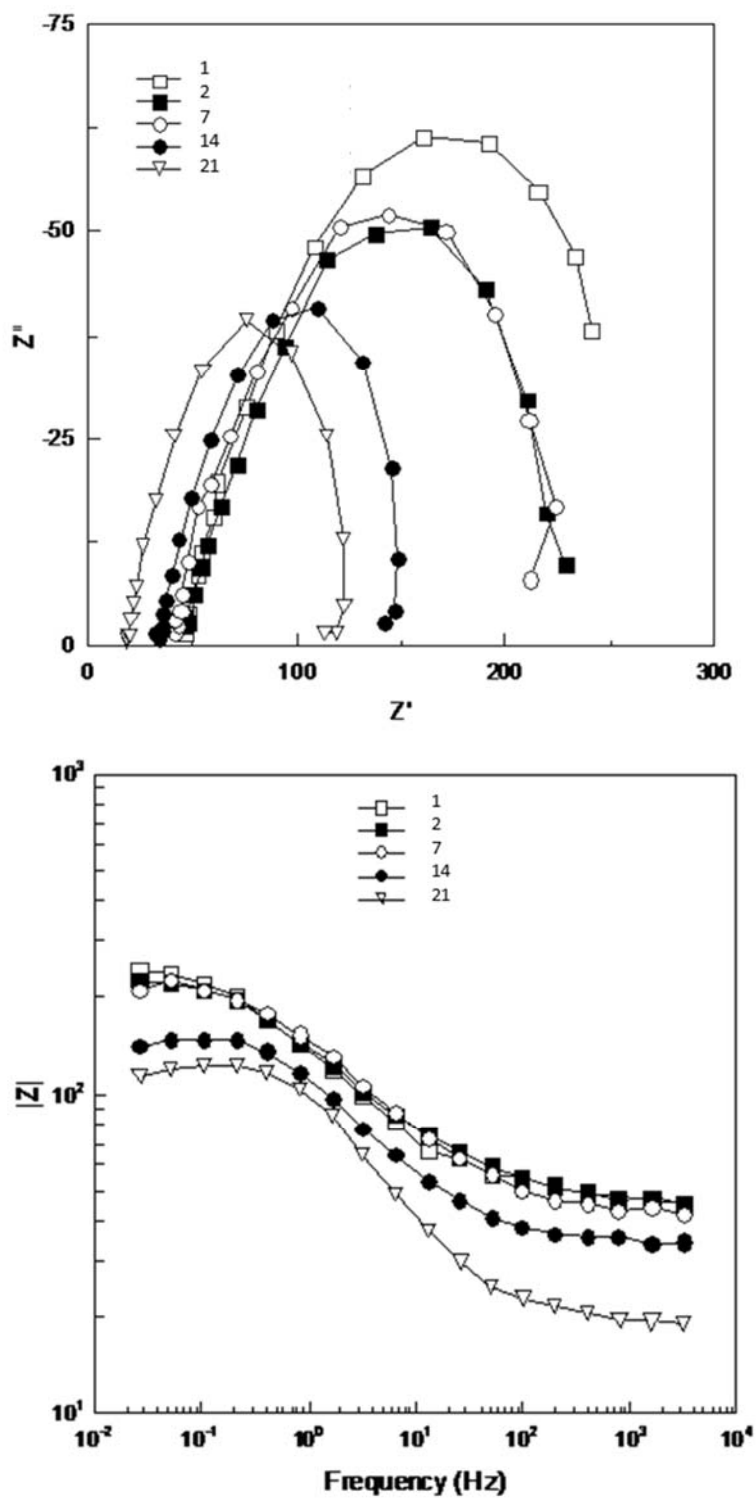


Figure 4. Nyquist and Bode plots for PMMA with MC film 7 μm thickness.

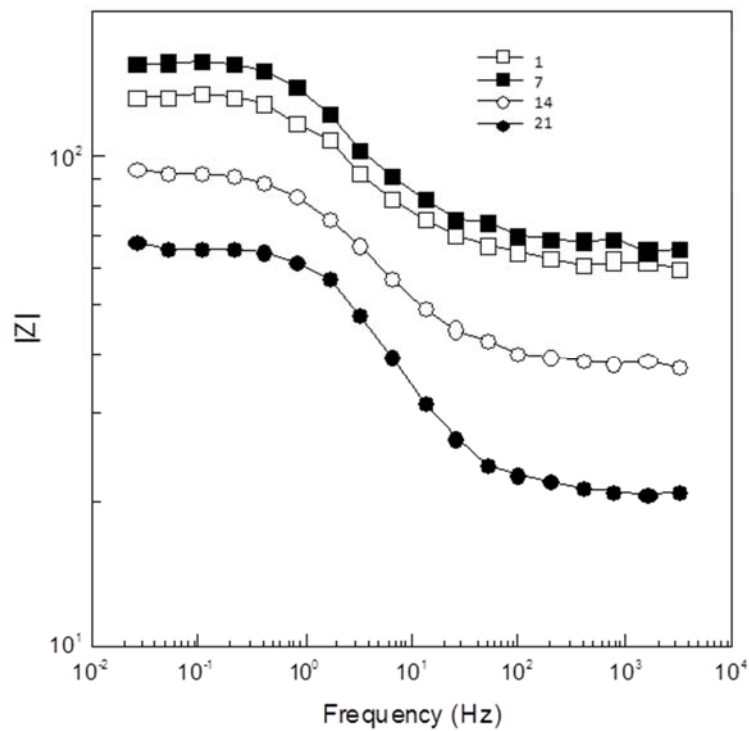
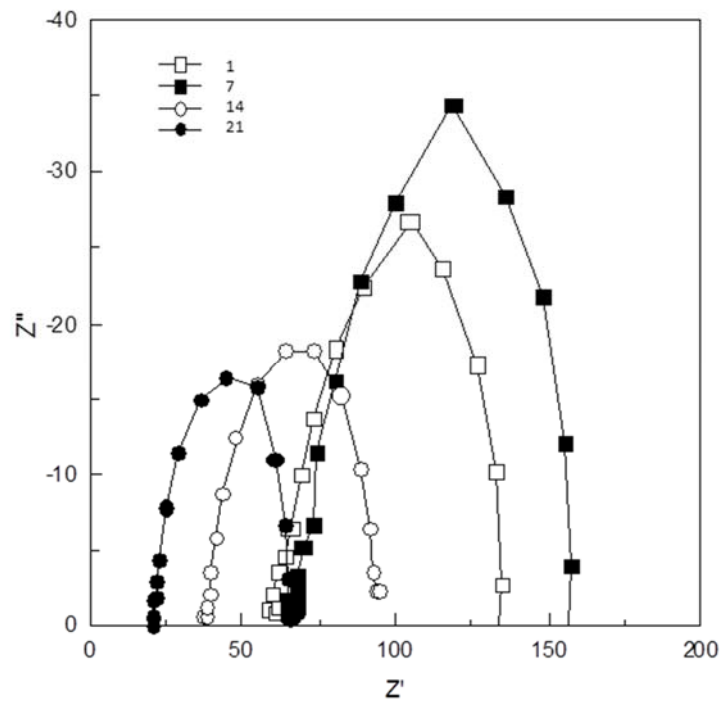


Figure 5. Nyquist and Bode plots for PMMA with MC film 14 μm thickness.

CONCLUSION

Changes in the properties of coatings containing MC were studied by electrochemical impedance spectroscopy. Barrier properties of films change with time depending on the amount of MC. Observed behavior can be explained by morphological changes related to swelling in voids and channels during ions diffusion. Obtained results allow more justified approach in the formulation of composition of coatings for medical and technical application.

ACKNOWLEDGMENTS

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DEVELOPMENT OF NANOTECHNOLOGY-BASED NANOCOMPOSITES

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ABSTRACT

The unique character of the nanocomposite lies in the high volume ratio of the phase boundaries and their strength. An important aspect of the nanocomposite synthesis is the use of the principles of self-organization and self-assembly. The study of scientific basics of synthesis of nanocomposites will lead to the development the technology for the creation new 3D products and functionally-graded coatings with a wide range of application.

Keywords: composite materials, nanocomposites, self-organizing system, structural organization, mechanochemical synthesis, high-temperature synthesis, functionally-graded coatings

INTRODUCTION

The science of composite materials as a section of the materials science dates back to the turn of the 60s. Over the last few years the research on the composites development for medical and biological purpose has extended due to the expanding of the features set implemented with polymer composites. The proceeding to the nanosize structures and substances has led to the introduction of a new substance - nanocomposites. Unfortunately, the lack of our understanding and knowledge of the nanoworld does not allow predicting not only what new features will appear by the introduction of new ingredients in the nanocomposites, but also their vector. These features may be radically different from the components features. Nanocomposites are completely unique structures, which from the point of view of materials science can help to create compositions that are impossible from the conventional point of view. The effect of the nanoparticles on the nanocomposite features and

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their use is considerably dependent on the environment in which the nanoparticles are dispersed (e.g., matrix). Of interest is the use of various physical fields for the synthesis of nanosize and nanocomposite films [1, 2, 3].

SOME PHYSICAL INTERPRETATION OF THE NANOCOMPOSITE SYNTHESIS

The unique character of the nanostructured and nanocomposite coatings lies in the high volume ratio of the phase boundaries and their strength, in the absence of dislocations within the crystallites and the possibility of changing the volume ratio of crystalline and amorphous phase, as well as in the mutual solubility of metallic and nonmetallic components. The presence of a large area of the phase interface in the nanocomposite coatings and films allows significant changing of their properties by modifying the structure and electronic structure as well as by alloying with various elements. Nanocomposite coatings are a new generation of materials [4, 5].

An important aspect of the nanocomposite synthesis is the use of the principles of self-organization and self-assembly. Any open system, where exchange processes take place, can be classified as a self-organizing system. Under the exchange processes are understood in general the exchange of substance, energy and information. The purpose of the self-organization is to bring up the particles in the system to unified measures under internal and external influence - the emergence and development of sources of self-ordering, the spontaneous information accumulation, structuring. Therefore, the process of self-organization can be considered in two ways - structural and functional. In the structural aspect a change of the internal structure of the system takes place, whereas in the functional aspect the system quality changes. Structural self-organization ensures the structural stability of the system, thereby a search of self-consistency between the system components takes place. The functional component finds and supports the optimal ways of the system components behavior, keeping the sequence of actions. As the system structure is characterized by the discrete determinacy, differentiated quantity, and the system function is in a certain way chosen quality, so in the first case, one should use methods for mathematical modeling of the system with the obligatory taking into account of the chemical component of the process, while in the second case - methods for the quality research. The structural organization is the distribution order of the system components as parts in a whole entity, a way of their connection, subordination, hierarchy of the system. Functional self-organization is a sequence in the performance of the system of necessary actions to achieve immediate and long-term objectives [6, 7, 8]. In order to influence on the self-assembly processes and to implement the efforts to manage them it is appropriate to apply weak and superweak effects of physical fields of different nature (electromagnetic, magnetic, electrical) [9, 10, 11] in combination with modeling of the synthesis processes of nanosize nanocomposite films and structures [12, 13].

PROMISING AREAS IN THE USE OF NANOCOMPOSITE STRUCTURES

The first area is connected with the study of scientific basics and the development of innovative technologies for the preparation of nanocomposite powder materials based on the controllable mechanochemical synthesis and self-spreading high-temperature synthesis for additive technologies, which means the analysis of the mechanism of interaction of the matrix plastic dispersion material with highly-rigid nanoparticles in the high-speed shock-wave interaction, conducting fundamental research of composite nanostructured powders for additive technologies and development on this basis of the technology for the composite powders creation. Therefore, mathematical modeling of the process of high-speed interaction of plastic matrix material particles with highly-rigid nanoparticles and fundamental study of physical and chemical processes of heterophase synthesis of composite nanostructured dispersed objects are necessary. Fulfilling these requirements will lead to the development and mastering the technology of the composite nanostructured powders preparation and their adaptation for the creation of 3D products with irregular shape and a wide range of common and special application using additive technologies.

The second area is the development of physical and chemical basics and highly efficient methods for the preparation of nanostructured composite functionally-graded coatings with the highest ever mechanical, thermal, adaptive and corrosive features for the work in extreme conditions. It means the study of the processes of physical and chemical interaction of dispersed materials of the “metal-nonmetal” system in the high-temperature flow by the formation of functionally-graded coatings with abnormally high features set and the development of computerized technology of their preparation for promising products of common and special application, based on the determination of common regularities in the formation of composite functionally-graded coatings with a controllable features set, the development and mastering the computerized technology of their preparation applied to promising products of precision engineering, energetics, transport, construction and agricultural machinery, medicine and industrial ecology.

Nanosize and nanostructured composite powder materials produced by means of high-speed controllable mechanosynthesis are very specific regarding the technological features by the preparation of functional coatings. One of the characteristics of such powders is their tendency to the agglomerate formation and structure degradation at temperatures much lower the liquidus temperature. To prevent these negative phenomena technologies of the functional nanostructured coatings preparation are developed, the spraying of these coatings is performed at low temperatures and at high speeds of heterophase transfer. In the Nanocenter “Prometey” the technology of supersonic cold gasdynamic spraying has been mastered, its main characteristics are low temperature of the particles in the heterophase flow (80-120°C) and high speed of particle transfer (up to 2,5 M). When using two or more off-line dispensers, the technology allows creating functionally gradient coatings with the required microhardness of the coating thickness due to the adjustable delivery of the nanosize powder from one of the dispensers (e.g., nanocorundum or WC fraction 30-80 nm). It ensures high adhesive and cohesive strength of the coating and a radical microhardness from the substrate to the surface. For example, for corrosion-resistant alloy Al-Zn-Sn microhardness can controllably change from 45 to 350 HRC by the simultaneous porosity decrease from 5 to 0.2-0.5%. This ensures a significant increase of wear and corrosion resistance of the coating when using in severe

conditions, which is particularly effective for friction pairs, locking systems, control systems elements and so on.

The speciality of the the Nanocenter “Prometey” is the development and mastering several related promising technologies of functional coatings preparation. This allows, firstly, obtaining coatings with a radically improved features set and, secondly, creating completely different as regards to functional tasks coatings. In particular, a method for robotic microplasma spraying has been developed and patented, this method enables to save without degrading the original structure of the sprayed material in the functional coating, as well as in contrast to conventional gas-thermal spraying methods to apply coatings on thin-walled products without the risk of overheating and deformation, providing high adhesion and cohesion strength of the coating with advanced adjustable multi-porosity [14, 15].

An important area is the research of the possibility of the gradient nanocomposite films formation, in particular, research to develop a technology for the creation of the structure “multilayer nanocomposite ferroelectric - dielectric substrate” as a basis for the building a new element base of Microwave and Terahertz radio-electronics. At present the main research areas for improving the features of created ferroelectric structures are in the field of the nanosize composites materials, the technology of their application on the substrates of different physical nature by means of modern methods: ion-cathode and ion-plasma reactive magnetron spraying, levitation-jet method, sol-gel technology, laser ablation, etc. Estimating the global trend of scientific and technological development over the last decade, it is clear that there is a positive dynamic in the elimination of negative factors in the ferroelectric films features. These technologies are used in the industrial production of analog Microwave and digital IC, as well as memory elements. Industry leaders do not reveal the secrets of their technological achievements because of the economic and technical benefit. Devices on the new element base have exceptional quality functionality: extended operating frequency and temperature range, high switching speed and low power loss, high radiation resistance, wider application spectrum as compared to their counterparts on the semiconductor, p-i-n diodes and ferrites [16, 17, 18].

The existing technological problems and the lack of research in materials science are a significant obstacle for the development of modern electronic component base. The use of magnetron spraying of the targets with various composition will significantly improve quality electrical parameters of the created multilayer ferroelectric structures, their use allows engineering and constructing passive and active phased antenna arrays with electronic control of the directional diagram, used in various radio-technical devices. The new ferroelectric structures will be used as the basis of the RAM and ROM computing devices elements. Micro- and nano-electronics on the new ferroelectric substrates should become the basis for the creation of analog and digital IC with ultra large integration level. Performing estimation comparison of elements on the ferroelectric substrates of the technology in question and existing technology, one can definitely say that the resulting structures will have a wide temperature operating range of the dielectric permittivity stabilization from -500°C to $+600^{\circ}\text{C}$, whereas currently the best temperature stabilization value is from -100°C to $+30^{\circ}\text{C}$. Creating new models of multicomponent ferroelectric materials taking into account energy interactions by the ion-plasma spraying will lead to a breakthrough in this technology. Its novelty lies in the formulation and solution of the optimizing selection procedure of technological parameters of nanocomposite layers spraying, which form the ferroelectric structure, using a modified model of the ferroelectric barium strontium titanate. Using the

multicomponent targets for the formation of a multi-layer ferroelectric substrate, taking into account the subsidence properties of each component of the substrate and each monolayer of the structure, allows synthesizing a nanocomposite film with the required electrophysical parameters [19].

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CURRENT SPECTROSCOPY OF NATURALLY DISORDERED Pb_3O_4 SEMICONDUCTOR

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ABSTRACT

Charge transfer in Pb_3O_4 layers. Temporal dependences of the current are investigated in the range of dc electric field 20 - 100 V. Experimental dependences agree with locations of the relay mechanism of charge transport with the participation of deep local levels.

1. INTRODUCTION

Among the components of the lead oxide series, Pb_3O_4 is distinguished by the stability of its phase composition in thin layers, photoelectric sensitivity in the visible spectral range, and pyroelectric and ferroelectric properties [1, 2]. Its high resistivity, combined with a high density of deep localized states, enables the use of the oxide Pb_3O_4 in electret structures. The defect and impurity states in high resistance Pb_3O_4 are responsible for the energy spectrum with a complex distribution of the energy levels of localized electron states in the band gap, which determines the charge state of the structure.

Polarization and charging processes determine the operation of most semiconductor devices, controlling the conditions of creation of the potential profile on the surface of photosensitive layers, as well as its variation under optical excitation. To establish the charge transport mechanisms and the nature of the local centers in high-resistivity photoconductors, experimental study and theoretical analysis of the mechanisms of polarization in electric fields of different intensities appeared to be effective.

Charge relaxation in semiconductor bulk can be assumed as one of the factors that determine the stability of characteristics of electronic elements. Relaxation phenomena in a high-resistivity structure are associated with the manifestation of any form of disorder since the possibility of revelation of relaxing elements in an ideally ordered system is reduced to a minimum. The investigation of temporal dependence of the currents of isothermal relaxation makes it possible to acquire information on the population kinetics of capture centers

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arranged nonuniformly over the semiconductor thickness as well as on the capture processes in near-electrode regions [3]. In the following, the results of the study of the polarization relaxation in photoconductive Pb_3O_4 layers are presented.

2. EXPERIMENTAL

Kinetic dependences of polarization currents were measured for the Pb_3O_4 layers with the binder—cyanoethyl ester of polyvinyl alcohol—deposited on a glass substrate with the ITO conducting film based on tin-doped indium oxides. A layer of current-conducting paste (aquadag) with the area of 1 cm^2 and $50 \text{ }\mu\text{m}$ thick was deposited on the surface of the material under study as the upper electrode. Currents of isothermal polarization were detected using a Keithley 6517A electrometric amplifier. The electric field strength was varied in the range $E = 2 \times 10^5 - 9 \times 10^5 \text{ V/m}$. The sample was heated using an electric furnace mounted into a holder. The furnace was dc-supplied from a stabilized current source. The heating rate in the limits of $3-5 \text{ K/min}$ could be fixed in the range $T = 300-370 \text{ K}$.

3. RESULTS AND DISCUSSION

Figure 1 shows the results of the study of the kinetics of isothermal polarization currents in Pb_3O_4 layers measured for different electric fields. The shape of the polarization relaxation curves for Pb_3O_4 indicates that there are two phases of the process (fast and slow) corresponding to time intervals $\Delta t_1 = 1-30 \text{ s}$ and $\Delta t_2 = 30-200 \text{ s}$. At the initial stage after switching the voltage on, rapid current decay is observed in polycrystalline Pb_3O_4 layers, obeying the empirical Curie–von Schweidler relation $I \sim t^{-n}$ ($n = 0.8$). A slow polarization kinetics component corresponds to the exponential dependence. As the voltage increases, the temporal range of the initial portion of the kinetics of the polarization current decreases, while the decay rate of function $I(t)$ increases.

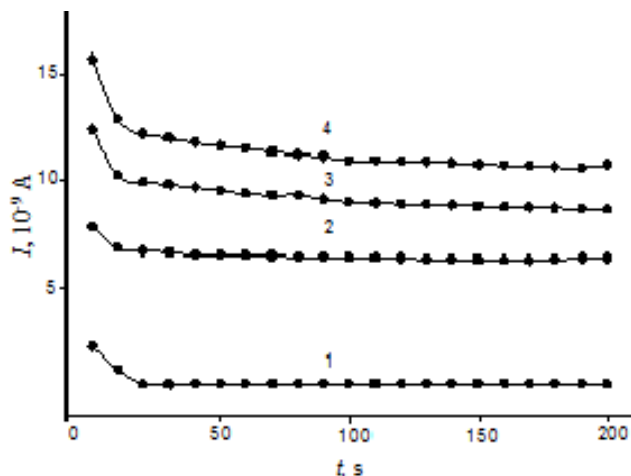


Figure 1. Kinetics of the polarization current measured for Pb_3O_4 layers at electric fields
1 - $2 \cdot 10^5$, 2 - $4 \cdot 10^5$, 3 - $6 \cdot 10^5$, 4 - $8 \cdot 10^5 \text{ V/m}$. $T = 300 \text{ K}$.

The data on the kinetics of the isothermal relaxation currents was interpreted within a model according to which the transfer of an electric charge injected into a crystal occurs through the relay-race mechanism [4, 5]. The charge transfer from the contact into the sample occurs through the mechanism of hopping conduction over the trap centers, which are located in the band gap and have deep trapping levels of free charge carriers. This process is also accompanied by the formation of an energy barrier at the boundary with the anode, which hinders the transfer of electrons (injected from the cathode) to the anode. The energy barrier at the boundary with the anode arises from the energy difference between the electron affinity for the local center and the work function of the anode metal. Thus, the electric current is limited by both the space charge in the bulk of the semiconductor and the energy barrier at the boundary with the anode, which leads to a redistribution of the voltage across the crystal and decrease of electric current passing through the crystal.

Long-time relaxation processes established for the structures under study on the basis of polycrystalline Pb₃O₄ layers can be also accompanied by the formation of depletion regions at the grain–intergrain layer boundary. A nonuniform potential profile of the boundary regions in the polycrystalline structure studied is the same as that created by a quasi-continuous energy spectrum of the traps.

The current relaxation decay observed for the structure is accompanied by the accumulation of charge whose value can be determined from the area lying under the curve of the time dependence of the current. In Figure 2, the values of this charge are plotted as functions of the applied electric field. We can notice that in low electric fields, the accumulated charge increases to a first approximation by the quadratic law, while with the further increase, the polarization varies according to linear dependence.

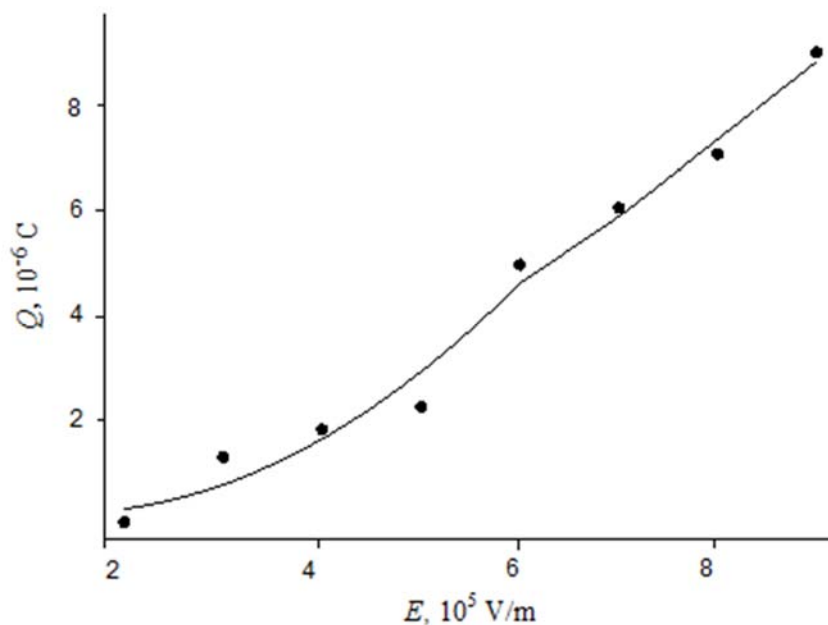


Figure 2. Charge accumulated in the Pb₃O₄ layer and measured as a function of the electric field E . $T=300$ K.

As follows from the theory developed in [5], the electric current passing through the system and the accumulated charge are related by the expression

$$Q = C_c U - \sqrt{\frac{C_c L^3 I}{\mu_{eff} d_c}} \quad (1)$$

It can be seen from expression (1) that, at each instant of time, the accumulated charge is proportional to the square root of the current flowing through the system. Relationship (1) holds for the voltages and times corresponding to the descending branches of the relaxation characteristics. It is worth noting that the lower the voltage and the shorter the time, the better the fit of relationship (1) to the experimental data.

Figure 3 shows the experimental dependences of the charge accumulated in the Pb_3O_4 within different time intervals on the electric current measured at the same times. These dependences were obtained at applied electric field $E=8.0 \cdot 10^5$ (curve 1) and $9.0 \cdot 10^5$ V/m (curve 2) in the range of the descending branches of the relaxation characteristics. In this case, the currents I are the experimental values after subtracting the background current I_b , which corresponds to the leakage current. The background current I_b was chosen equal to the minimum value in the descending branch of the relaxation characteristic at a specified voltage and a longer time. The dependences constructed in the $\sqrt{I}-Q$ coordinates exhibit linear behavior in accordance with relationship (1).

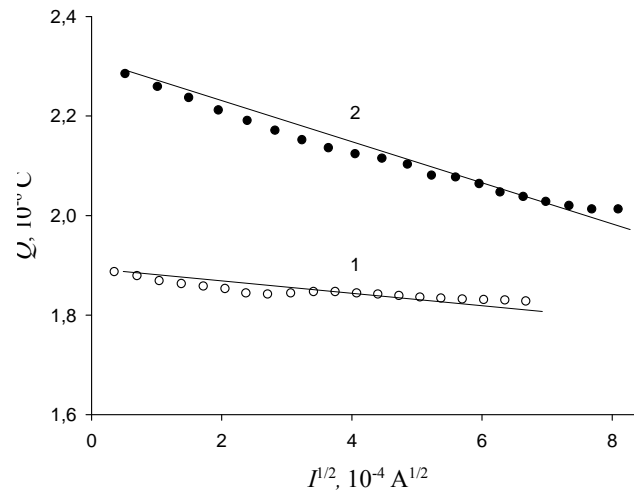


Figure 3. Charge accumulated in the Pb_3O_4 layers for fixed time intervals of the effect of voltage as a function of the current corresponding to the ends of these intervals for the electric fields E : 1 - $8.0 \cdot 10^5$, 2 - $9.0 \cdot 10^5$. $T=300$ K.

The curves of current decay for Pb_3O_4 layers at different temperatures are shown in Figure 4. It was noted that at high temperatures, the power dependence $I(t)$ goes into exponential. The main contribution to conductivity is probably caused by thermal activation of charge carriers from deep capture levels. In accordance with the relay mechanism, their electron drift mobility μ exponentially depends on temperature [4].

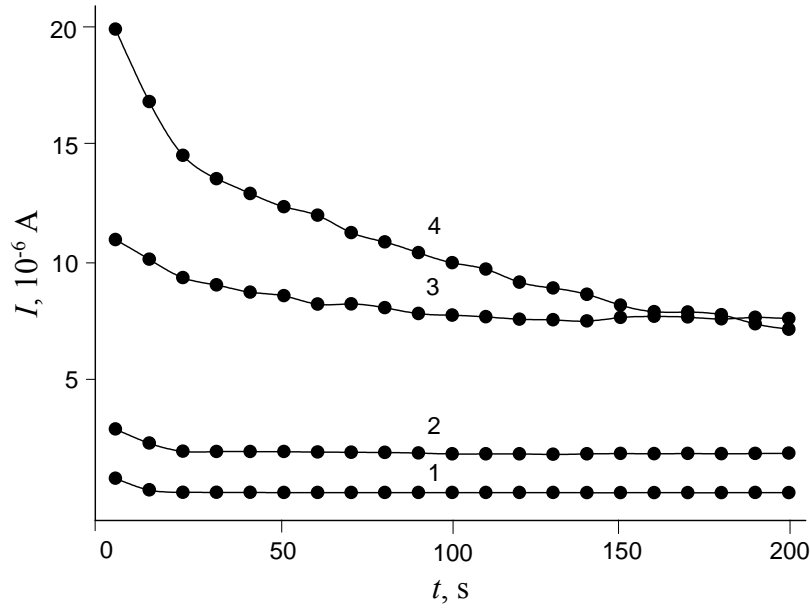


Figure 4. Kinetics of the polarization current measured for Pb₃O₄ layers at temperature: 1- 320, 2 - 340, 3 - 360, 4 - 370 K. $E = 5 \cdot 10^5$ V/m.

The exponential decay of current can be determined by following expression [6]:

$$I(t) = \frac{q\mu n_i SE}{\tau_d} \exp\left(-\frac{t}{\tau_d}\right) \quad (2)$$

with

$$\tau_d = \frac{1}{N_c \sigma_t} \exp\left(-\frac{E_t}{kT}\right), \quad (3)$$

where n_i is the initial density of trapped electrons, S the area through which the current is following, E intensity of applied electric field, σ_t – the conduction of trapped electrons, N_c – the concentration of electrons in the conduction band, E_t – the energy of trapped electrons, k – Boltzmann constant.

According to (2) and (3) the current decays exponentially in time with a time constant equal to τ_d .

Thus, if the measurements are repeated at slightly different temperature, τ_d can be obtained as a function of temperature by plotting $\ln(I)$ versus t . Therefore, on the basis of (3), E_t can be deduced from the slope and the intercept, respectively, of the straight line representing $\ln \tau_d$ against $1/kT$.

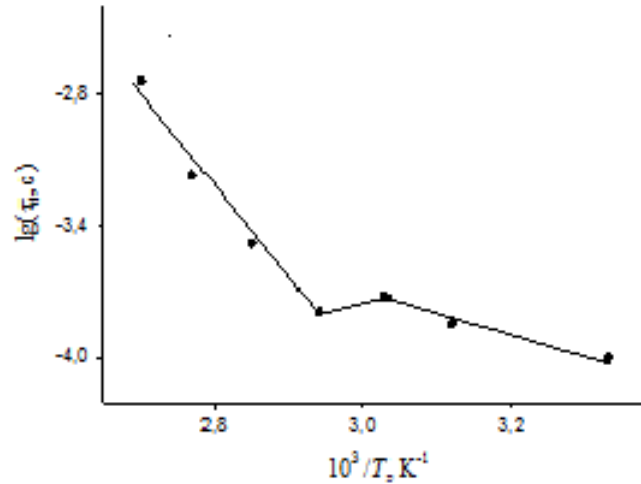


Figure 5. Semi-logarithmic plot of $\lg \tau_d (I/T)$ for Pb_3O_4 layers. $E = 5 \cdot 10^5$ V/m.

In Figure 5 the plot of $\ln \tau_d$ versus $1/kT$ for Pb_3O_4 is reported. Temperature dependence of $N_c \sigma_t$ has been neglected in comparison with the exponential term of the temperature. The slopes of dependence $\ln \tau_d (10^3/T)$ was determined to be $E_{t1} = 0.13$ eV and $E_{t2} = 0.38$ eV.

The data on the kinetics of the isothermal relaxation currents was interpreted within a model according to which the transfer of an electric charge injected into a crystal occurs through the relay-race mechanism [2, 3]. The charge transfer from the contact into the sample occurs through the mechanism of hopping conduction over the trap centers, which are located in the band gap and have deep trapping levels of free charge carriers. This process is also accompanied by the formation of an energy barrier at the boundary with the anode, which hinders the transfer of electrons (injected from the cathode) to the anode. The energy barrier at the boundary with the anode arises from the energy difference between the electron affinity for the local center and the work function of the anode metal. Thus, the electric current is limited by both the space charge in the bulk of the semiconductor and the energy barrier at the boundary with the anode, which leads to a redistribution of the voltage across the crystal and decrease of electric current passig through the crystal.

Long-time relaxation processes established for the structures under study on the basis of polycrystalline Pb_3O_4 layers can be also accompanied by the formation of depletion regions at the grain–intergrain layer boundary. A nonuniform potential profile of the boundary regions in the polycrystalline structure studied is the same as that created by a quasi-continuous energy spectrum of the traps.

CONCLUSION

Thus, the behavior of main characteristics of the relaxation process occurring in Pb_3O_4 layers are in agreement with the theory of the relay mechanism of charge transport under the conditions of nonuniform distribution of local centers in metal–(high-resistivity semiconductor)–metal structures. The study of current relaxation related to the accumulation

and redistribution of space charge extends our understanding of photoconductivity mechanisms and charge transport in IV–VI compounds with variable ionic–covalent bonding and a tendency towards the formation of naturally disordered structure.

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INFLUENCE OF THE HETEROATOMIC INTERACTION BETWEEN METAL AND NITROGEN ON TRIBOCHEMICAL PROPERTIES OF COPPER WITH ADSORPTED QUATERNARY AMMONIUM COMPOUNDS

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ABSTRACT

In this research the influence of consistent chemisorption of triamon and alkamon on copper powder on anti-frictional properties of Cu-containing lubricants was studied. The integral index of friction (proportional to force of friction) of systems with lubricants with different types of Cu-additives was measured. The data about electronic interaction (Cu←N) between metal and adsorpted ammonium-containing molecules was obtained for all Cu-samples by using XPS method. It was found that the strong interaction of a surfactant film with the solid support is the most important factor in attaining the highest anti-frictional and protective properties of modified samples.

Keywords: chemisorption of quaternary ammonium compounds, copper, anti-frictional effect, surface of metal, tribochemistry, hydrophobicity, substituent effect

INTRODUCTION

It has been earlier demonstrated that sequential chemisorption of triamon and alkamon (the formulations based on quaternary ammonium compounds with C₁-C₂ and C₁₆-C₁₈ substituents at the nitrogen atom, respectively) at dispersed aluminum leads to the synergetic increase of the high-temperature metal oxidation by at least 45% [1, 2]. The adsorption of surfactants with varied length of the alkyl chain is of interest in view of adjustment of the

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solid surface reactivity as well as the effect on the water-repellent and anti-frictional properties of the modified metal [2-5]. The interest towards study of the effect of triamon and alkamon adsorption on copper tribochemical properties has been directed by the two following major reasons. Firstly, the surface of copper powders is generally "cleaner" than that of Al samples, capable of heteroatomic interaction with quaternary ammonium compounds [2]. Secondly, the systems containing lubricants with Cu-additives have exhibited the non-wear Kragelsky-Garkunov effect resulting in decrease of the friction coefficient by an order of magnitude [4].

EXPERIMENT AND RESULTS

The PM-1 grade copper powder (GOST 4960-75) with the specific surface area of $0.34 \pm 0.02 \text{ m}^2/\text{g}$ was treated with triamon and (or) alkamon vapor at room temperature as described in [2, 6]. The content of the major component of the mentioned ammonium compounds was $>95 \text{ wt } \%$ in the liquid phase (TU 2482-030-05744685-2003 and GOST 10106-75) and $>99.5 \text{ wt } \%$ in the vapor. The water-repellent properties of the samples were determined from the water vapor adsorption as measured by the gravimetric desiccator method at the relative pressure of $p/p_0 = 0.98 \pm 0.02$. The integral index of friction D of the tribological pair (steel-steel) with the lubricant was determined via the acoustic emission method using the certified instrument ARP-11 at 20-300 kHz according to the procedure described in GOST 27655-88. The integral index of friction D is proportional to the force of friction. The oil I-20 was used as the lubricant; the modified copper powder was added into the oil, the copper content being equal in all the experiments.

According to the EDX spectroscopy data (an EDAX/TSL analytical attachment, recording at 6 kV), the initial copper powder did not contain any noticeable amounts of nitrogen or sulfur. The content of other elements was as follows: copper at least 91.6 mol %, oxygen 3.1 mol %, and carbon 4.7 mol %. After treatment in alkamon vapor, the copper sample with the specific surface area of $0.35 \text{ m}^2/\text{g}$ contained 0.2 mol % of nitrogen, 0.3 mol % of sulfur, 3.7 mol % of oxygen, and 5.8 mol % of carbon. The relative mass increase due to water vapor adsorption at the Cu-alkamon material was $a_1 = 0.0299$, significantly lower than that in the case of initial copper ($a = 0.0445$). The similarly prepared Cu-triamon sample with specific surface area of $0.32 \text{ m}^2/\text{g}$ contained 0.4 mol % of nitrogen, 0.4 mol % of sulfur, 3.7 mol % of oxygen, and 5.0 mol % of copper; the water vapor adsorption was $a_2 = 0.0268$. The Cu-triamon-alkamon material (prepared via sequential treatment in the triamon and alkamon vapors) with the specific surface area of $0.36 \text{ m}^2/\text{g}$ contained 0.7 mol % of nitrogen, 0.8 mol % of sulfur, 3.1 mol % of oxygen, and 6.3 mol % of carbon; the water vapor adsorption was $a_3 = 0.0260$ [5].

Measurement of the integral index of friction of the test system with the addition of the copper powders at the loading pressure of 40 MPa gave the following results: $D_1 = 1300$ (Cu-alkamon), $D_2 = 1100$ (Cu-triamon), $D_3 = 270$ (Cu-triamon-alkamon) [5], $D = 1580$ (initial copper), and $D_0 = 1690 \pm 50$ (no copper additive). Hence, copper modification resulted in the decreased friction in the test system. Comparison of the corresponding D values demonstrated that the sequential treatment with both modifiers was 4-5 times more efficient than that of the individual components. So, there is a synergetic effect, which clearly manifests itself in the reduction of D for a lubricant with added copper samples whose surface consistently treated

with quaternary ammonium compounds with different sizes of organic radicals on the nitrogen atom - triamon ($[(\text{HOC}_2\text{H}_4)_3\text{N}^+\text{CH}_3][\text{CH}_3\text{SO}_3^-]$) and alkamon with C_{16} - C_{18} -radicals.

Interestingly, the somewhat weaker synergetic effect was observed as far as water vapor adsorption was considered: comparison of the a_1 , a_2 , and a_3 values revealed that the sample obtained via sequential treatment with the both modifiers exhibited the lowest a value. Interestingly, the copper sample treated with the low-molecular triamon showed lower adsorption of water as compared with the case of modification with alkamon. That was likely due to the horizontal orientation of the organic substituents at the Cu- triamon sample surface and to the better stabilization of the smaller triamon molecules at the metal surface; both factors prevented interaction of water molecules with hydrophilic sites at the copper surface [7].

The XPS data evidenced that the strongest Cu←N electronic interaction between the metal and the adsorbed ammonium molecules occurred in the case of the Cu-triamon-alkamon sample. The determined bond energies of the electrons of the characteristic levels were as follows: $E_b(\text{Cu}2p) = 932.8$ eV and $E_b(\text{N}1s) = 404.0$ eV (Cu-alkamon-triamon); $E_b(\text{Cu}2p) = 933.5$ eV and $E_b(\text{N}1s) = 402.1$ eV (Cu-alkamon); $E_b(\text{Cu}2p) = 933.2$ eV and $E_b(\text{N}1s) = 402.5$ eV (Cu- triamon); and $E_b(\text{Cu}2p) = 933.8$ eV (initial copper). The spectra were excited with AlK_α radiation (1486.6 eV), the analyzer chamber pressure during the recording was below 1.3 mPa. Stability of the surfactants adsorbed at the copper surface in the course of the spectra recording was confirmed by the constant pressure in the analyzer chamber and the intensity of the characteristic N1s peak in the spectra during the experiment. The spectra were obtained using an Escalab 220 iXL instrument (Leipzig University, Germany).

The synergetic change of the tribochemical properties of the studied systems could at the first approximation be due to the strengthening of the adhesion between copper and the surfactants, other conditions (the loading pressure, the dispersion state, and the additive content) being the same. Under the harsh conditions of the tribology test ($p = 40$ MPa, close to the dry friction conditions [4]), the I-20 oil was pushed out the friction pair contact zone [6]. The friction was then to a large extent determined by the anti-frictional effect of the solid additive. According to the commonly accepted views, the highest anti-frictional and the protective properties of the surfactant film at the solid surface are attained in the case of the film hydrophobicity and its good adhesion to the solid support [3, 4]. The results of this work coincided with these fundamental views and underscored the importance of the adhesion factor [2, 6, 7]. The reasons for the increased bond energy of the N1s level in the metal-triamon-alkamon samples have been earlier discussed in [1].

CONCLUSION

The XPS studies conducted in this work demonstrated that sequential chemisorption of triamon and alkamon at the dispersed copper resulted in enhancement of the metal-nitrogen interaction in the surface layer. The water-repellent properties of the metal were improved, and addition of the modified metal to the lubricant of the tribological pair led to synergetic decrease of the integral index of friction (the friction force) at least four times.

ACKNOWLEDGMENTS

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**THESES OF THE INTERNATIONAL SYMPOSIUM
“NANOPHYSICS AND NANOMATERIALS” – 2015
ST. PETERSBURG, MINING UNIVERSITY
NOVEMBER 24 – 25 2015**

NIN-2015 was organized with the assistance of the Ministry of Education and Science of the Russian Federation and with the support of Soligorst branch of “Belgorhimprom” Ltd. Regional affiliation of Unesco Symposium was divided into two general sections: nanophysics and nanomaterials, and practical implementation of nanotechnologies in industry (including the mining industry) in Russia and abroad.

Theses are organized by the following subjects.

- Alloy and Oxide Nanometallurgy
- Electrochemistry and Corrosion Protection
- Nanoporous and Nanostructured Materials
- Nanocomposite Systems with Optical Properties
- Plasma Technologies, Diagnostical Methods, Fractal Structures, and Nano-Sized Structures
- Semiconductors and Thin-Film Technologies

FORMATION AND OPTICAL PROPERTIES OF CuCl NANOCRYSTALS IN FLUOROPHOSPHATE GLASS

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We study the possibility of formation of CuCl nanocrystals in fluorophosphate glass ($\text{NaPO}_3\text{-Ba}(\text{PO}_3)_2\text{-AlF}_3$) by heat treatment technique. Using the optical absorption technique, the position of the CuCl nanocrystal exciton absorption band was studied as a function of heat treatment time and the radius of CuCl nanocrystals increased from 3 to 9 nm.

Keywords: fluorophosphate Glass, CuCl nanocrystals, excitons

INVESTIGATION OF INTERNAL STRUCTURE OF NANOPARTICLES BASED ON POROUS SILICON POWDERS

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Nanoparticles of porous silicon were obtained by electrochemical anodic etching. Morphology and structure of the particles was investigated with using atomic force and scanning electron microscopy and methods of sorbometrii such as measurement of specific surface area BET and capillary condensation. The influence of technological conditions of preparation on geometrical parameters of the porous silicon particles (particle size distribution, pore shape and size, the specific surface area of the porous silicon) is discussed.

Keywords: porous silicon nanoparticles, electrochemical etching, capillary condensation

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NANOSTRUCTURED FUNCTIONALLY GRADIENT COATING FOR THE PROTECTION OF STRUCTURAL ELEMENTS FROM CORROSION AND WEAR

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A technology for creating nanostructured composite powders for spraying was developed. Studies on the development and application of thermal spraying methods for functionally graded coatings production have been conducted. A hardness gradient over the cross section of the coating was investigated. The present study shows the possibility of the formation of thick coatings with controlled hardness.

Keywords: nanostructured composite powders, coating, functionally gradient coating, hardness gradient, combining methods of spraying

FORMATION OF NANO-DIMENSIONAL STRUCTURES IN AMORPHOUS AND NON-CRYSTALLINE MATERIALS FOR DEVELOPMENT OF MODERN OPTOELECTRONIC SYSTEMS

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In accordance with modern understanding of the role of micro- and nano-inhomogeneities in the processes of formation of surface micro relief the problems of the synthesis of materials with pre-defined properties are discussed. The formation of nanoscale structures in the photosensitive glass opens up new possibilities in the preparation of glasses for special purposes. Change in the conditions of synthesis of glasses, their composition, the introduction of activators demonstrates the ability to create modern optoelectronic systems. As model systems, well-known compositions of photosensitive silicate and germanate glasses are investigated. The silver ions are introduced into the test glass by ion exchange diffusion.

Keywords: nanoscale structures, photosensitive glass, ion exchange processes, optoelectronic devices

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WATER TREATMENT SYSTEMS WITH THE USE OF MAGNETRON NANOSTRUCTURED COATINGS Ti-RU-O

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The feasibility of making a dimensionally stable anode (DSA) with an active coating Ti-Ru-O prepared by reactive magnetron sputtering was demonstrated through the present work. In addition, it was shown a utilization efficiency of water treatment systems the main element of which is the developed anode.

Keywords: dimensionally stable anodes, magnetron sputtering, nanostructured coating, water treatment

DEVELOPMENT OF MECHANICAL PROPERTIES OF ALUMINUM-SILICON ALLOYS

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An effect of modification has been studied for the aluminum-silicon alloys. Different types of modifiers have been studied such as sodium, strontium, various phosphides and aluminum-based alloys containing titanium and antimony. Segregation has been investigated during sampling and casting ingots. Carbothermic technology has been proposed for producing aluminum-silicon alloys in a melting furnace. It will produce alloys with finer granularity and improve its mechanical properties.

Keywords: aluminum, silicon, modifying silumin, carbothermic technology, modifier

INVESTIGATION OF THE DEPENDENCE OF THE DISPERSION FORCES ON THE PROPERTIES OF THE METALLIZATION LAYER IN MDS-STRUCTURES

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We presented the new results of calculations dispersion force pressure with different material used as metal layer in metal–dielectric–semiconductor (MDS) structures. The calculations are based on the Lifshitz theory at nonzero temperature. We discuss the range of the typical value of the thickness a dielectric layer used in modern electronics. As an example, we show how the value of the dispersion force pressure depends on of changes electro-optical properties of the metal layer in MDS-structures.

Keywords: metal–dielectric–semiconductor (MDS) structures, Silicon, Metallization, Dispersion forces, Lifshitz theory

NANO- AND THE MICRODIMENSIONAL COATS POLYCRYSTALTITANIUM-CONTAINING THE BASES OF A METHOD OF ELECTROCHEMICAL BORONIZING

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The technology for the production of wettablealuminium coating was implemented using the method of electro-chemical borating of the carbon-titanium cathode directly at the electrolytic reduction of cryolite-alumina melts in laboratory conditions.

TiC and TiB₂, responsible for the wetting effect, were detected by X-ray phase analysis of cathode surface layer. The mechanism of electro-chemical and chemical processes of Ti-B-Ccompound formation in the subsurface cathode volume is proposed for the discussion.

Keywords: electro-chemical deposition, borating, carbon-titanium cathode, wettable coating

PROSPECTS OF NANOMETALURGY APPLICATION IN THE PREPARATION OF MASTER ALLOYS AND COMPOSITE MATERIALS

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The prospects of nanometalurgy application in the preparation of master alloys and composite materials with rare earth metals (REM) are covered. In the field of production of master alloys based on aluminum and magnesium the determinedresults are achieved at the Department of Metallurgy Mining University.

Keywords: aluminium, magnesium, alloys, master alloys

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STUDY OF LUMINESCENCE AND SURFACE PROPERTIES OF Y_{1-x}Eu_xV_{1-y}P_yO₄ PHOSPHORS

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The composition of Y_{1-x}Eu_xV_{1-y}P_yO₄ phosphors is optimized to provide the highest luminescence brightness achieved for samples with P and Eu contents 10 and 7 mol.%, respectively. The observed brightness growth prominently correlates with the content of specific centers on the phosphor surface reflecting the formation of species responsible for the luminescence efficiency.

Keywords: luminescence, phosphors, yttrium vanadate, surface functional groups

MICROCRYSTALLINE CELLULOSE ADDITIVE FOR MODIFICATION OF PROPERTIES OF POLYMER FILMS

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In this study, polymer coating was modified with microcrystalline cellulose (MCC). The progress of water uptake inside the coating was studied by electrochemical impedance spectroscopy (EIS). Observed results show morphological changes related to swelling in ions and channels during ions propagation.

Conducted study allows more justified approach in the formulation of composition of coatings for medical and technical application.

Keywords: coatings, electrochemical impedance spectroscopy, microcrystalline cellulose, polymethylmethacrylate, moisture uptake, thin films

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PENZA STATE UNIVERSITY THE EFFECT OF SYNTHESIS CONDITIONS ON THE QUANTITATIVE COMPOSITION OF THE NANOSTRUCTURED METAL OXIDES BASED ON SiO₂ - SnO₂

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The growing interest in nanostructured materials has stimulated considerable activity in the study of their structure. One of the basic and versatile experimental techniques to determine qualitative and quantitative composition of substances are X-ray diffraction methods and Fourier spectroscopy.

The relevance of this study is determined by scientific and practical interest in the development of new nanocrystalline materials with high catalytic activity, selectivity to analysed gases, thermal stability.

Therefore, the aim of this work is to develop a methodology and research of quantitative structure of nanocomposite materials based on SiO₂-SnO₂ with an infrared Fourier transform spectrometer.

The objects of study are nanocomposite materials based on SiO₂-SnO₂ with different composition obtained by sol-gel technology.

Keywords: nanostructured, oxide, concentration, synthesis, Fourier-spectroscopy, Sol-gel, temperature, spectrograms

THE USE OF NANO-COATING TO PROTECT PARTS OF MINING MACHINES FROM FRETTING-CORROSION

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The application of nano-coatings based on fluorocarbon polymer composition, friction-mechanical brass, fullerene C₆₀ and surface treatment of vibrorolling with the regular roughness for the protection of heavily loaded mating parts of machines, working in conditions of fretting-corrosion. Studied the mechanisms of friction of nano-coating, which will considerably reduce the fretting-wear mechanisms of friction in engineering products.

Keywords: nano-coating, fretting corrosion, vibrorolling, fullerene C₆₀

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EFFECT OF ZNS: CU, CL PHOSPHOR SURFACE MODIFICATION WITH SHUNGITE CARBON ON ELECTROLUMINESCENT LIGHT SOURCE PERFORMANCES

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The deposition of shungite carbon micro-additive onto the surface of a commercial ZnS: Cu, Cl phosphor surface provides an adjustable modification of its luminescence spectrum, particularly the control over the ratio between the intensities of “blue” and “green” luminescence bands depending on the deposited additive content.

Keywords: Zinc sulfide, phosphors, electroluminescence spectra, shungite

FRACTAL STRUCTURE AND ELECTRICAL PROPERTIES OF PERCOLATION SENSOR LAYERS

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A model of percolation sensor layers with fractal structure near percolation threshold based on Mandelbrot-Given curve was proposed. Sensitivity values of these layers to reducing gases exceeding the typical values by several orders of magnitude were explained using developed model. The peculiarities of electrical properties of percolation sensor layers were studied by impedance spectroscopy in air and in the presence of reducing gases.

Keywords: gas sensors, percolation cluster, Mandelbrot-Given fractal, impedance spectroscopy

EVOLUTION OF COPPER (II) OXIDE NANOSTRUCTURES IN POROUS GLASS MATRIX

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Controllable accumulation of copper(II) oxide in porous glass was carried out by repeated impregnation of the carrier by $\text{Cu}(\text{NO}_3)_2$ aqueous solutions with subsequent thermal decomposition of the salt. The results of measuring electric conductivity of a series of modified plates make it possible to characterize the trend in the oxide distribution on a silica surface. In the case of its cyclic accumulation by small portions, a two-dimensional structure of monolayer filling the surface is presumably formed in a narrow range of CuO concentration.

Keywords: porous glass, CuO, monolayer, electrical conductivity

EFFECT OF THE SYNTHESIS METHODS ON THE CRYSTAL STRUCTURE AND LUMINESCENCE OF $\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$ PHOSPHORS

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$\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$ phosphors powders were synthesized with different concentration of activator ions by using sol-gel (SG) method and solution combustion (SC) technique. The effect of the method of synthesis and concentration of Eu^{3+} ions on the structure and luminescence properties of zinc aluminate phosphor were investigated. X-ray diffraction pattern confirmed that the fibers were composed of the cubic ZnAl_2O_4 phase. The calculation of the crystallite size according to Scherrer formula and the maximum were for obtained 0.12 % of Eu^{3+} ions by using SG and for samples prepared by SC was 0.15%. Luminescence spectra shown peaks at 612 and 618 nm. The intensity of all the emission bands reached at 0.12% and 0.24% depending on activator concentration by using SG and SC techniques, respectively. So the crystallinity, luminescence spectrum profiles and luminescence of phosphors can be effectively adjusted by the variation of method and dopant (activator) concentration.

Keywords: zinc aluminate phosphor, zinc aluminate spinel, phosphor, XRD, luminescence

STUDY OF THE DEPOSITION PROCESS OF VINPOCETINE ON THE SURFACE OF POROUS SILICON FOR THE PURPOSE OF ESTABLISHMENT OF THE TARGETED DRUG DELIVERY SYSTEMS

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Currently the most prospective way in pharmacotherapy is the obtaining of nanoparticles involving pharmaceutical substances. Application of porous inorganic materials on the basis of silicon is among the main tendencies in solving of this problem. The present work is concerned with the problem of the deposition of pharmaceutical drug with nootropic activity – vinpocetine – into porous silicon. Silicon nanoparticles were obtained by electrochemical anodic etching of Si plates. The process of vinpocetine deposition was studied in a dependence of the deposition time. As a result of the investigations it was found that infrared transmission spectra of porous silicon with the deposited vinpocetine revealed the absorption bands characteristic of vinpocetine substance.

Keywords: nanoparticles, porous silicon, vinpocetine

ANALYTICAL CAPABILITIES OF REM IN THE MODE OF SCATTERED ELECTRON REGISTRATION WITH ENERGY SELECTION FOR DIAGNOSTICS OF NANOSTRUCTURES

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The report encompasses capabilities of scanning electron microscopy for quantitative diagnostics of morphology and ultimate composition of soft matter nanostructures in the mode of scattered electron registration with energy selection.

Keywords: scanning electron microscopy, scattering electrons, imaging contrast

CHARGE TRANSFER PROCESSES IN Bi₁₂SiO₂₀ SINGLE CRYSTAL

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Charge transfer in Bi₁₂SiO₂₀ structures is investigated. Electric current dependences on time at temperature of 300 K in the dc electric field strength of the 2·10⁵–10⁶ V/m range are measured. Flowing of relaxation polarizing current is shown to result in charge accumulation in the sample surface area. Experimental regularities coordinate with provisions of the relay mechanism of transfer of a charge with the participation of deep local levels.

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Keywords: electric field, charge transfer, charge accumulation, conductivity, polarization, local states

INVESTIGATION OF LASER MICROMACHINING OF ZINC OXIDE

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Big size (~1,4M²) silicon-based thin-film solar module (SM) consists of elements connected between each other in a way to get the maximum efficient solar energy conversion in the output. In solar modules production the technological process of separating elements is realized using laser scribing. As a result, the SM area will consist of “active area”, where the photoeffect occurs, providing the current constituent part of the converted energy, and “dead zone”, which does not participate in photo-electric current generation, but it is a required element for effective separate elements commutation.

The research includes analysis of possibility to decrease the “dead zone” and to increase the parameters of electrical energy output. This can be achieved both by decreasing the width of scribes and by optimizing the commutative connections of SM elements. In terms of precision and quality of manufacture the shape and type of the scribes depend on laser irradiance parameters used in technological process of division of SM into separate elements.

Keywords: ablation, laser ablation, scribe, transparent conductive thin films of zinc oxide (ZnO), “dead zone,” shunting effect, laser beam energy, scribe profile

GRAPHENES, STACKS AND GLOBULES IN NANOPARTICLES OF SHUNGITE CARBON AND NEW MATERIALS

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Shungite carbon (ShC) is considered as the natural carbon allotrope of a multi-level fractal structure produced by the consecutive aggregation of ~ 1 nm graphene fragments. Turbostratic stacks of ~ 1.5 x 2.5 nm and the globular composition of the stacks ~ 6 nm are responsible for the secondary and tertiary levels of the structure. Aggregates of globules, measuring tens of nanometres, form 3D-nets and complete the structure. All structural levels could be released through stable aqueous dispersion of ShC nanoparticles. Each level is important for obtaining special properties in new materials with ShC nanoparticles.

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Keywords: Nanocarbon, shungite carbon, graphene, nanotechnology

STRUCTURAL TRANSFORMATIONS IN IRON THIN FILMS ON SILICON SUBSTRATE

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During annealing of iron films (20-270 nm) on silicon substrate phase-formation process consists of two stages. Under temperature less than 130°C the increasing of iron lattice parameter from 2.8663 (traditional bcc lattice) Å up to 2.8737 Å is observed and solid solution Fe(Si) is formed. The width of transition region (Fe/Si) is increasing up to 30 nm. Under temperature 180°C the phase Fe₅Si₃ which is an ordered solid solution and which exists under 800°C only is formed and stabilized in thin film state. The forming of Fe(Si)-phase is initiated by polygonization process of iron structure. Recrystallization process of iron structure is observed only at film thickness more than 100 nm.

Keywords: iron thin film, structure, polygonization, recrystallization

ATOMIC-FORCE VISUALISATION OF MOTT-TRANSITION IN VO₂ NANOCOMPOSITE

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The electron beam can be used to control the temperature of the semiconductor–metal phase transition. The structure that is formed on the VO₂-nanocomposite surface using electron beam irradiation is studied with the aid atomic force methods. The physical principle of such a control is based on the donor properties of the backdonation σ bonds

Keywords: Vanadium dioxide, phase transition, strong correlations

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CORRELATION MECHANISM OF THE ELECTRONIC COMPONENT OF THE METAL-INSULATOR PHASE TRANSITION IN VO₂ NANOCOMPOSITE

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Development of a method for separating of purely electronic phase transition component of VO₂-films and the determination of its characteristics is main result of this study.

Keywords: Vanadium dioxide, phase transition, strong correlations

ON THE MODELING OF GAS-SENSITIVE PROPERTIES OF THE POROUS COMPOSITES SiO₂-Me_xO_y WITH FRACTAL STRUCTURE

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A model of gas sensitivity, taking into account the molecular and Knudsen diffusion of gases in porous nanocomposites SiO₂-Me_xO_y is developed. It has been shown that their gas sensing properties depend not only on the qualitative and quantitative composition, but also on the prevailing type of gas diffusion, which is determined by the concentration and size of the pores in the material.

Keywords: sol-gel technology, nanocomposites, diffusion, gas sensors, modeling

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INFLUENCE OF THE TRIAMON UNDERLAYERS ADSORPTED ON THE INTERFACE ON TRIBOCHEMICAL CHARACTERISTICS OF THE METAL-LUBRICANT SYSTEM

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In this research the influence of mixed and consistent chemisorption of differently sized molecules of quaternary ammonium compounds (alkamon and triamon) on disperse aluminum on its properties. As a part of the research the lubricants containing modified aluminum were tested. It was discovered that as the hydrophobicity of Al-additives increases, the force of friction (F_{fr}) and coefficient of friction (f) decrease. It was discovered that Al-additives with external layer of ethylhydridesiloxane and only one underlayer of triamon has the best anti-frictional effect. The addition more T-underlayers (from 1 to 3) did not give a significant improvement. The force of friction (F_{fr}) and coefficient of friction (f) were measured for tribosystems, containing ten types of differently modified Al-additives.

Keywords: chemisorption of quaternary ammonium compounds, aluminum, anti-frictional effect, influence of the triamon underlayers, ethylhydridesiloxane on surface of metal, Al-containing lubricants

INVESTIGATION OF COVERED COLLOIDAL QUANTUM DOTS CdSe/ZnS AND CdSeZnS/ZnS AS A BASIS OF DETECTOR COATING

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Covered colloidal quantum dots CdSe/ZnS and CdSeZnS/ZnS were examined. High efficiency of luminescence was shown in the range of wavelengths from 500 to 700 nm. Simulation of CQDs' energy and dimensional properties was run; it was shown that particles vary in diameters in the range from 2 to 5 nm. Using a mixture of CQDs as a basis, detector coating were created; such covers are promising for use in non-contact surface quality diagnostics.

Keywords: colloidal quantum dots, Luminescence, dimensional parameters

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INFLUENCE OF CHROME-OXIDE NANOSTRUCTURES ON THE CONDITION OF THE DISPERSE BORON NITRIDE SURFACE AND HEAT CONDUCTIVITY OF THE POLYMERIC COMPOSITE

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The solution of the problem of creation of the high-heat-conducting materials possessing good dielectric properties is an actual problem of materials science. One of the solutions of this task is using of the polymers which have high insulating properties, simplicity of receiving, light weight and low cost. However low thermal conductivity of polymers is their essential disadvantage. For improvement of the heat exchange the fillers with rather high heat conductivity are entered into polymeric material composition. But there are some limiting factors during the exploitation of such composites and the main one is the limit of phase boundary between a matrix and a filler, which reduces conductivity of composites. It is possible to reduce the influence of phase boundary on composite's heat conductivity by increasing of the adhesion between two phases (filler and polymer matrix). The most perspective way of increasing of the adhesion is the modification of a filler's surface, which allows to form strong and homogeneous bonding with a matrix.

Keywords: heat conductivity, composite materials, surface modification

THESES “METHODOLOGICAL CONCEPT OF ESTIMATION OF FACTORS AFFECTING THE QUALITY OF THE STRETCHABLE NANOROD GEOMETRY”

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The mathematical models are offered which adequately describe the process of nanorod stretching, considering all significant factors affecting the rod shaping, including not only viscous properties of the glass melt, but also its relaxation ability. The conditions of stable course of the stretching process were revealed, that allow to choose areas of technological parameters (stretching rate, viscoelastic characteristics of zone of formation) under which the process would be resistant to uncontrollable disturbances. The method is offered for determining characteristics of the formation zone, based on a forced oscillation team of stretchable nanorod.

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Keywords: viscosity, stretching rate, surface tension, viscoelastic characteristics, elongation rod, method

EFFECT OF MARTENSITE CRYSTALS SIZE OF THE MATERIAL STRUCTURE OF THE ROCK-CUTTING TOOL ON ITS WEAR RESISTANCE

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The results of experiments on the effect of the size of the crystal structure of martensite steel 30HGSA (steel of rock cutting tools) to its hardness and wear resistance are presented. Wear experiments were performed on the sandstone (rock is most common during operation of roadheaders). The results showed that high-temperature thermomechanical treatment of steel (strain at 900° C, water quenching, tempering at 230° C) is leading to a shift in the size of the martensite crystals on its structure in the submicron area (0.2 - 2 microns). This is the causes of increasing of hardness (23%) and wear resistance (38%) of the material as compared to a typical steel heat treatment (quenching and tempering), which is used in the manufacture of cutting tools manufacture. Grinding grains in the structure of metal structural materials of cutting tools is an effective way to improving its wear resistance was concluded.

Keywords: steel 30HGSA, thermomechanical treatment, submicron size of grain, wear resistance

JOINT SYNTHESIS OF NANOSIZED POWDERS IN THE B₄C–SiC–TiB₂ SYSTEM

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The increasing interest in ceramic materials with a submicron grains size, naturally leads to developing of new ways of synthesis multicomponent powders with submicron and nanosized range of dispersion. The technology of mechanical grinding and thin milling of coarse powders, classical for powder metallurgy, isn't always reasonable,

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especially for a milling of highly rigid compounds, such as boron carbide, silicon carbide and titanium diboride. The synthesis methods lead to receive powders not only with the demanded phase and chemical composition, but also with necessary dispersion are perspective for such compounds.

Keywords: nanosized powders, ceramic materials, metallurgy, dispersion

INFLUENCE OF POROSITY ON THE PERFORMANCE OF A CUTTING CERAMICS

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Now more and more widely used is a ceramic cutting tool, which is used for processing precision machine parts. On the performance of ceramic tool in addition to other factors is greatly influenced by the porosity of the material. The smaller the porosity, the better cutting properties and performance of ceramic tool. Under normal conditions to determine the number of pores, the size of which is 0.1 to 10 nm, using methods whose use in production conditions difficult.

To solve this problem, we propose to use correlation between the porosity of the cutting ceramics the magnitude of the electrical resistivity of this material. Studies have shown the presence of such dependence and have enabled the identification of quantitative component.

In cutting ceramics with the magnitude of the electrical resistance $R \approx 100 \Omega$ quantity and pore size will be minimal compared with the ceramics with the magnitude of the electrical resistance $R \approx 10 \Omega$. Thus, it can be concluded that the greater would be the value of the specific electric resistance of the cutting ceramics, the greater would be the operation of the instrument.

Keywords: cutting ceramics, performance tool, the porosity of the material.

TRANSITION METAL DOPED ZINC SELENIDE NANOCRYSTALS SYNTHESIZED IN AQUEOUS AND ORGANIC SOLUTIONS

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Colloidal quantum dots (QDs) of zinc selenide doped with manganese and copper were obtained in water medium using mercaptopropionic acid as a surfactant. Nucleation doping technique was implemented to synthesize ZnSe:Mn QDs in non-coordinating solvent octadecene. Samples were characterized by means of absorption and photoluminescence spectroscopies. Synthesized nanocrystals may be an alternative to

conventional cadmium chalcogenide nanocrystals for visible range applications including biomedical detection.

Keywords: colloidal quantum dots, surfactant, absorption

PLASMA NANOTECHNOLOGIES FOR NOVEL PLASMA ENERGETICS

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Experimental studies of the properties of a condensate of cesium excited states are analyzed. Theoretical and experimental data of different authors are compared. We discuss the concept of the practical use of the Rydberg matter in the working process of a low-temperature thermionic converter (TIC) of energy at the emitter temperature below 1600 K, the collector temperature below 700 K, and the generalized index of energy loss in a TIC (barrier index) of $V_b \sim 1.6$ eV.

Keywords: Rydberg matter, low-temperature thermionic converter, plasma energetic

CORRECT CALCULATION OF THE TEMPERATURE DEPENDENCES OF KINETIC COEFFICIENTS IN THE TWO-BAND MODEL

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It is known that most semiconductors have a complex structure of the valence band. Therefore, several types of holes with different effective masses are involved in transport phenomena. This circumstance greatly complicates the analysis of experimental data. In such an event, experimental data are usually analyzed on the basis of the two-band model.

Keywords: semiconductors, two band model

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CO-PRECIPIATION OF NANO-SIZED Al_2O_3 - ZrO_2 - Y_2O_3 SINTERING ADDITIVE FOR SiC LIQUID-PHASE SINTERING

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and S. S. Ordan'yan*

The nano-sized mixture in system Al_2O_3 - ZrO_2 - Y_2O_3 (respectively, 63 mol. %; 37 mol. %, and 4 mol. % above 100%) was obtained by the precipitation of respective hydroxides on the "substrate" of submicron SiC powder with total concentration of oxide additive 10 vol. %. After the calcination at 1250°C in vacuum and sonication obtained mixture was characterized by the X-Ray diffraction, SEM and EDX analysis. Liquid phase formation temperature (1700-1730°C) of resulting system SiC- Al_2O_3 - ZrO_2 - Y_2O_3 was estimated during its spark plasma sintering.

Keywords: alumina, zirconium, plasma sintering

DEVIATION OF THE LAMBERT-BEER LOW FOR THE CARBON NANOPARTICLES DIFFERENT KINDS AT THE NEAR THZ FREQUENCY RANGE

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This work concerns the peculiarities of the electromagnetic waves absorption by different kinds of nanocarbon particles in THz frequency range. Lot of much the different nanocarbon clusters - the fullerenes (C-60 and C-70), two types of multiwall carbon nanotubes (arc and gas phase technology made), colloid graphite, astralenes, sulfo-adducts of the two or three-layer graphenes and carbon nanoporous microfiber (CNPMF) have been studied by Ph.D. Irina Khromova in work. It was found, that for the most famous kinds of the carbon nanoparticles concentration (1%-25% mass.) the relations between the absorption coefficients and the concentrations of these particles in the transparent media (high density polyethylene(HDPE)) are rather goodly confirm the Lambert-Beer low for the wide frequency diapason (0,005 – 3 NHz). However, it is not so for the astralenes and for the CNPMF. For this case the relations between the absorption coefficients and concentrations of the carbon nanoparticles are non-linear even for not so high concentrations (3%-4 % mass.), and for highest value of concentrations the absorption coefficient arise strongly, especially at the near THz frequency range.

Keywords: terahertz frequency, carbon nanoparticles

GEOLOGICAL AND MINERALOGICAL JUSTIFICATION OF THE APPLICATION OF PROCESSED SHUNGITE RAW MATERIALS IN NANOTECHNOLOGY

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Carbon-rich shungite rocks are promising raw materials for production of adsorbents, catalysts and fillers for polymers of different polarity and inorganic blends. Recently shungite rocks attract attention as a natural source of nanosized carbon. However, heterogeneity of shungite rocks and poor reproducibility of its composition and properties lead to inability to use this valuable raw material in high-tech processes. The ways of homogenization of the raw material obtained of shungite rocks and improvement the efficiency of its application are suggested.

Keywords: shungite rocks, raw materials, nanosized quartz, hybrid materials, nanotechnology

INFLUENCE OF ALKALI METALS ON THE STRUCTURE OF CARBON GRAPHITE MATERIALS OF KATHODE LINING OF ALUMINUM REDUCTION CELL

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The main indicator of work of the aluminum reduction cells is the life of the cathode device. The cathode device is a basic unit of aluminum reduction cell. Increasing resistance of the cathode device is determined by ability of carbon graphite lining, and silicon carbide side lining to keep their properties as much as possible within a given period of time. The weakest point in the carbon graphite linings are interblock and peripheral joints of cathode devices of aluminum reduction cell. The carbon ramming paste is used for taps interblock and peripheral joints. The carbon ramming paste is carbon graphite materials, which is produced by mixing the calcined anthracite (filler), and coal tar pitch (binder). Additive of low-fusible oil is used to reduce the softening temperature of paste and taps at low temperatures. The last factor is very important because it allows the taps joints without preheating. Such a mass is called cold carbon ramming paste and that it is by far the dominant material for the production of cathode blocks. The cold carbon ramming paste is a mixture of coke and coal tar pitch with a softening point most suitable at low degree of volatility grade, which determines the life of cathode device. Ease of installation and environmental benefits was an additional factor that led to the transition to the cold carbon ramming paste.

Keywords: graphite, cathode, aluminum reduction cell

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DONOR-ACCEPTOR CHARACTERISTICS OF SURFACE AND FUNCTIONAL PROPERTIES OF SOLIDS

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Surface characteristics of solid influences interface interaction in which this solid participates and thus influences some functional properties of solids. Distribution of active surface centers (DAC) spectroscopy is applied to study donor-acceptor characteristics of surface of solid materials, especially luminescent ones.

Keywords: spectroscopy, luminescent materials

PRODUCTION AND RESEARCH OF NANOCRYSTALLINE ZNO FILMS

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³St. Petersburg University of Information Technologies, Mechanics and Optics,
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Some results are provided in this work confirming that modifying the 1 microns thick films of zinc fabricated on glass substrates by method of a laser ablation by a resulting effect of heat treatment in the atmosphere of dry air and action of cross electric field manufacturing of ZnO with the extended surface consisting of one-dimensional monocrystals of the nanometer sizes is possible. By method of the scanning electronic microscopy the morphology of a surface of all films was investigated, and the micro x-ray spectral analysis was used to investigate their element structure.

Keywords: nanocomposite films, ZnO, spectral analysis.

NANOPOROUS CATALYTIC COMPOSIT FOR THE STEAM METHANE REFORMING SYSTEMS

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and A. A. Deev*

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The catalytic porous coatings on the base alumina were produced by microplasma spraying. The positive influence of the heat treatment coatings on the characteristics of

porosity was established. The nanostructured porous coatings are efficiency for the steam methane reforming systems.

Keywords: syngas, steam methane reforming systems, porous coating, metallic support, nanostructured catalysts, micro-plasma spraying, super surface area, pore size distribution.

ALLOY AND OXIDE NANOMETALLURGY

DEVELOPMENT OF MECHANICAL PROPERTIES OF ALUMINUM-SILICON ALLOYS

S. N. Fedorov and V. Y. Bazhin
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An effect of modification has been studied for the aluminum-silicon alloys. Different types of modifiers have been studied such as sodium, strontium, various phosphides and aluminum-based alloys containing titanium and antimony. Segregation has been investigated during sampling and casting ingots. Carbothermic technology has been proposed for producing aluminum-silicon alloys in a melting furnace. It will produce alloys with finer granularity and improve its mechanical properties.

Keywords: aluminum, silicon, modifying silumin, carbothermic technology, modifier.

PROSPECTS OF NANOMETALURGY APPLICATION IN THE PREPARATION OF MASTER ALLOYS AND COMPOSITE MATERIALS

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The prospects of nanometalurgy application in the preparation of master alloys and composite materials with rare earth metals (REM) are covered. In the field of production of master alloys based on aluminum and magnesium the determined results are achieved at the Department of Metallurgy Mining University.

Keywords: aluminium, magnesium, alloys, master alloys

INVESTIGATION OF LASER MICROMACHINING OF ZINC OXIDE

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Big size (~1,4m²) silicon-based thin-film solar module (SM) consists of elements connected between each other in a way to get the maximum efficient solar energy conversion in the output. In solar modules production the technological process of separating elements is realized using laser scribing. As a result, the SM area will consist of “active area”, where the photoeffect occurs, providing the current constituent part of the converted energy, and “dead zone”, which does not participate in photo-electric current generation, but it is a required element for effective separate elements commutation.

The research includes analysis of possibility to decrease the “dead zone” and to increase the parameters of electrical energy output. This can be achieved both by decreasing the width of scribes and by optimizing the commutative connections of SM elements. In terms of precision and quality of manufacture the shape and type of the scribes depend on laser irradiance parameters used in technological process of division of SM into separate elements.

Keywords: ablation, laser ablation, scribe, transparent conductive thin films of zinc oxide (ZnO), “dead zone,” shunting effect, laser beam energy, scribe profile

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In this research the influence of mixed and consistent chemisorption of differently sized molecules of quaternary ammonium compounds (alkamon and triamon) on disperse aluminum on its properties. As a part of the research the lubricants containing modified aluminum were tested. It was discovered that as the hydrophobicity of Al-additives increases, the force of friction (F_{fr}) and coefficient of friction (f) decrease. It was discovered that Al-additives with external layer of ethylhydridesiloxane and only one underlayer of triamon has the best anti-frictional effect. The addition more T-underlayers (from 1 to 3) did not give a significant improvement. The force of friction (F_{fr}) and coefficient of friction (f) were measured for tribosystems, containing ten types of differently modified Al-additives.

Keywords: chemisorption of quaternary ammonium compounds, aluminum, anti-frictional effect, influence of the triamon underlayers, ethylhydridesiloxane on surface of metal, Al-containing lubricants

INFLUENCE OF CHROME-OXIDE NANOSTRUCTURES ON THE CONDITION OF THE DISPERSE BORON NITRIDE SURFACE AND HEAT CONDUCTIVITY OF THE POLYMERIC COMPOSITE

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The solution of the problem of creation of the high-heat-conducting materials possessing good dielectric properties is an actual problem of materials science. One of the solutions of this task is using of the polymers which have high insulating properties, simplicity of receiving, light weight and low cost. However low thermal conductivity of polymers is their essential disadvantage. For improvement of the heat exchange the fillers with rather high heat conductivity are entered into polymeric material composition. But there are some limiting factors during the exploitation of such composites and the main one is the limit of phase boundary between a matrix and a filler, which reduces conductivity of composites. It is possible to reduce the influence of phase boundary on composite's heat conductivity by increasing of the adhesion between two phases (filler and polymer matrix). The most perspective way of increasing of the adhesion is the modification of a filler's surface, which allows to form strong and homogeneous bonding with a matrix.

Keywords: heat conductivity, composite materials, surface modification.

EFFECT OF MARTENSITE CRYSTALS SIZE OF THE MATERIAL STRUCTURE OF THE ROCK-CUTTING TOOL ON ITS WEAR RESISTANCE

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Mining University, St. Petersburg, Russia

The results of experiments on the effect of the size of the crystal structure of martensite steel 30HGSA (steel of rock cutting tools) to its hardness and wear resistance are presented. Wear experiments were performed on the sandstone (rock is most common during operation of roadheaders). The results showed that high-temperature thermomechanical treatment of steel (strain at 900° C, water quenching, tempering at 230° C) is leading to a shift in the size of the martensite crystals on its structure in the submicron area (0.2 - 2 microns). This is the causes of increasing of hardness (23%) and wear resistance (38%) of the material as compared to a typical steel heat treatment

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(quenching and tempering), which is used in the manufacture of cutting tools manufacture. Grinding grains in the structure of metal structural materials of cutting tools is an effective way to improving its wear resistance was concluded.

Keywords: steel 30HGSA, thermomechanical treatment, submicron size of grain, wear resistance

JOINT SYNTHESIS OF NANOSIZED POWDERS IN THE B₄C–SiC–TiB₂ SYSTEM

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The increasing interest in ceramic materials with a submicron grains size, naturally leads to developing of new ways of synthesis multicomponent powders with submicron and nanosized range of dispersion. The technology of mechanical grinding and thin milling of coarse powders, classical for powder metallurgy, isn't always reasonable, especially for a milling of highly rigid compounds, such as boron carbide, silicon carbide and titanium diboride. The synthesis methods lead to receive powders not only with the demanded phase and chemical composition, but also with necessary dispersion are perspective for such compounds.

Keywords: nanosized powders, ceramic materials, metallurgy, dispersion

CO-PRECIPIATION OF NANO-SIZED AL₂O₃-ZrO₂-Y₂O₃ SINTERING ADDITIVE FOR SiC LIQUID-PHASE SINTERING

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The nano-sized mixture in system Al₂O₃-ZrO₂-Y₂O₃ (respectively, 63 mol. %; 37 mol. %, and 4 mol. % above 100%) was obtained by the precipitation of respective hydroxides on the “substrate” of submicron SiC powder with total concentration of oxide additive 10 vol. %. After the calcination at 1250 °C in vacuum and sonication obtained mixture was characterized by the X-Ray diffraction, SEM and EDX analysis. Liquid phase formation temperature (1700-1730°C) of resulting system SiC-Al₂O₃-ZrO₂-Y₂O₃ was estimated during its spark plasma sintering.

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Keywords: XRD, SEM, EDX, silicon carbide, nano-sized particles

THE EFFECT OF SYNTHESIS CONDITIONS ON THE QUANTITATIVE COMPOSITION OF THE NANOSTRUCTURED METAL OXIDES BASED ON SiO₂ - SnO₂

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The growing interest in nanostructured materials has stimulated considerable activity in the study of their structure. One of the basic and versatile experimental techniques to determine qualitative and quantitative composition of substances are roentgen diffraction methods and Fourier spectroscopy.

The relevance of this study is determined by scientific and practical interest in the development of new nanocrystalline materials with high catalytic activity, selectivity to analyzed gases, thermal stability.

Therefore, the aim of this work is to develop a methodology and research of quantitative structure of nanocomposite materials based on SiO₂-SnO₂ with an infrared Fourier transform spectrometer.

The objects of study are nanocomposite materials based on SiO₂-SnO₂ with different composition obtained by sol-gel technology.

Keywords: nanostructured, oxide, concentration, synthesis, Fourier-spectroscopy, Sol-gel, temperature, spectrograms

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ELECTROCHEMISTRY AND CORROSION PROTECTION

NANOSTRUCTURED FUNCTIONALLY GRADIENT COATING FOR THE PROTECTION OF STRUCTURAL ELEMENTS FROM CORROSION AND WEAR

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A technology for creating nanostructured composite powders for spraying was developed. Studies on the development and application of thermal spraying methods for functionally graded coatings production have been conducted. A hardness gradient over the cross section of the coating was investigated. The present study shows the possibility of the formation of thick coatings with controlled hardness.

Keywords: nanostructured composite powders, coating, functionally gradient coating, hardness gradient, combining methods of spraying

NANO- AND THE MICRODIMENSIONAL COATS POLYCRYSTAL TITANIUM-CONTAINING THE BASES A METHOD OF ELECTROCHEMICAL BORONIZING

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The technology for the production of wettable aluminium coating was implemented using the method of electro-chemical borating of the carbon-titanium cathode directly at the electrolytic reduction of cryolite-alumina melts in laboratory conditions.

TiC and TiB₂, responsible for the wetting effect, were detected by X-ray phase analysis of cathode surface layer. The mechanism of electro-chemical and chemical processes of Ti-B-C compound formation in the subsurface cathode volume is proposed for the discussion.

Keywords: electro-chemical deposition, borating, carbon-titanium cathode, wettable coating.

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MICROCRYSTALLINE CELLULOSE ADDITIVE FOR MODIFICATION OF PROPERTIES OF POLYMER FILMS

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Studying structure and properties of various coatings used in medicine, technique, and other areas is very important nowadays, and in particular understanding the electromagnetic response to the microstructure and electrochemical response to the chemistry of the coating. Changes in the properties of coatings containing microcrystalline cellulose (MCC) were studied by electrochemical impedance spectroscopy. It was shown that barrier properties of films change with time depending on the amount of MCC. This result can be explained by morphological changes related to swelling in voids and channels during ions diffusion. This study allows a more scientifically justified approach in the formulation of composition of coatings for medical and technical application.

Keywords: coatings, electrochemical impedance spectroscopy, microcrystalline cellulose, polymethylmethacrylate, moisture uptake, thin films

THE USE OF NANO-COATING TO PROTECT PARTS OF MINING MACHINES FROM FRETTING-CORROSION

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The application of nano-coatings based on fluorocarbon polymer composition, friction-mechanical brass, fullerene C₆₀ and surface treatment of vibroroling with the regular roughness for the protection of heavily loaded mating parts of machines, working in conditions of fretting-corrosion. Studied the mechanisms of friction of nano-coating, which will considerably reduce the fretting-wear mechanisms of friction in engineering products.

Keywords: nano-coating, fretting corrosion, vibroroling, fullerene C₆₀

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INFLUENCE OF ALKALI METALS ON THE STRUCTURE OF CARBON GRAPHITE MATERIALS OF KATHODE LINING OF ALUMINUM REDUCTION CELL

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The main indicator of work of the aluminum reduction cells is the life of the cathode device. The cathode device is a basic unit of aluminum reduction cell. Increasing resistance of the cathode device is determined by ability of carbon graphite lining, and silicon carbide side lining to keep their properties as much as possible within a given period of time. The weakest point in the carbon graphite linings are interblock and peripheral joints of cathode devices of aluminum reduction cell. The carbon ramming paste is used for taps interblock and peripheral joints. The carbon ramming paste is carbon graphite materials, which is produced by mixing the calcined anthracite (filler), and coal tar pitch (binder). Additive of low-fusible oil is used to reduce the softening temperature of paste and taps at low temperatures. The last factor is very important because It allows the taps joints without preheating. Such a mass is called cold carbon ramming paste and that it is by far the dominant material for the production of cathode blocks. The cold carbon ramming paste is a mixture of coke and coal tar pitch with a softening point most suitable at low degree of of volatility grade, which determines the life of cathode device. Ease of installation and environmental benefits was an additional factor that led to the transition to the cold carbon ramming paste.

Keywords: graphite, cathode, aluminum reduction cell

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NANOPOROUS AND NANOSTRUCTURED MATERIALS

INVESTIGATION INTERNAL STRUCTURE OF NANOPARTICLES BASED ON POROUS SILICON POWDERS

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Nanoparticles of porous silicon were obtained by electrochemical anodic etching. Morphology and structure of the particles was investigated with using atomic force and scanning electron microscopy and methods of sorbometrii such as measurement of specific surface area BET and capillary condensation. The influence of technological conditions of preparation on geometrical parameters of the porous silicon particles (particle size distribution, pore shape and size, the specific surface area of the porous silicon) is discussed.

Keywords: Porous silicon nanoparticles, electrochemical etching, capillary condensation

EVOLUTION OF COPPER(II) OXIDE NANOSTRUCTURES IN POROUS GLASS MATRIX

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Controllable accumulation of copper(II) oxide in porous glass was carried out by repeated impregnation of the carrier by $\text{Cu}(\text{NO}_3)_2$ aqueous solutions with subsequent thermal decomposition of the salt. The results of measuring electric conductivity of a series of modified plates make it possible to characterize the trend in the oxide distribution on a silica surface. In the case of its cyclic accumulation by small portions, a two-dimensional structure of monolayer filling the surface is presumably formed in a narrow range of CuO concentration.

Keywords: porous glass, CuO, monolayer, electrical conductivity

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STUDY OF THE DEPOSITION PROCESS OF VINPOCETINE ON THE SURFACE OF POROUS SILICON FOR THE PURPOSE OF ESTABLISHMENT OF THE TARGETED DRUG DELIVERY SYSTEMS

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Currently the most prospective way in pharmacotherapy is the obtaining of nanoparticles involving pharmaceutical substances. Application of porous inorganic materials on the basis of silicon is among the main tendencies in solving of this problem. The present work is concerned with the problem of the deposition of pharmaceutical drug with nootropic activity – vinpocetine – into porous silicon. Silicon nanoparticles were obtained by electrochemical anodic etching of Si plates. The process of vinpocetine deposition was studied in a dependence of the deposition time. As a result of the investigations it was found that infrared transmission spectra of porous silicon with the deposited vinpocetine revealed the absorption bands characteristic of vinpocetine substance.

Keywords: nanoparticles, porous silicon, vinpocetine

GRAPHENES, STACKS AND GLOBULES IN NANOPARTICLES OF SHUNGITE CARBON AND NEW MATERIALS

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Shungite carbon (ShC) is considered as the natural carbon allotrope of a multi-level fractal structure produced by the consecutive aggregation of ~ 1 nm graphene fragments. Turbostratic stacks of ~ 1.5 x 2.5 nm and the globular composition of the stacks ~ 6 nm are responsible for the secondary and tertiary levels of the structure. Aggregates of globules, measuring tens of nanometres, form 3D-nets and complete the structure. All structural levels could be released through stable aqueous dispersion of ShC nanoparticles. Each level is important for obtaining special properties in new materials with ShC nanoparticles.

Keywords: Nanocarbon, shungite carbon, graphene, nanotechnology

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METHODOLOGICAL CONCEPT OF ESTIMATION OF FACTORS AFFECTING THE QUALITY OF THE STRETCHABLE NANOROD GEOMETRY

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The mathematical models are offered which adequately describe the process of nanorod stretching, considering all significant factors affecting the rod shaping, including not only viscous properties of the glass melt, but also its relaxation ability. The conditions of stable course of the stretching process were revealed, that allow to choose areas of technological parameters (stretching rate, viscoelastic characteristics of zone of formation) under which the process would be resistant to uncontrollable disturbances. The method is offered for determining characteristics of the formation zone, based on a forced oscillation team of stretchable nanorod.

Keywords: viscosity, stretching rate, surface tension, viscoelastic characteristics, elongation rod, method

INFLUENCE OF POROSITY ON THE PERFORMANCE OF A CUTTING CERAMICS

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Now more and more widely used is a ceramic cutting tool, which is used for processing precision machine parts. On the performance of ceramic tool in addition to other factors is greatly influenced by the porosity of the material. The smaller the porosity, the better cutting properties and performance of ceramic tool. Under normal conditions to determine the number of pores, the size of which is 0.1 to 10 nm, using methods whose use in production conditions difficult.

To solve this problem, we propose to use correlation between the porosity of the cutting ceramics the magnitude of the electrical resistivity of this material. Studies have shown the presence of such dependence and have enabled the identification of quantitative component.

In cutting ceramics with the magnitude of the electrical resistance $R \approx 100 \Omega$ quantity and pore size will be minimal compared with the ceramics with the magnitude of the electrical resistance $R \approx 10 \Omega$. Thus, it can be concluded that the greater would be the value of the specific electric resistance of the cutting ceramics, the greater would be the operation of the instrument.

Keywords: cutting ceramics, performance tool, the porosity of the material

NANOPOROUS CATALITIC COMPOSIT FOR THE STEAM METHANE REFORMING SYSTEMS

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The catalytic porous coatings on the base alumina were produced by microplasma spraying. The positive influence of the heat treatment coatings on the characteristics of porosity was established. The nanostructured porous coatings are efficiency for the steam methane reforming systems.

Keywords: syngas, steam methane reforming systems, porous coating, metallic support, nanostructured catalysts, micro-plasma spraying, super surface area, pore size distribution

**NANOCOMPOSITE SYSTEMS
WITH OPTICAL PROPERTIES**

FORMATION AND OPTICAL PROPERTIES OF CuCl NANOCRYSTALS IN FLUOROPHOSPHATE GLASS

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We study the possibility of formation of CuCl nanocrystals in fluorophosphate glass ($\text{NaPO}_3\text{-Ba(PO}_3)_2\text{-AlF}_3$) by heat treatment technique. Using the optical absorption technique, the position of the CuCl nanocrystal exciton absorption band was studied as a function of heat treatment time and the radius of CuCl nanocrystals increased from 3 to 9 nm.

Keywords: Fluorophosphate Glass, CuCl nanocrystals, excitons

STUDY OF LUMINESCENCE AND SURFACE PROPERTIES OF $\text{Y}_{1-x}\text{Eu}_x\text{V}_{1-y}\text{P}_y\text{O}_4$ PHOSPHORS

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The composition of $\text{Y}_{1-x}\text{Eu}_x\text{V}_{1-y}\text{P}_y\text{O}_4$ phosphors is optimized to provide the highest luminescence brightness achieved for samples with P and Eu contents 10 and 7 mol. %, respectively. The observed brightness growth prominently correlates with the content of specific centers on the phosphor surface reflecting the formation of species responsible for the luminescence efficiency.

Keywords: luminescence, phosphors, yttrium vanadate, surface functional groups

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EFFECT OF ZNS: CU, CL PHOSPHOR SURFACE MODIFICATION WITH SHUNGITE CARBON ON ELECTROLUMINESCENT LIGHT SOURCE PERFORMANCES

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The deposition of shungite carbon micro-additive onto the surface of a commercial ZnS: Cu, Cl phosphor surface provides an adjustable modification of its luminescence spectrum, particularly the control over the ratio between the intensities of “blue” and “green” luminescence bands depending on the deposited additive content.

Keywords: Zinc sulfide, phosphors, electroluminescence spectra, shungite

EFFECT OF THE SYNTHESIS METHODS ON THE CRYSTAL STRUCTURE AND LUMINESCENCE OF ZnAl₂O₄:Eu³⁺ PHOSPHORS

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ZnAl₂O₄:Eu³⁺ phosphors powders were synthesized with different concentration of activator ions by using sol-gel (SG) method and solution combustion (SC) technique. The effect of the method of synthesis and concentration of Eu³⁺ ions on the structure and luminescence properties of zinc aluminate phosphor were investigated. X-ray diffraction pattern confirmed that the fibers were composed of the cubic ZnAl₂O₄ phase. The calculation of the crystallite size according to Scherrer formula and the maximum were for obtained 0.12% of Eu³⁺ ions by using SG and for samples prepared by SC was 0.15%. Luminescence spectra shown peaks at 612 and 618 nm. The intensity of all the emission bands reached at 0.12% and 0.24% depending on activator concentration by using SG and SC techniques, respectively. So the crystallinity, luminescence spectrum profiles and luminescence of phosphors can be effectively adjusted by the variation of method and dopant (activator) concentration.

Keywords: zinc aluminate phosphor, zinc aluminate spinel, phosphor, XRD, luminescence

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INVESTIGATION OF COVERED COLLOIDAL QUANTUM DOTS CdSe/ZnS AND CdSeZnS/ZnS AS A BASIS OF DETECTOR COATING

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Covered colloidal quantum dots CdSe/ZnS and CdSeZnS/ZnS were examined. High efficiency of luminescence was shown in the range of wavelengths from 500 to 700 nm. Simulation of CQDs' energy and dimensional properties was run; it was shown that particles vary in diameters in the range from 2 to 5 nm. Using a mixture of CQDs as a basis, detector coating were created; such covers are promising for use in non-contact surface quality diagnostics.

Keywords: colloidal quantum dots, luminescence, dimensional parameters

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**PLASMA TECHNOLOGIES, DIAGNOSTICAL
METHODS, FRACTAL STRUCTURES,
AND NANO-SIZED STRUCTURES**

WATER TREATMENT SYSTEMS WITH THE USE OF MAGNETRON NANOSTRUCTURED COATINGS Ti-RU-O

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The feasibility of making a dimensionally stable anode (DSA) with an active coating Ti-Ru-O prepared by reactive magnetron sputtering was demonstrated through the present work. In addition, it was shown a utilization efficiency of water treatment systems the main element of which is the developed anode.

Keywords: dimensionally stable anodes, magnetron sputtering, nanostructured coating, water treatment

PLASMA NANOTECHNOLOGIES FOR NOVEL PLASMA ENERGETICS

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Experimental studies of the properties of a condensate of cesium excited states are analyzed. Theoretical and experimental data of different authors are compared. We discuss the concept of the practical use of the Rydberg matter in the working process of a low-temperature thermionic converter (TIC) of energy at the emitter temperature below 1600 K, the collector temperature below 700 K, and the generalized index of energy loss in a TIC (barrier index) of $V_b \sim 1.6$ eV.

Keywords: Rydberg matter, low-temperature thermionic converter, plasma energetics

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CO-PRECIPIATION OF NANO-SIZED $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-Y}_2\text{O}_3$ SINTERING ADDITIVE FOR SiC LIQUID-PHASE SINTERING

*D. D. Nesmelov, O. A. Kozhevnikov,
S. N. Perevislov and S. S. Ordan'yan*

The nano-sized mixture in system $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-Y}_2\text{O}_3$ (respectively, 63 mol. %; 37 mol. %, and 4 mol. % above 100%) was obtained by the precipitation of respective hydroxides on the "substrate" of submicron SiC powder with total concentration of oxide additive 10 vol. %. After the calcination at 1250 °C in vacuum and sonication obtained mixture was characterized by the X-Ray diffraction, SEM and EDX analysis. Liquid phase formation temperature (1700-1730 °C) of resulting system SiC- $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-Y}_2\text{O}_3$ was estimated during its spark plasma sintering.

Keywords: alumina, zirconium, plasma sintering

FRACTAL STRUCTURE AND ELECTRICAL PROPERTIES OF PERCOLATION SENSOR LAYERS

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A model of percolation sensor layers with fractal structure near percolation threshold based on Mandelbrot-Given curve was proposed. Sensitivity values of these layers to reducing gases exceeding the typical values by several orders of magnitude were explained using developed model. The peculiarities of electrical properties of percolation sensor layers were studied by impedance spectroscopy in air and in the presence of reducing gases.

Keywords: gas sensors, percolation cluster, Mandelbrot-Given fractal, impedance spectroscopy

ANALYTICAL CAPABILITIES OF REM IN THE MODE OF SCATTERED ELECTRON REGISTRATION WITH ENERGY SELECTION FOR DIAGNOSTICS OF NANOSTRUCTURES

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The report encompasses capabilities of scanning electron microscopy for quantitative diagnostics of morphology and ultimate composition of soft matter nanostructures in the mode of scattered electron registration with energy selection.

Keywords: scanning electron microscopy, scattering electrons, imaging contrast.

DEVIATION OF THE LAMBERT-BEER LOW FOR THE CARBON NANOPARTICLES DIFFERENT KINDS AT THE NEAR THZ FREQUENCY RANGE

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This work concerns the peculiarities of the electromagnetic waves absorption by different kinds of nanocarbon particles in THz frequency range. Lots of different nanocarbon clusters - the fullerenes (C-60 and C-70), two types of multiwall carbon nanotubes (arc and gas phase technology made), colloid graphite, astralenes, sulfo-adducts of the two or three-layer graphenes and carbon nanoporous microfiber (CNPMF) have been studied by Ph.D. Irina Khromova in work. It was found, that for the most famous kinds of the carbon nanoparticles concentration (1%-25% mass.) the relations between the absorption coefficients and the concentrations of these particles in the transparent media (high density polyethylene(HDPE)) are rather goodly confirm the Lambert-Beer law for the wide frequency diapason (0,005 – 3 THz). However, it is not so for the astralenes and for the CNPMF. For this case the relations between the absorption coefficients and concentrations of the carbon nanoparticles are non-linear even for not so high concentrations (3%-4% mass), and for highest value of concentrations the absorption coefficient arises strongly, especially at the near THz frequency range.

Keywords: terahertz frequency, carbon nanoparticles

GEOLOGICAL AND MINERALOGICAL JUSTIFICATION OF THE APPLICATION OF PROCESSED SHUNGITE RAW MATERIALS IN NANOTECHNOLOGY

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Carbon-rich shungite rocks are promising raw materials for production of adsorbents, catalysts and fillers for polymers of different polarity and inorganic blends.

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Recently shungite rocks attract attention as a natural source of nanosized carbon. However, heterogeneity of shungite rocks and poor reproducibility of its composition and properties lead to inability to use this valuable raw material in high-tech processes. The ways of homogenization of the raw material obtained of shungite rocks and improvement the efficiency of its application are suggested.

Keywords: shungite rocks, raw materials, nanosized quartz, hybrid materials, nanotechnology

SEMICONDUCTORS AND THIN-FILM TECHNOLOGIES

INVESTIGATION OF THE DEPENDENCE OF THE DISPERSION FORCES ON THE PROPERTIES OF THE METALLIZATION LAYER IN MDS-STRUCTURES

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We presented the new results of calculations dispersion force pressure with different material used as metal layer in metal–dielectric–semiconductor (MDS) structures. The calculations are based on the Lifshitz theory at nonzero temperature. We discuss the range of the typical value of the thickness a dielectric layer used in modern electronics. As an example, we show how the value of the dispersion force pressure depends on of changes electro-optical properties of the metal layer in MDS-structures.

Keywords: metal–dielectric–semiconductor (MDS) structures, silicon, metallization, dispersion forces, Lifshitz theory

STRUCTURAL TRANSFORMATIONS IN IRON THIN FILMS ON SILICON SUBSTRATE

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During annealing of iron films (20-270 nm) on silicon substrate phase-formation process consists of two stages. Under temperature less than 130°C the increasing of iron lattice parameter from 2.8663 (traditional bcc lattice) Å up to 2.8737 Å is observed and solid solution Fe(Si) is formed. The width of transition region (Fe/Si) is increasing up to 30 nm. Under temperature 180°C the phase Fe₅Si₃ which is an ordered solid solution and which exists under 800°C only is formed and stabilized in thin film state. The forming of Fe(Si)-phase is initiated by polygonization process of iron structure. Recrystallization process of iron structure is observed only at film thickness more than 100 nm.

Keywords: iron thin film, structure, polygonization, recrystallization

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ATOMIC-FORCE VISUALISATION OF MOTT-TRANSITION IN VO₂ NANOCOMPOSITE

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The electron beam can be used to control the temperature of the semiconductor–metal phase transition. The structure that is formed on the VO₂-nanocomposite surface using electron beam irradiation is studied with the aid atomic force methods. The physical principle of such a control is based on the donor properties of the backdonation σ bonds.

Keywords: Vanadium dioxide, phase transition, strong correlations

CORRELATION MECHANISM OF THE ELECTRONIC COMPONENT OF THE METAL-INSULATOR PHASE TRANSITION IN VO₂ NANOCOMPOSITE

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Development of a method for separating of purely electronic phase transition component of VO₂-films and the determination of its characteristics is main result of this study.

Keywords: Vanadium dioxide, phase transition, strong correlations

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TRANSITION METAL DOPED ZINC SELENIDE NANOCRYSTALS SYNTHESIZED IN AQUEOUS AND ORGANIC SOLUTIONS

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Colloidal quantum dots (QDs) of zinc selenide doped with manganese and copper were obtained in water medium using mercaptopropionic acid as a surfactant. Nucleation doping technique was implemented to synthesize ZnSe:Mn QDs in non-coordinating solvent octadecene. Samples were characterized by means of absorption and photoluminescence spectroscopies. Synthesized nanocrystals may be an alternative to conventional cadmium chalcogenide nanocrystals for visible range applications including biomedical detection.

Keywords: Colloidal quantum dots, surfactant, absorption

CORRECT CALCULATION OF THE TEMPERATURE DEPENDENCES OF KINETIC COEFFICIENTS IN THE TWO-BAND MODEL

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It is known that most semiconductors have a complex structure of the valence band. Therefore, several types of holes with different effective masses are involved in transport phenomena. This circumstance greatly complicates the analysis of experimental data. In such an event, experimental data are usually analyzed on the basis of the two-band model.

Keywords: semiconductors, two band model

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DONOR-ACCEPTOR CHARACTERISTICS OF SURFACE AND FUNCTIONAL PROPERTIES OF SOLIDS

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Surface characteristics of solid influences interface interaction in which this solid participates and thus influences some functional properties of solids. Distribution of active surface centers (DAC) spectroscopy is applied to study donor-acceptor characteristics of surface of solid materials, especially luminescent ones.

Keywords: spectrtrosopy, luminescent materials

PRODUCTION AND RESEARCH OF NANOCRYSTALLINE ZNO FILMS

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Some results are provided in this work confirming that modifying the 1 microns thick films of zinc fabricated on glass substrates by method of a laser ablyation by a resulting effect of heat treatment in the atmosphere of dry air and action of cross electric field manufacturing of ZnO with the extended surface consisting of one-dimensional monocrystals of the nanometer sizes is possible. By method of the scanning electronic microscopy the morphology of a surface of all films was investigated, and the micro x-ray spectral analysis was used to investigate their element structure.

Keywords: nanocomposite films, ZnO, spectral analysis

CHARGE TRANSFER PROCESSES IN B112SiO20 SINGLE CRYSTAL

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Charge transfer in $\text{Bi}_{12}\text{SiO}_{20}$ structures is investigated. Electric current dependences on time at temperature of 300 K in the dc electric field strength of the $2 \cdot 10^5$ – 10^6 V/m range are measured. Flowing of relaxation polarizing current is shown to result in charge accumulation in the sample surface area. Experimental regularities coordinate with provisions of the relay mechanism of transfer of a charge with the participation of deep local levels.

Keywords: electric field, charge transfer, charge accumulation, conductivity, polarization, local states

ON THE MODELING OF GAS-SENSITIVE PROPERTIES OF THE POROUS COMPOSITES SiO_2 - Me_xO_y WITH FRACTAL STRUCTURE

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A model of gas sensitivity, taking into account the molecular and Knudsen diffusion of gases in porous nanocomposites SiO_2 - Me_xO_y is developed. It has been shown that their gas sensing properties depend not only on the qualitative and quantitative composition, but also on the prevailing type of gas diffusion, which is determined by the concentration and size of the pores in the material.

Keywords: sol-gel technology, nanocomposites, diffusion, gas sensors, modeling

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