РЕЗЮМЕТА НА ПУБЛИКАЦИИТЕ

на доц. д-р Марио Йорданов Митов

за участие в конкурса за професор по професионално направление 4.2. Химически науки (неорганична химия – електрохимия), обявен в Държавен вестник бр. 33/ 27.04.2012 г.

I. Публикации

І.1. Статии в чуждестранни реферирани списания с импакт фактор

1. M. Mitov, R. Rashkov, N. Atanassov, A. Zielonka

Effects of Nickel Foam Dimensions on Catalytic Activity of Supported Co-Mn-B Nanocomposites for Hydrogen Generation from Stabilized Borohydride Solutions *J.Mat.Sci.*, **42** (2007) 3367-3372. **IF 2.325** (http://rd.springer.com/article/10.1007/s10853-006-0786-0)

In the present work, the catalytic activity of electrodeposited Co–Mn–B nanocomposites towards controllable hydrolysis of sodium borohydride was studied. Deposition was performed on two types of Ni foam (RECEMAT Int.) with different pore size, specific surface area and thickness. Higher deposit loading, as well as bigger real surface area, was obtained with foam samples possessing bigger pore size. The catalyst deposited on bigger pore foam promoted hydrogen generation with higher rates than the other one when contacted with a base-stabilized NaBH₄ solution. The same activation energy value, however, was determined for both supported catalysts. On the base of the obtained results, it may be concluded that the geometric factor plays predominant role for the catalytic activity of studied catalysts.

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doi:10.1016/j.ijhydene.2012.04.021

2. M.Mitov, G.Hristov, E.Hristova, R.Rashkov, M.Arnaudova, A.Zielonka

Complex performance of novel CoNiMnB electrodeposits in alkaline borohydride solutions *Environm.Chem.Lett.* **7** (2) (2009)167-173.

IF 2,051

(http://www.mendeley.com/research/complex-performance-novel-conimnb-electrodepositsalkaline-borohydride-solutions/)

The complex performance of newly synthesized CoNiMnB electrodeposits in basestabilized sodium borohydride solutions was examined. The rate of hydrogen generation due to borohydride hydrolysis was determined at different temperatures. Activation energy of approximately 33 kJ/mol was estimated, which is lower than the values reported for other catalysts. At electrochemical conditions, there is a competition between borohydride hydrolysis and electrooxidation reactions. The electrooxidation of borohydride takes place with low overpotentials at relatively high current densities. The long-term discharge at galvanostatic conditions as well as possibilities for partial storage of generated hydrogen indicates potentials for application of studied electrodeposits as anode material in direct borohydride fuel cells (DBFC).

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3. M.Mitov, E.Hristova, G.Hristov, R.Rashkov, M.Arnaudova, A.Popov Catalytic activity of Ni-W electrodeposits *Environm.Chem.Lett.* 7 (3) (2009) 249-253.
IF 2,051 (http://www.springerlink.com/content/9257276884665516/)

NiW systems are known as one of the best catalysts for various desulfurization processes. In this study, we examined catalytic properties of NiW electrodeposits, produced from two different electrolytes, towards sulfide ion oxidation in alkaline solution. Despite the big difference in morphology and structure of both materials, they exhibit almost the same catalytic activity for the examined reaction. A possible explanation of this experimental fact is that the overall reaction is controlled by the transport of oxygen through the catalyst samples.

4. J.Zaharieva, M.Milanova, **M.Mitov**, L.Lutov, S.Manev, D.Todorovsky Corrosion of aluminium and aluminium alloy in ethylene glycol–water mixtures *Journal of Alloys and Compounds*, **470** (2009) 397-403. **IF 2.134** (<u>http://www.sciencedirect.com/science/article/pii/S0925838808003587</u>)

Samples of pure aluminium and aluminium alloy were heated at 150 kPa and 130 \circ C in ethylene glycol (EG)–water mixture (volume ratio 1:1) for 172 h (8–12 h heating, 12–16 h pause). The corrosion of the metals was characterised by the transfer of Al into solution, changes in the surface morphology of the samples and their electrochemical behaviour. Formation of a white crystalline aluminium-organic precipitate was found during the heating of metals and some of its characteristics were determined. The effect of the addition of glycolic, citric and sebacic acid to the EG–water mixture on the metal corrosion behaviour was investigated. A significant corrosive action of glycolic acid and a protective effect of sebacic acid were found.

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Potential application of Candida melibiosica in biofuel cells *Bioelectrochemistry* 78 (2010) 57-61.
IF 3.520
(http://www.sciencedirect.com/science/article/pii/S1567539409001315)

Various prokaryote species have been widely studied for microbial fuel cell (MFC) application. However, the information about yeast utilization into biofuel cells is still scanty. The aim of this investigation is to verify if *Candida melibiosica 2491*, a yeast strain, possessing high phytase activity, could be applied as a biocatalyst in a yeast biofuel cell. The microbiological requirements were coupled with the electrochemical ones tracing main biochemical pathway metabolites such as different carbohydrate and inorganic phosphates and their assimilation with time. The obtained results show that from the three carbohydrates investigated — glucose, fructose and sucrose, fructose is the most suitable for the yeast cultivation. The presence of yeast extract and peptone improves the performance into the

biofuel cell. The relationship between the yeast cell amount and the biofuel cell characteristics was determined. Analyses showed that electricity was generated by the yeast culture even in the absence of an artificial mediator. The addition of methylene blue at concentrations higher than 0.1 mM improves the current and power density output. The obtained experimental results proved that *C. melibiosica 2491* belongs to the electrogenic strains.

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Characterisation of yeastmicrobial fuel cellwith the yeast *Arxula adeninivorans* as the biocatalyst

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 Catalytic activity of baker's yeast in a mediatorless microbial fuel cell BIOELECTROCHEMISTRY 86: 97-101, AUGUST 2012 doi: 10.1016/j.bioelechem.2012.02.001

6. Y.Hubenova, R.Rashkov, V.Buchvarov, M.Arnaudova, S.Babanova, **M.Mitov** Improvement of Yeast-biofuel cell output by electrode modifications *Industrial & Engineering Chemistry Research* **50**(2) (2011) 557-564. doi: 10.1021/ie1000949

IF 2.072 (http://pubs.acs.org/doi/abs/10.1021/ie1000949)

In this study, a methodology for electrodeposition of nickel nanostructures on carbon felt was developed on the base of pulse plating technique. Different in size, shape, and distribution, Ni-island nanostructures were deposited varying the potential, current, pulse duration, and cycle reiteration. The biocompatibility and nontoxicity of the newly created materials toward *Candida melibiosica* yeast cells was proven. The prepared Ni-nanomodified carbon felts were investigated as anodes in a two-chamber mediatorless yeast-biofuel cell. Maximum power density values of 720 and 390 mW/m² were achieved with the electrodes modified under galvanostatic and potentiostatic conditions, respectively, against 36 mW/m² for the nonmodified ones. The better biofuel cell performance obtained with the Ni-modified electrodes is assigned to an improved electron transfer.

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High-performance amperometric biosensors and biofuel cell based on chitosan strengthened cast thin films of chemically synthesized catecholamine polymers with glucose oxidase effectively entrapped

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Effect of bed expansion height on electrogenesis capacity of anaerobic fluidized bed membraneless microbial fuel cell.

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Electricity Generation from Wastewater Using an Anaerobic Fluidized Bed microbial Fuel Cell

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5. Rawson, F.J., Gross, A.J., Garrett, D.J., Downard, A.J., Baronian, K.H.R. Mediated electrochemical detection of electron transfer from the outer surface of the cell wall of *Saccharomyces cerevisiae*

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 Catalytic activity of baker's yeast in a mediatorless microbial fuel cell BIOELECTROCHEMISTRY 86: 97-101, AUGUST 2012 doi: 10.1016/j.bioelechem.2012.02.001

7. Y.Hubenova, R.Rashkov, V.Buchvarov, S.Babanova, **M.Mitov** Nanomodified NiFe- and NiFeP-carbon felt as anode electrocatalysts in yeast-biofuel cell *Journal of Materials Science* **46**(22) (2011) 7074-7081, doi: 10.1007/s10853-011-5502-z IF **2.325**

(http://www.springerlink.com/content/e307854720333xv2/)

The improvement of the electron transfer from the microorganisms to the anode is considered to be one of the most important factors for increasing the biofuel cell fficiency. In our recent study, a significant improvement of the yeast-biofuel cell output was achieved by application of Ni-modified carbon felt anodes. In this study, the electrocatalytic properties of new nanomodified carbon materials were investigated. Nickel–iron and nickel–iron– phosphorous nanostructures were electrodeposited on carbon felt by means of pulse plating technique. The produced materials were analyzed for cytotoxicity and applied as anodes in a double-chamber mediatorless yeast-biofuel cell. The use of all modified electrodes resulted in increase of the biofuel cell outputs in comparison with those obtained with non-modified carbon felt; however, higher maximum power density values, exceeding up to 5-folds that of the control, have been achieved with NiFeP-carbon felt anodes. The observed electrocatalytic effects were connected with the particular elemental content, size distribution, and morphology of modified materials as well as with a hypothesis for switching on adaptive mechanisms as a response to Ni and Fe presence, resulting in facilitated electron transfer across the cell membrane.

Цитати: 2 бр.

1. Rawson, F.J., Gross, A.J., Garrett, D.J., Downard, A.J., Baronian, K.H.R. Mediated electrochemical detection of electron transfer from the outer surface of the cell wall of *Saccharomyces cerevisiae*

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 Catalytic activity of baker's yeast in a mediatorless microbial fuel cell BIOELECTROCHEMISTRY 86: 97-101, AUGUST 2012 doi: 10.1016/j.bioelechem.2012.02.001

8. S.Babanova, Y.Hubenova, M.Mitov

Influence of artificial mediators on yeast-biofuel cell performance *Journal of Bioscience and Bioengineering* **112**(4) (2011) 379–387. doi:10.1016/j.jbiosc.2011.06.008

IF 2.312

(http://www.mendeley.com/research/influence-artificial-mediators-yeastbased-fuel-cell-performance/)

Soluble artificial mediators are often applied to enhance the electron transfer from living cells to an anode in microbial fuel cells. Recently, we have demonstrated that the

Candida melibiosica 2491 yeast strain possesses electrogenic properties and can be used as a biocatalyst in yeast-based fuel cells even in the absence of artificial mediators. To enhance the generated electrical power, the potential application of several organic compounds as mediators in a C. melibiosica-based fuel cell was examined in this study. The choice of compounds was based upon observed cyclic voltammetry reversible electrochemical behavior at potentials appropriate for mediated electron transfer. Among the studied mediators, methylene blue, methyl orange, methyl red and neutral red significantly increased the current and power outputs in comparison with those obtained with a mediatorless yeast-based fuel cell.

9. S. Babanova, Y.Hubenova, **M. Mitov**, P.Mandjukov Uncertainties of yeast-based biofuel cell operational characteristics *Fuel Cells* (2011) doi: 10.1002/fuce.201100086 **IF 3.320** (http://onlinelibrary.wiley.com/doi/10.1002/fuce.201100086/abstract)

The commonly used parameters characterizing fuel cells and in particular microbial fuel cells (MFCs) electrical performance are open circuit voltage (*OCV*), maximum power and short circuit current. These characteristics are usually obtained from polarization and power curves building. In the present study, the expanded uncertainties of operational characteristics for yeast-based microbial fuel cell were evaluated and the main sources of uncertainty were determined. Two approaches were used: the uncertainty budget building for sources uncertainty estimation and a statistical treatment of identical MFCs results – for operational characteristics uncertainty calculation. It was found that in this particular bioelectrochemical system the major factor contributing to operational characteristics uncertainties were decreased from 19% to 13% for *OCV*, from 42% to 14% for maximal power and for short circuit current from 46% to 13% with the usage of electrodes with resistance in the interval 6- 7Ω . The described approaches can be used for operational characteristics expanded uncertainties calculation of all types of fuel cells using data from polarization measurements.

10. M.Mitov, E.Chorbadjijska, Y.Hubenova, R.Rashkov

Novel nanostructured electrocatalysts for hydrogen evolution reaction in neutral and weak acidic solution

Int. J. Hydr.Energy (2012) doi:10.1016/j.ijhydene.2012.02.102 **IF 4,053** (http://www.sciencedirect.com/science/article/pii/S0360319912004661)

Microbial electrolysis cells (MECs) provide an innovative bioelectrochemical approach for hydrogen production using microorganisms as biocatalysts. The development of costeffective cathodes for near-neutral pH and ambient temperature conditions is the most critical challenge for the practical application of MEC technology. In this study, the electrocatalytic properties of electrodeposited onto carbon felt NiFe-, NiFeP- and NiFeCoP nanostructures towards HER in neutral and weak acidic solutions were investigated. The voltage needed to initiate hydrogen production and the current production rates were estimated from obtained linear voltammograms. The developed composite materials possess much higher catalytic activity than bare carbon felt. The highest current production rate corresponding to $1.7 \pm 0.1 \text{ m}^3\text{H}_2/\text{day/m}^2$ was achieved with NiFeCoP/carbon felt electrodes. In addition, the applied modifications result in improvement of the corrosion resistance. The obtained results demonstrate that Ni-based nanomodified materials are promising

electrocatalysts for HER in near-neutral electrolytes and could be applied as cathodes in MECs.

11. Y.Hubenova, M.Mitov

Conversion of solar energy into electricity by using duckweeds in Direct Photoshyntetic Plant Fuel Cell *Bioelectrochemistry* (2012) doi:10.1016/j.bioelechem.2012.02.008 **IF 3.520** (http://www.sciencedirect.com/science/article/pii/S1567539412000436)

In the present study we demonstrate for the first time the possibility for conversion of solar energy into electricity on the principles of Direct Photosynthetic Plant Fuel Cell (DPPFC) technology by using aquatic higher plants. Lemna minuta duckweed was grown autotrophically in specially constructed fuel cells under sunlight irradiation and laboratory lighting. Current and power density up to 1.62±0.10 A.m⁻² and 380±19 mW.m⁻², respectively, were achieved under sunlight conditions. The influence of the temperature, light intensity and day/night sequencing on the current generation was investigated. The importance of the light intensity was demonstrated by the higher values of generated current (at permanently connected resistance) during daytime than those through the nights, indicating the participation of light-dependent photosynthetic processes. The obtained DPPFC outputs in the night show the contribution of light-independent reactions (respiration). The electron transfer in the examined DPPFCs is associated with a production of endogenous mediator, secreted by the duckweed. The plants' adaptive response to the applied polarization is also connected with an enhanced metabolism resulting in an increase of the protein and carbohydrate intracellular content. Further investigations aiming at improvement of the DPPFC outputs and elucidation of the electron transfermechanismare required for practical application.

І.2. Статии в други чуждестранни специализирани издания

12. Y. Hubenova, M.Mitov

The new era has begun: renewable bioenergy production as a progressing interdisciplinary research approach

In: Alpine Space - Man & Environment, vol. 7, edited by R. Jandl, A. Borsdorf, H. van Miegroet, R. Lackner, R. Psenner, Innsbruck University Press, ISBN 978-3-902571-97-7, 2008, pp.141-148.

(http://www.uibk.ac.at/alpinerraum/publications/vol7/hubenova.pdf)

The aim of this study is a verification of possibilities for introducing budding yeast cells as a microreactor into biofuel cells. The investigation includes optimization of conditions for high efficiency utilization of in vivo produced electrons within the main biochemical pathways, which naturally cover the energy needs of the living cells. We trace out the three stages of cellular respiration - glycolysis, citric acid cycle and oxidative phosphorylation in eukaryotic cells, aspiring to shuttle the electrons between the biological system and the fuel cell anode by using appropriate mediator. The challenge is to use the biological energy from subcellular level. We modulate the biofuel cell/cell suspension elements in such manner that the mediator could capture the electrons from the biological electron transport chains and transfer them subsequently through the double mitochondrial membrane and outer membrane

of intact cells and/or from cytosol under anaerobic conditions and finally, to the electrode, where they are transmuted into electricity.

Цитати: 1 бр.

 Бабанова, София Малинова
 Генериране на електричество чрез дрожден биогоривен елемент Дисертация, Благоевград, 2012

13. M.Arnaudova, G.Avdeev, R.Rashkov, **M.Mitov**, A.Zielonka, E.Theodoridou Electrodeposition and characterization of Ni-Mo and Ni-Mo-W layers on carbon fibers *Journal of International Scientific Publications: Materials, Methods & Technology* **4**(2) (2010) 275-283. ISSN: 1313-2539.

Ni-based systems (Ni-W and Ni-Mo-W) were electrodeposited on oxidized and nonoxidized carbon fiber from the electrolyte containing nickel sulphamate, sodium molybdate and sodium tungstate under potentiostatic conditions. The morphology, structure and chemical state of the components on the surface were analyzed by scanning electron microscopy (SEM), X-ray diffraction (XRD) methods and X-ray photoelectron spectroscopy (XPS). The kinetics of the composite deposition and corrosion behaviour was studied. The NiMoW layers on oxidized carbon fibers possess the best catalytic characteristics for HER.

14. Y.Hubenova, M.Mitov

Bacterial mutalism in the mosses roots applicable in Bryophyta-microbial fuel cell *Communications in Agricultural and Applied Biological Sciences* **76**(2) (2011) 63-65. (<u>http://www.ncbi.nlm.nih.gov/pubmed/21404937</u>)

The Microbial Fuel Cell (MFC) technology is rapidly developed the last few years. It is based on the utilization of whole microorganism cells and the conversion of a part of their biochemical energy into electrical one. The investigations of higher organisms such as plants as a future bioenergy source in the so-called Plant Microbial Fuel Cell, however, have just begun. Actually the Plant-MFC technology re-creates on a small scale the fundamental norms of the circulation of substances and energy in the nature. The aim of this *ab initio* study is to investigate a new type plant MFC, called by us Bryophyta-MFC (B-MFC). This technological approach is based on both natural developed species interactions combined with the MFC requirements for harvesting *in situ* produced bioenergy.

І.З. Статии в български реферирани списания с импакт фактор

15. E.Hristova, M.Mitov, R.Rashkov, M.Arnaudova, A.Popov Sulfide oxidation on electrodeposited Ni-Mo-W catalysts *Bulg.Chem.Comm.*, 40 (2008) 291-294.
IF 0.171 (http://cl.bas.bg/hosted-journals-of-the-bulgarian-academy-of-sciences/bulgarian-chemicalcommunications/bbc)

In this study, the catalytic activity of novel Ni-Mo-W electrodeposits for sulfide oxidation in alkaline media has been investigated. The studies were performed by obtaining partial anodic and cathodic polarization curves with sodium hydroxide and alkaline sodium sulfide electrolytes, respectively, and applying the additivity principle, proposed by Wagner

and Traud, for reaction rate determination. In addition, catalytic test were carried out in static reactor and the process kinetics was registered by UV- spectroscopy determination of sulfide concentration decrease. The results from both experiments were compared and discussed.

16. G.Hristov, M.Mitov, R.Rashkov, S.Hristov, A.Popov
Electrooxidation of alkaline borohydrides on metal hydride electrodes *Bulg.Chem.Comm.*, 40 (2008) 306-309.
IF 0.171
(http://cl.bas.bg/hosted-journals-of-the-bulgarian-academy-of-sciences/bulgarian-chemical-communications/bbc)

In this paper, commercial AB_5 metal hydride alloy has been investigated as an anode material for borohydride electrooxidation. Polarization and discharge characteristics in stabilized sodium borohydride solutions as well as in strong base electrolyte have been obtained by means of electrochemical methods. The results have been analyzed and compared with those of previously studied nanocomposite electrodeposits.

Цитати: 1 бр.

 Santos, D.M.F., Sequeira, C.A.C.
 Sodium borohydride as a fuel for the future RENEWABLE AND SUSTAINABLE ENERGY REVIEWS 15(8), 3980-4001, OCTOBER 2011

17. В.Димитрова, М.Митов, Ст.Манев

Водородните технологии в обучението по Химия и опазване на околната среда *Химия*, **17** (2008) 89. **SJR 0.032** (<u>http://khimiya.org/pdfs/KHIMIYA_17_2_MANEV.pdf</u>)

Статията предлага идеи и примери за включване на основните принципи и постижения на водородните технологии в учебния процес по дисциплините "Човекът и природата" (за по-ранните етапи на обучение по природните науки) и "Химия и опазване на околната среда" (за учениците от средния курс).

18. Y.Hubenova, M.Mitov

Electricity generation during sauerkraut fermentation process *Bulg.Chem.Comm.* (in press) **IF 0.171** (http://cl.bas.bg/hosted-journals-of-the-bulgarian-academy-of-sciences/bulgarian-chemicalcommunications/bbc)

The possibility to use a sauerkraut juice as an anolyte in microbial fuel cell (MFC) was previously proved by us. In this study, fifty days long MFC-experiments, covering the total term of the sauerkraut fermentation process, were performed. A change of the electrochemical behavior of sauerkraut juice, associated with the successive loading of different dominating microbial species in the mixed microflora as well as accumulation of various intermediate and end metabolites, was observed by means of cyclic voltammetry. The highest MFC power density of 1.87 W/m³ was achieved by using a fresh sauerkraut juice at the early stage of fermentation, when heterofermentative species are developed into the medium, as anolyte.

However, the maximum power density of a permanently loaded by external resistance MFC was obtained after a month operation, corresponding to the lower development of heterofermentative lactic acid bacteria and their substitution with homo-fermentative bacteria. Stable current density of 1.05 ± 0.10 A/m³ was generated at a long-term of the later fermentation stages.

І.4. Статии в други български специализирани списания

19. M.Mitov, K.Lekova

UV-Spectroscopy Determination of Sulfide Ions in Alkaline Solutions *Ann.Shumen Univ.*, Vol. XVIII B2 (2008) 116-120.

A simple method for determination of sulfide ions in alkaline solutions is presented. The sample preparation consists only of controllable dilution of a solution to proper concentrations. UV-spectra are measured from 190 to 400 nm by using UV-VIS-NIR Spectrophotometer (Agilent technology). Concentration dependent peak of sulfide ions appears at 230 nm. The determination is not interfered by the presence of sodium hydroxide. The method has been designed for kinetics control of catalyzed oxidation of sulfide ions in alkaline solutions. It could be also used for other analytical purposes, for example, monitoring of sulfide content in sea or dinking waters.

20. Y. Hubenova, M.Mitov

Comparison of *Candida melibiosica* and *Saccharomyces cerevisiae* Performance in Experimental Biofuel Cell

Annual of Konstantin Preslavski University of Shumen vol. XIX B2 (2009) 164-170.

The aim of this study is to compare the performance of both *Candida melibiosica* and *Saccharomyces cerevisiae* yeast as a microreactor in experimental biofuel cell. For this purpose different modified yeast media were developed so that the microbiological requirements of these strains could be coupled with the electrochemical ones. Various carbohydrate sources, cultivation temperatures and pH of media were examined. Polarization measurements with suspension of yeast cells, carbohydrate, phosphate buffer and mediator methylene blue at variable as well as at constant load resistance were carried out in a two-chamber electrochemical cell. Higher electric characteristics (generated current, voltage and power) values were achieved with *Saccharomyces cerevisiae*. However, much more stable characteristics within time were obtained with *Candida melibiosica* yeast during long-term polarization tests.

21. Y. Hubenova, S. Babanova, D. Georgiev, **M. Mitov** Influence of the Catholyte Composition on the Microbial Fuel Cell Performance *Annual of Konstantin Preslavski University of Shumen* vol.XX B2 (2010) 195-203.

Most of the research in the field of Microbial Fuel Cells is directed to elucidation of the electron transfer mechanism from microorganisms, serving as biomicroreactors, to the anode. In many cases, however, the cathode semi-reaction is the rate-determining one of the overall current generating process. In this study, the performance of yeast biofuel cell using different soluble oxidizers as a final electron acceptor was investigated and compared. The electrochemical behavior of the catholytes used was also examined by means of cyclic voltammetry measurements.

22. Y. Hubenova, M. Mitov

In situ Generation of Electricity by Bryophyta Microbial Fuel Cell Annual of Konstantin Preslavski University of Shumen vol.XX B2 (2010) 186-194.

The objectives of this study are based on the concept of the novel technology of Microbial Fuel Cells utilizing the energy transfer processes from the plant (Phylum Bryophyta) to the microorganisms and to the fuel cell anode. For the first time the possibility for utilization of symbiotic Bryophyta-microorganisms society as a natural bioreactor in Microbial Fuel Cell (MFC) was proved. A forest moss was taken and placed in a single-chamber MFC. The investigations were performed under semi-natural conditions for 70 days over two seasons. No additions of any nutrients, except compensation of water loss, were made during the whole experiment. Open circuit voltage and current were recorded three times per day. Resistance of 1 k Ω was used for the assays. Voltage values between 550 - 790 mV and current density between 20 - 40 ± 5 mA/m² were achieved.

23. **M.Mitov**, Y.Hubenova, A.Kaisheva, R.Rashkov Innovative microbiological fuel cells as green power sources *Advances in Bulgarian Science* **1** (2010) 36-44. ISSN 1312-6164

Electricity generation from renewable sources and effective waste treatment are key challenges for the sustainable development. Microbiological (Microbial or Bio-) Fuel Cells provide an elegant solution by linking both tasks. Biofuel cells, which can directly generate electricity from biodegradable substances, have rapidly gained increasing research attention. Widely available fuel sources and moderate operational conditions make them promising in renewable energy generation, wastewater treatment, as power sources for remote or implantable devices, etc. The aim of this студъ is a verification of possibilities for conversion of bioenergy into electricity by development and testing of biofuel cells, utilizing whole microorganisms as biocatalysts. Complex microbiological and biochemical analyses are carried out for preliminary selection of proper microorganisms (prokaryotes and eukaryotes), which electrochemical behavior is further analyzed in biofuel cells. Various traditionally used and novel synthesized materials are examined as potential electrodes. The selection of appropriate mediator is based on cytotoxicity tests as well as on electrochemical measurements. An optimization of the microorganisms-mediator-electrode system as well as the whole biofuel cell performance in regards to improvement of its output characteristics (cell voltage, generated current and power density) is also carried out.

I.5. Статии в сборници от международни научни форуми

24. **M. Mitov**, E.Hristova, G.Hristov, R. Rashkov, M. Arnaudova, N. Atanasov, A. Popov Performance of cobalt-nickel-manganese-boron electrodeposits in borohydride solutions In: Nanoscience & Nanotechnology, **7**, Ed. by E. Balabanova and I.Dragieva, Heron Press, Sofia, 2007, pp.146-148.

In this study, results for performance of newly synthesized CoNiMnB elevtrodeposits in borohydride containing solutions are presented. These nanocomposites were produced from complex electrolytes containing cobalt (II), nickel (II) and manganese (II) sulphamates as well as boric acid. Such multilayers, electrodeposited on Ni-foam, were tested as catalysts for hydrolysis of stabilized borohydride solutions. The reaction kinetics was monitored by volumetric measurement of generated hydrogen. Rate constants and activation energy were calculated from recorded kinetic data. The obtained results were compared with those for CoMnB catalysts and discussed.

25. M.Arnaudova, R.Rashkov, V.Bachvarov, M.Mitov, A. Zielonka
Studying Ni Based Systems as Catalyst Materials for HER
In: "Nanoscale Phenomena and Structures", edited by D. Kashchiev, Prof. M. Driniov
Publishing House, Sofia, 2008, pp. 313-316.

Morphology and electrocatalytic activity of newly synthesized NiWTiO_x and NiMoW electrodeposits were examined. On these electrodes, the kinetics of hydrogen evolution reaction in strong alkaline media was studied by means of galvanostatic step polarization technique. The obtained results were compared with those for Ni and NiW.

Цитати: 1 бр.

 Mirkova, L., Monev, M., Petkova, N.
 Hydrogen Evolution, Diffusion and Solution in Ni / Based Composite Electrodeposits ECS TRANSACTIONS 19 (10):105-112, 2009

26. M. Mitov, Y. Hubenova, S.Manev

Demonstration Fuel Cell in Chemical Education

In: Proceedings of the Thirds International Scientific Conference FMNS-2009, vol.1, Blagoevgrad, pp.247-250.

A fuel cell prototype for demonstrations and training purposes is presented. A set of experiments has been developed and included in specialized handbook. An educational kit for school and extracurricular training is under development.

Цитати: 1 бр.

1. Георгиев, Д., Богданов, Б., Костов, Г., Кирякова, Д. Водородни технологии. Горивни елементи – състояние и перспективи. НАУЧНИ ТРУДОВЕ НА РУСЕНСКИЯ УНИВЕРСИТЕТ - 2011, том 50, серия 9.1, 160-165

27. M.Mitov, R.Rashkov, St.Hristov, A.Kaisheva

A novel approach to the fuel cell technology

In: Proceedings of the Thirds International Scientific Conference FMNS-2009, vol.2, Blagoevgrad, pp.3-10.

In this paper, results from implementation the first year program of a project "Metal Hydride – Air Cell" are presented and discussed. Conventional and newly synthesized materials have been studied as anode and cathode electrocatalysts for borohydride oxidation and oxygen reduction reactions, respectively. Initial tests with experimental fuel cell were also conducted. Based on analysis of results, some of studied materials are proposed for further investigations during next stages of the project.

28. S. Babanova, Y. Hubenova, **M. Mitov** Biofuel Cells – Alternative Power Sources In: Proceedings of the Thirds International Scientific Conference FMNS-2009, vol.2, Blagoevgrad, pp.24-29.

Energy generation from renewable sources and effective waste treatment are two key challenges for the sustainable development. Microbiological (or Bio-) Fuel Cells provide an elegant solution by linking both tasks. Biofuel cells, which can directly generate electricity from biodegradable substances, have rapidly gained increasing research attention. Widely available fuel sources and moderate operational conditions make them promising in renewable energy generation, wastewater treatment, power sources for remote devices, etc. This paper reviews the use of microorganisms as biocatalysts in microbiological fuel cells. The principle of biofuel cells and their construction elements are discussed.

Цитати: 1 бр.

1. Георгиев, Д., Богданов, Б., Костов, Г., Кирякова, Д. Водородни технологии. Горивни елементи – състояние и перспективи. НАУЧНИ ТРУДОВЕ НА РУСЕНСКИЯ УНИВЕРСИТЕТ - 2011, том 50, серия 9.1, 160-165

29. G. Hristov, E. Hristova, M. Mitov

Investigation of Metal Hydride Electrodes for Application in Direct Borohydride Fuel Cells In: Proceedings of the Thirds International Scientific Conference FMNS-2009, vol.2, Blagoevgrad, pp.167-173.

The commercialization of fuel cell technology is going to solve the global problem with satisfying rising energy demands as well as those of environmental pollution and global warming. The use of hydrogen rich compounds, such as alkaline borohydrides, is a possible solution of the problem connected with safety hydrogen storage and transportation. Alkaline borohydrides can also undergo direct electrooxidation. The purpose of this study is to determine the share of possible processes taking place in the complex system AB_5 metal hydride electrode/sodium borohydride electrolyte. The obtained results allow selecting the appropriate conditions for application in direct borohydride fuel cells or hydrogen-on-demand systems.

30. G.Hristov, E.Chorbadzhiyska, R.Rashkov, Y.Hubenova, M.Mitov

Comparison of sodium borohydride hydrolysis kinetics on Co-based nanocomposite catalysts In: Proceedings of the Fourth International Scientific Conference FMNS-2011, vol.1, Blagoevgrad, pp. 295 – 300

In this study, we compared the results, obtained with several Co-based nanocomposites (CoMnB, CoNiMnB and CoNiMoW) produced by electrodeposition on Nifoam, as catalysts for the sodium borohydride hydrolysis reaction. Based on the comparative analyses, we propose CoNiMnB electrodeposits as most proper catalysts for development of Hydrogen-on-Demand (HOD) system, while CoNiMoW ones as potential anodes for Direct Borohydride Fuel Cells (DBFCs).

31. E.Chorbadzhiyska, Y.Hubenova, G.Hristov, M.Mitov

Microbial electrolysis cells as innovative technology for hydrogen production In: Proceedings of the Fourth International Scientific Conference FMNS-2011, vol.1, Blagoevgrad, pp. 422-427 Hydrogen production is becoming increasingly important in view of using hydrogen in fuel cells. However, most of the production of hydrogen so far comes from the combustion of fossil fuels and water electrolysis. Microbial Electrolysis Cell (MEC), also known as Bioelectrochemically Assisted Microbial Reactor, is an ecologically clean, renewable and innovative technology for hydrogen production. Microbial electrolysis cells produce hydrogen mainly from waste biomass assisted by various bacteria strains. The principle of MECs and their constructional elements are reviewed and discussed.

32. G.Hristov, E.Chorbadzhiyska, R.Rashkov, Y.Hubenova, M.Mitov

Comparative investigation of CoMnB, CoNiMnB and CoNiMoW-supported anodes for Direct Borohydride Fuel Cells

In: Proceedings of the Fourth International Scientific Conference FMNS-2011, vol.1, Blagoevgrad, pp. 428-433

A direct borohydride fuel cell (DBFC) is a device that converts chemical energy of alkaline borohydride electrooxidation into electricity. Many materials are object of investigation with the importance of operating parameters on the fuel cell performance. In this study, we investigated and compared the results, obtained with DBFC using Co-based nanocomposites (CoMnB, CoNiMnB and CoNiMoW) as anodes and air gas-diffusion electrodes as cathodes. The Co-based nanocomposite electrodes were prepared by electrodepositon on Ni-foam.

І.6. Статии в сборници от национални научни форуми

33. В. Димитрова, Р. Петкова, М. Митов, Ст. Манев

Използване на модели за строеж на атома и химична връзка в обучението по химия в средното училище

В: Сборник от Юбилейна научна конференция "Педагогическото образование в България: състояние и тенденции", т.2, Университетско издателство "Неофит Рилски", 2007, стр.239-244

В статията се прави анализ на използването на разнообразни модели за строежа на атома и химична връзка в задължителната подготовка по "Химия и опазване на околната среда" и "Физика и астрономия" в средния курс. Налага се извода, че използваните модели не винаги са съобразени с възможностите на учениците, ДОИ и учебните програми. Препоръчително е използването на по-опростени, но достатъчно информативни еднотипни модели, което би улеснило ефективното усвояване на учебното съдържание и реализиране на вътрешнопредметни и междупредметни връзки.

34. М.Митов, Д.Николова, Е.Далева, Д.Митов, С.Манев

Демонстрационен модел на екологосъобразна енергийна система

В: Сборник с доклади на XXXV национална конференция по въпроси на обучението по физика "Експериментът в обучението по физика", Съюз на физиците в България, 2007, стр. 89-92

В статията е представен демонстрационен модел на екологосъобразна енергийна система, онагледяващ принципа на възлови технологии, залегнали в концепцията на водородната енергетика. Разработеният лабораторен модулен стенд се състои от слънчев панел – електролизьор - газ-холдери – горивен елемент – краен консуматор.

Електролизьорът и горивният елемент са саморъчно изработени от сравнително достъпни и евтини материали. Важно предимство на разработения лабораторен стенд е, че всеки от основните модули може да бъде заменен с аналогични по действие устройства.

35. М.Митов, Г.Христов, Е.Христова, С.Манев

Експерименти с демонстрационен горивен елемент *DeMi Cell*

В: Сборник с доклади на XXXV национална конференция по въпроси на обучението по физика "Експериментът в обучението по физика", Съюз на физиците в България, 2007, стр. 106-109

В настоящата рабоота са представени основни експерименти, демонстриращи принципа на действие на регенеративен горивен елемент *DeMi Cell* в режим на електролизьор и като източник на ток. Демонстрационният горивен елемент *DeMi Cell* е разработен в катедра "Химия" на Югозападен университет "Неофит Рилски" – Благоевград и може да бъде използван както в часовете по химия и физика, така и в извънкласни форми на обучение.

36. М.Митов

Демонстрационни модели на високи технологии за образователни цели В: Сборник доклади от 42-ра Национална конференция на учителите по химия "Качество на обучението по химия в средното училище", Сдружение "PHTC с ДНТ –

Пловдив", Пловдив, 2007, стр. 92-93

В настоящия доклад е споделен опитът на автора от участието му в Европейския фестивал "Наука на сцената 2", проведен от 1 до 6 април 2007 г. в Гренобъл, Франция. В рамките на фестивала той организира и ръководи дискусионен семинар на тема "Демонстрационни модели на високи технологии за образователни цели". Идеята за този семинар възникна във връзка с натрупания опит по създаване и демонстриране на действащи прототипи, представящи перспективни технологии за получаване на енергия от възобновяеми източници. Представеният на българския щанд проект "Демонстрационен модел на еко-енергийна система", разработен с участието на ученици от ПМГ "Акад.С.П.Корольов" и Югозападен университет "Неофит Рилски" – Благоевград, бе удостоен многонационалното жури с Втората награда на фестивала в конкуренцията на над 500 преподаватели от 28 страни.

37. Й.Хубенова, М.Митов

Връзка между обучението по химия в средните и висши учебни заведения

В: Сборник доклади от 42-ра Национална конференция на учителите по химия "Качество на обучението по химия в средното училище", Сдружение "РНТС с ДНТ – Пловдив", Пловдив, 2007, стр. 161-163

В доклада се прави кратък анализ на някои особености на обучението по химия в българските средни училища, свързани със занижения хорариум, липсата на адекватна материална база и не на последно място, липсата на заинтересованост от учениците, което от една страна контрастира с високите държавни образователни изисквания, а от друга води до съществени пропуски в знанията на бъдещите студенти. Въз основата на дългогодишния си педагогически опит и наблюдения, свързани със затрудненията на голяма част от студентите-химици при използването на основния понятиен апарат (маса, обем, количество вещество, концентрация и др.) авторите правят конкретни предложения, които считат че биха могли да подпомогнат по-плавния преход между учебния материал в средните и висшите училища.

38. Й.Хубенова, Д.Георгиев, М.Митов

Химичното образование и наука в България – традиции и настояще

В: Сборник доклади от Юбилейна научна конференция с международно участие "Науката, образованието и времето като грижа", Смолян, 2007, стр. 89-94.

Химичното образование и наука в България имат богати традиции от втората половина на 19 век. Понастоящем, обаче, съществуват редица проблеми, свързани с намаляващия интерес към природните науки, остарялата материалмна база в повечето от съществуващите химични институти, ниското ниво на заплащане в бранша и др. В настоящата статия са посочени и дискутирани някои подходи за преодоляване на тези проблеми.

39. S. Babanova, K. Bojanov, Y. Hubenova, M. Mitov
Bioelectrochemical Analyses of *Lactobacillus plantarum* for MFC-Application
In: Proceedings of XIII National Conference for Young Scientists, Plovdiv, 2009, pp. 44-49.

Lactobacillus plantarum plays an important role as a natural preserve in food and canning industries. It belongs to the homofermentative microorganisms, which main metabolite is lactic acid. In this study, *Lactobacillus plantarum* 226-15 strain was investigated as a potential biocatalyst in mediatorless microbial fuel cell (ML-MFC). The optimal cultivation medium and conditions as well as the growth phases of the culture were examined. The cell number in suspension was determined in order to use an appropriate cell amount as anolyte in the MFC. The lactic acid quantity formed within time during cell cultivation was measured by means of neutralization titration. Polarization curves and cyclic voltammograms were taken in a two-chamber fuel cell by using carbon felt electrodes. A stable power and current density output was obtained without addition of artificial mediator. For the first time, it is demonstrated that Lactobacillus plantarum can be used for electricity generation in a ML-MFC.

20.06.2012 Благоевград Подпис: /доц.д-р Марио Митов/