Božić, B., Korać, J., Stanković, D.M., Stanić, M., Popović-Bijelić, A., Bogdanović Pristov, J., Spasojević, I., Bajčetić, M.
Mechanisms of redox interactions of bilirubin with copper and the effects of penicillamine
(2017) Chemico-Biological Interactions, 278, pp. 129-134.

https://doi.org/10.1016/j.cbi.2017.10.022

ABSTRACT: Toxic effects of unconjugated bilirubin (BR) in neonatal hyperbilirubinemia have been related to redox and/or coordinate interactions with Cu2+. However, the development and mechanisms of such interactions at physiological pH have not been resolved. This study shows that BR reduces Cu2+ to Cu1+ in 1:1 stoichiometry. Apparently, BR undergoes degradation, i.e. BR and Cu2+ do not form stable complexes. The binding of Cu2+ to inorganic phosphates, liposomal phosphate groups, or to chelating drug penicillamine, impedes redox interactions with BR. Cu1+ undergoes spontaneous oxidation by O2 resulting in hydrogen peroxide accumulation and hydroxyl radical production. In relation to this, copper and BR induced synergistic oxidative/damaging effects on erythrocytes membrane, which were alleviated by penicillamine. The production of reactive oxygen species by BR and copper represents a plausible cause of BR toxic effects and cell damage in hyperbilirubinemia. Further examination of therapeutic potentials of copper chelators in the treatment of severe neonatal hyperbilirubinemia is needed. © 2017 Elsevier B.V.

Pašti, I., Milojević-Rakić, M., Junker, K., Bajuk-Bogdanović, D., Walde, P., Ćirić-Marjanović, G.
Superior capacitive properties of polyaniline produced by a one-pot peroxidase/H2O2-triggered polymerization of aniline in the presence of AOT vesicles
(2017) Electrochimica Acta, 258, pp. 834-841.

https://doi.org/10.1016/j.electacta.2017.11.133

ABSTRACT: The development of novel electrode materials for electrochemical capacitors requires innovative approaches with an imperative to produce highly active materials while holding to simple and scalable synthetic approaches. For the first time we have addressed capacitances of polyaniline (PANI) obtained by enzymatic polymerization. PANI was synthesized in an aqueous system containing aniline, horseradish peroxidase isoenzyme C (HRPC)/hydrogen peroxide (H2O2) as catalyst/oxidant, and 80-100 nm-sized vesicles formed from sodium bis(2-ethylhexyl) sulfosuccinate (AOT). The vesicles served as templates to produce PANI in its emeraldine salt (ES) form. Electrochemical properties of the obtained material were investigated using cyclic voltammetry and galvanostatic charge/discharge experiments. Under galvanostatic conditions and the current load of 1 A g−1 a specific capacitance of 770 F g−1 was measured in 0.5 M H2SO4 solution. We observed that the presence of AOT vesicles in the reaction mixture is crucial for the synthesized polymer product to exhibit redox activity. The applied mild enzymatic PANI-ES synthesis procedure led to a highly stable and processable PANI-AOT vesicle suspension which can be applied directly for the production of active electrodes without any isolation and purification of the reaction products. We believe that the presented results can open a new perspective in the production of conductive polymers for application in electrochemical capacitors. © 2017 Elsevier Ltd

Jovanovic, Z., Bajuk-Bogdanović, D., Jovanović, S., Mravik, Ž., Kovač, J., Holclajtner-Antunović, I., Vujković, M.
The role of surface chemistry in the charge storage properties of graphene oxide
(2017) Electrochimica Acta, 258, pp. 1228-1243.

https://doi.org/10.1016/j.electacta.2017.11.178

ABSTRACT: In the present study we have evaluated the contribution of particular oxygen functional groups in the charge storage properties of graphene oxide (GO). This was achieved by a gradual thermal reduction of GO in an inert atmosphere (up to 800 °C) and thorough examination of functional groups which remained after each de-functionalization step. After identification of functional groups, the character of additional cyclovoltammetric peak, less pronounced than the main redox quinone/hydroquinone pair, and overall charge storage properties of GO were discussed from the perspective of different thermal stability of its surface groups. The results indicated three-stage deoxidation process of GO, each comprising of specific surface chemistry, structural changes and electrochemical behavior. The low capacitance, ~50 F g−1, at T ≤ 300 °C was attributed to the presence of epoxy and carboxyl groups. The highest capacitance (120–130 F g−1) was observed in the case of GO reduced at 400 and 500 °C, which we attributed to positive effects of phenol and carbonyl/quinone groups, while at high temperatures (T ≥ 600 °C, ~30 F g−1) the extensive desorption of functional groups and structural changes were emphasized as the main reasons for additional decrease of capacitance. Our results highlight the cases where the duality of interpretation of surface functional groups is likely to happen and indicate that not all functional groups play a positive role in charge storage behavior of graphene oxide. © 2017 Elsevier Ltd

Tošović, J., Marković, S., Dimitrić Marković, J.M., Mojović, M., Milenković, D.
Antioxidative mechanisms in chlorogenic acid
(2017) Food Chemistry, 237, pp. 390-398.

https://doi.org/10.1016/j.foodchem.2017.05.080

ABSTRACT: Although chlorogenic acid (5CQA) is an important ingredient of various foods and beverages, mechanisms of its antioxidative action have not been fully clarified. Besides electron spin resonance experiment, this study includes thermodynamic and mechanistic investigations of the hydrogen atom transfer (HAT), radical adduct formation (RAF), sequential proton loss electron transfer (SPLET), and single electron transfer – proton transfer (SET-PT) mechanisms of 5CQA in benzene, ethanol, and water solutions. The calculations were performed using the M06-2X/6-311++G(d,p) level of theory and CPCM solvation model. It was found that SET-PT is not a plausible antioxidative mechanism of 5CQA. RAF pathways are faster, but HAT yields thermodynamically more stable radical products, indicating that in acidic and neutral media 5CQA can take either HAT or RAF pathways. In basic environment (e.g. at physiological pH) SPLET is the likely antioxidative mechanism of 5CQA with extremely high rate. © 2017 Elsevier Ltd

Smarun, A.V., Petković, M., Shchepinov, M.S., Vidović, D.
Site-Specific Deuteration of Polyunsaturated Alkenes
(2017) Journal of Organic Chemistry, 82 (24), pp. 13115-13120.

https://doi.org/10.1021/acs.joc.7b02169

ABSTRACT: Selective deuteration of drugs and biologically relevant molecules is becoming increasingly important in the pharmaceutical industry. Site-selective isotopic reinforcement of polyunsaturated fatty acids (PUFAs) at their bis-allylic sites has been identified as a unique approach in preventing oxidative damage in these molecules, which had been linked to neuronal and retinal diseases, atherosclerosis, and aging. Typical methods for preparation of site-selectively deuterated PUFAs require rather long, laborious, and expensive syntheses. In this report, we disclose a very efficient catalytic protocol for site-specific deuteration of PUFAs and analogous poly-alkenes under exceptional kinetic control. Deuterium oxide (D2O) has been identified not only as a deuterium source but also as a crucial component in the overall reaction mechanism responsible for averting the formation of thermodynamically favored side-products. © 2017 American Chemical Society.

Dordević, N., Ganguly, R., Petković, M., Vidović, D.
E-H (E = B, Si, C) Bond Activation by Tuning Structural and Electronic Properties of Phosphenium Cations
(2017) Inorganic Chemistry, 56 (23), pp. 14671-14681.

https://doi.org/10.1021/acs.inorgchem.7b02579

ABSTRACT: In this work, strategic enhancement of electrophilicity of phosphenium cations for the purpose of small-molecule activation was described. Our synthetic methodology for generation of novel two-coordinate phosphorus(III)-based compounds [{C6H4(MeN)2C}2C·PR]2+ ([2a]2+, R = NiPr2; [2b]2+, R = Ph) was based on the exceptional electron-donating properties of the carbodicarbene ligand (CDC). The effects of P-centered substituent exchange and increase in the overall positive charge on small substrate activation were comparatively determined by incorporating the bis(amino)phosphenium ion [(iPr2N)2P]+ ([1]+) in this study. Implemented structural and electronic modifications of phosphenium salts were computationally verified and subsequently confirmed by isolation and characterization of the corresponding E-H (E = B, Si, C) bond activation products. While both phosphenium mono- and dications oxidatively inserted/cleaved the B-H bond of Lewis base stabilized boranes, the increased electrophilicity of doubly charged species also afforded the activation of significantly less hydridic Si-H and C-H bonds. The preference of [2a]2+ and [2b]2+ to abstract the hydride rather than to insert into the corresponding bond of silanes, as well as the formation of the carbodicarbene-stabilized parent phosphenium ion [{C6H4(MeN)2C}2C·PH2]+ ([2·PH2]+) were experimentally validated. © 2017 American Chemical Society.

Bubanja, I.N., Ivanović-Šašić, A., Čupić, Ž., Anić, S., Kolar-Anić, L.
Intermittent Chaos in the Bray−Liebhafsky Oscillator. Dependence of Dynamic States on the Iodate Concentration

(2017) Russian Journal of Physical Chemistry A, 91 (13), pp. 2525-2529.

https://doi.org/10.1134/S0036024417130076

ABSTRACT: Chaotic dynamic states with intermittent oscillations were generated in a Bray–Liebhafsky (BL) oscillatory reaction in an isothermal open reactor i.e., in the continuously-fed well-stirred tank reactor (CSTR) when the inflow concentration of potassium iodate was the control parameter. They are found between periodic oscillations obtained when [KIO3]0 < 3.00 × 10–2 M and stable steady states when [KIO3]0 > 4.10 × 10–2 M. It was shown that the most chaotic states obtained experimentally somewhere in the middle of this region are in high correlation with results obtained by means of largest Lyapunov exponents and phenomenological analysis based on the quantitative characteristics of intermittent oscillations. © 2017, Pleiades Publishing, Ltd.

Gigov, M., Jovanović, J., Adnađević, B.
Isothermal kinetics of C60 polyhydroxylation in a two-phase system in the presence of tetrabutylammonium hydroxide
(2017) Reaction Kinetics, Mechanisms and Catalysis, 122 (2), pp. 741-755.

https://doi.org/10.1007/s11144-017-1268-x

ABSTRACT: The isothermal kinetics of fullerene (C60) polyhydroxylation with sodium hydroxide in the presence of phase-transfer catalyst tetrabutylammonium hydroxide (TBAH) in a two-phase system was investigated. A spectrophotometric method for the determination of the degree of C60 polyhydroxylation was developed. The isothermal kinetic curves of C60 polyhydroxylation were measured in the temperature range from 300 to 328 K. The dependence of effective activation energy on the degree of polyhydroxylation was calculated by using the isoconversional method. The kinetics of polyhydroxylation is mathematically described successfully with the kinetic model of first order chemical reaction. The values of the rate constants, activation energy and pre-exponential factor of polyhydroxylation were calculated. The thermodynamic parameters of activated complex formation for C60 polyhydroxylation [standard enthalpy of activation (ΔH*), standard entropy of activation (ΔS*) and standard free Gibbs energy of activation (ΔG*)] were calculated by using Eyring equation. The effect of stirring speed on the reaction rate constants of polyhydroxylation in the presence of the two types of phase transfer catalysts, TBAH and cetyltrimethylammonium bromide (CTAB) was determined. The reaction mechanism of phase-transfer catalyst and activation of C60 molecule for the reaction of polyhydroxylation was suggested. © 2017, Akadémiai Kiadó, Budapest, Hungary.

Pavićević, A., Luo, J., Popović-Bijelić, A., Mojović, M.
Maleimido-proxyl as an EPR spin label for the evaluation of conformational changes of albumin
(2017) European Biophysics Journal, 46 (8), pp. 773-787.

https://doi.org/10.1007/s00249-017-1257-z

ABSTRACT: Albumin is the most abundant plasma protein and as such has been the subject of many studies using a variety of techniques. One of

them, capable of monitoring the conformational changes and the binding capacity of proteins, is electron paramagnetic resonance spectroscopy (EPR) spin labeling. To date, albumin has been investigated using a number of different spin labels, mostly spin-labeled fatty acids (SLFAs). However, albumin can bind up to seven equivalents of fatty acids, making it difficult to determine which parts of the molecule undergo conformational changes. To obtain information from a specific site on a protein, spin labels that bind to free cysteine residues may be used. In this work, the applicability of such a label, 3-maleimido proxyl (5-MSL), was evaluated for monitoring conformational changes of bovine serum albumin (BSA) at different temperatures and pH values. Also, the effect of ethanol, reactive oxygen species (hydrogen peroxide and superoxide radical), and the binding of ligands specific for albumin, namely fatty acids, and several drugs were evaluated. The results indicate that the labeling of albumin at its free cysteine residue (Cys-34) using 5-MSL may successfully be used for the detection of conformational changes, even in the case of the subtle alterations induced by ligand binding. © 2017, European Biophysical Societies' Association.

Stanojević, A., Marković, V.M., Čupić, Ž., Vukojević, V., Kolar-Anić, L.
Modelling of the Hypothalamic-Pituitary-Adrenal Axis Perturbations by Externally Induced Cholesterol Pulses of Finite Duration and with Asymmetrically Distributed Concentration Profile
(2017) Russian Journal of Physical Chemistry A, 91 (13), pp. 2600-2607.

https://doi.org/10.1134/S0036024417130027

ABSTRACT: A model was developed that can be used to study the effect of gradual cholesterol intake by food on the HPA axis dynamics. Namely, well defined oscillatory dynamics of vital neuroendocrine hypothalamic-pituitary-adrenal (HPA) axis has proven to be necessary for maintaining regular basal physiology and formulating appropriate stress response to various types of perturbations. Cholesterol, as a precursor of all steroid HPA axis hormones, can alter the dynamics of HPA axis. To analyse its particular influence on the HPA axis dynamics we used stoichiometric model of HPA axis activity, and simulate cholesterol perturbations in the form of finite duration pulses, with asymmetrically distributed concentration profile. Our numerical simulations showed that there is a complex, nonlinear dependence between the HPA axis responsiveness and different forms of applied cholesterol concentration pulses, indicating the significance of kinetic modelling, and dynamical systems theory for the understanding of large-scale self-regulatory, and homeostatic processes within this neuroendocrine system. © 2017, Pleiades Publishing, Ltd.

Rac, V., Rakić, V., Damjanović-Vasilić, L., Dondur, V., Auroux, A.
Complementary approach to the adsorption of CO and N2O on bimetallic ion exchanged ZMS-5 zeolite: Microcalorimetric and FTIR spectroscopy study
(2017) Applied Surface Science, 423, pp. 1134-1140.

https://doi.org/10.1016/j.apsusc.2017.06.269

ABSTRACT: Room temperature adsorption of CO and N2O using isothermal calorimetry and in situ FTIR spectroscopy on bimetallic and monometallic forms of Cu, Fe and Mn exchanged zeolite ZSM-5 was studied. The two complementary techniques allowed the assessment of the strengths of interactions as well as the identification of the cations active in adsorption. In bimetallic samples containing Cu, a synergistic effect was observed for CO adsorption, i.e higher strengths of adsorption were detected than for corresponding monometallic samples. Such an effect was not detected for N2O. Furthermore, FTIR measurements revealed that N2O adsorption was somewhat restricted for the cation which was introduced the first in bimetallic samples. These findings imply the importance of the order of cation introduction and the procedure of ion exchange process for the adsorptive properties of bimetallic ZSM-5 and, consequently, catalytic reactions where adsorption of N2O is an important reaction step. © 2017 Elsevier B.V.

Avdović, E.H., Milenković, D., Dimitrić-Marković, J.M., Vuković, N., Trifunović, S.R., Marković, Z.
Structural, spectral and NBO analysis of 3-(1-(3-hydroxypropylamino)ethylidene)chroman-2,4-dione
(2017) Journal of Molecular Structure, 1147, pp. 69-75.

https://doi.org/10.1016/j.molstruc.2017.06.094

ABSTRACT: The structure of the newly synthesized coumarin derivative, 3-(1-(3-hydroxypropylamino)-ethylidene)-chroman-2,4-dione, was investigated experimentally and theoretically. FTIR, 1H and 13C NMR spectroscopic methods along with the density functional theory calculations, with B3LYP functional (and with empirical dispersion corrections D3BJ) in combination with the 6−311+G(d,p) basis set, are performed in order to characterize the molecular structure and spectroscopic behavior of the investigated coumarin derivative. Molecular docking analysis was carried out in order to identify the potency of inhibition of the title molecule against human C-reactive protein. The inhibition activity was obtained for ten conformations of ligand inside protein. © 2017 Elsevier B.V.

Omerašević, M., Ružić, J., Vasiljević, B.N., Baščarević, Z., Bučevac, D., Orlić, J., Matović, L.
Transformation of Cs-exchanged clinoptilolite to CsAlSi5O12 by hot-pressing
(2017) Ceramics International, 43 (16), pp. 13500-13504.

https://doi.org/10.1016/j.ceramint.2017.07.055

ABSTRACT: Dense CsAlSi5O12 was successfully obtained by hot pressing of Cs-exchanged clinoptilolite at 900 °C. Simultaneous application of high temperature and mechanical pressure allowed formation of CsAlSi5O12 at temperature considerably lower than 1150 °C which was the lowest reported temperature of CsAlSi5O12 formation in pressureless sintered Cs-exchanged clinoptilolite. CsAlSi5O12 formation was preceded by complete amorphisation of Cs-exchanged clinoptilolite in temperature range between 700 and 900 °C. Bearing in mind that clinoptilolite possesses high affinity for Cs cation it is believed that hot pressing of Cs-exchanged clinoptilolite might be an efficient way to immobilize radioactive Cs by its incorporation into crystal lattice of stable

CsAlSi5O12. The samples sintered at 950 °C had relative density about 84% of theoretical density and open porosity of only 6% which is expected to result in low Cs leaching rate. © 2017 Elsevier Ltd and Techna Group S.r.l.

Bajuk-Bogdanović, D., Jović, A., Nedić Vasiljević, B., Milojević-Rakić, M., Kragović, M., Krajišnik, D., Holclajtner-Antunović, I., Dondur, V.
12-Tungstophosphoric acid/BEA zeolite composites – Characterization and application for pesticide removal
(2017) Materials Science and Engineering B: Solid-State Materials for Advanced Technology, 225, pp. 60-67.

https://doi.org/10.1016/j.mseb.2017.08.011

ABSTRACT: Tungstophosphoric acid and BEA zeolite composites were synthesized by wetness impregnation, followed by ultrasonication and calcination. Composites were characterized using Raman spectroscopy, thermal analysis and pH-dependent zeta potential. Spectroscopic measurements indicated the interaction of acid and the support by binding of polyanion terminal oxygens and BEA extra framework H+ via hydrogen bonds. Evaluation of prepared composites revealed their higher efficiency in nicosulfuron adsorption, in comparison to parent zeolite. All prepared composites showed excellent adsorption properties for pesticide removal in the range 12.1–25.8 mg of nicosulfuron per gram of investigated sample. Better adsorption capacity was found for sonicated samples in comparison to as-synthesized and calcined ones. It was found that the amount of polyanion in the composites and the extent of the particles surface charge are not crucial for the adsorption application, it is rather the uniformity of the zeolite surface coverage with the polyanion that is was more important. © 2017 Elsevier B.V.

Begović, N.N., Vasić, M.M., Blagojević, V.A., Filipović, N.R., Marinković, A.D., Malešević, A., Minić, D.M.
Synthesis and thermal stability of cis-dichloro[(E)-ethyl-2-(2-((8-hydroxyquinolin-2-il)methylene)hidrazinyl)acetate-κ2 N]-palladium(II) complex
(2017) Journal of Thermal Analysis and Calorimetry, 130 (2), pp. 701-711.

https://doi.org/10.1007/s10973-017-6458-2

ABSTRACT: The structure of new cis-dichloro[(E)-ethyl-2-(2-((8-hydroxyquinolin-2-il)methylene)hidrazinyl)acetate-κ2N]-palladium(II) complex was determined using a combination of XRD and IR measurements and DFT calculations. Inherent flexibility of its structure is evident from the complexity of its IR spectrum, which could only be theoretically reproduced as a combination of several closely related structures, involving rotation around C–O bond and changes in hydrogen interactions of its –OH group. Its thermal stability and decomposition were studied non-isothermally, and the thermal decomposition mechanism was proposed using correlation with DFT calculations at the molecular level. It was determined that the initial degradation step consists of the release of Cl free radical, which then reacts with both the initial compound and the degradation products. Besides the endothermic steps, there are exothermic ones, contributing to the complex shape of the DSC curve, consisted of overlapping endothermic and exothermic peaks.

Deconvolution of DTG curve allowed identification of primary fragments of the initial degradation process and, in conjunction with DFT calculations, construction of the most likely reaction mechanism. © 2017, Akadémiai Kiadó, Budapest, Hungary.

Bošnjaković-Pavlović, N., Bajuk-Bogdanović, D., Zakrzewska, J., Yan, Z., Holclajtner-Antunović, I., Gillet, J.-M., Spasojević-de Biré, A.
Reactivity of 12-tungstophosphoric acid and its inhibitor potency toward Na+/K+-ATPase: A combined 31P NMR study, ab initio calculations and crystallographic analysis
(2017) Journal of Inorganic Biochemistry, 176, pp. 90-99.

https://doi.org/10.1016/j.jinorgbio.2017.08.014

ABSTRACT: Influence of 12-tungstophosphoric acid (WPA) on conversion of adenosine triphosphate (ATP) to adenosine diphosphate (ADP) in the presence of Na+/K+-ATPase was monitored by 31P NMR spectroscopy. It was shown that WPA exhibits inhibitory effect on Na+/K+-ATPase activity. In order to study WPA reactivity and intermolecular interactions between WPA oxygen atoms and different proton donor types (D = O, N, C), we have considered data for WPA based compounds from the Cambridge Structural Database (CSD), the Crystallographic Open Database (COD) and the Inorganic Crystal Structure Database (ICSD). Binding properties of Keggin's anion in biological systems are illustrated using Protein Data Bank (PDB). This work constitutes the first determination of theoretical Bader charges on polyoxotungstate compound via the Atom In Molecule theory. An analysis of electrostatic potential maps at the molecular surface and charge of WPA, resulting from DFT calculations, suggests that the preferred protonation site corresponds to WPA bridging oxygen. These results enlightened WPA chemical reactivity and its potential biological applications such as the inhibition of the ATPase activity. © 2017 Elsevier Inc.

Čupić, Ž., Stanojević, A., Marković, V.M., Kolar-Anić, L., Terenius, L., Vukojević, V.
The HPA axis and ethanol: a synthesis of mathematical modelling and experimental observations
(2017) Addiction Biology, 22 (6), pp. 1486-1500.

https://doi.org/10.1111/adb.12409

ABSTRACT: Stress and alcohol use are interrelated—stress contributes to the initiation and upholding of alcohol use and alcohol use alters the way we perceive and respond to stress. Intricate mechanisms through which ethanol alters the organism's response to stress remain elusive. We have developed a stoichiometric network model to succinctly describe neurochemical transformations underlying the stress response axis and use numerical simulations to model ethanol effects on complex daily changes of blood levels of cholesterol, 6 peptide and 8 steroid hormones. Modelling suggests that ethanol alters the dynamical regulation of hypothalamic–pituitary–adrenal (HPA) axis activity by affecting the amplitude of ultradian oscillations of HPA axis hormones, which defines the threshold with respect to which the response to stress is being set. These effects are complex—low/moderate acute ethanol challenge (<8 mM) may reduce, leave unaltered or increase the amplitude of ultradian cortisol (CORT) oscillations, giving rise to an intricate response at the organism level, offering also a potential explanation as to why apparently discordant results were observed in experimental studies. In contrast, high-dose acute ethanol challenge (>8 mM) increases instantaneous CORT levels and the amplitude of ultradian CORT oscillations in a dose-dependent manner, affecting the HPA axis activity also during the following day(s). Chronic exposure to ethanol qualitatively changes the HPA axis dynamics, whereas ethanol at intoxicating levels shuts down this dynamic regulation mechanism. Mathematical modelling gives a quantitative biology-based framework that can be used for predicting how the integral HPA axis response is perturbed by alcohol. © 2016 Society for the Study of Addiction

Jovanović, Z., Holclajtner-Antunović, I., Bajuk-Bogdanović, D., Jovanović, S., Mravik, Ž., Vujković, M.
Effect of thermal treatment on the charge storage properties of graphene oxide/12-tungstophosphoric acid nanocomposite
(2017) Electrochemistry Communications, 83, pp. 36-40.

https://doi.org/10.1016/j.elecom.2017.08.017

ABSTRACT: The influence of thermal treatment in an inert atmosphere on the charge storage properties of graphene oxide (GO)/12-tungstophosphoric acid (WPA) nanocomposite was examined. The transmission electron microscopy analysis revealed high dispersion of WPA on GO matrix, while the surface analysis showed thermal activation of structural changes of WPA and desorption of oxygen functional groups from GO and GO/WPA nanocomposite. Initial GO/WPA nanocomposite had approximately two times higher capacitance compared to initial GO. The thermal treatment of initial GO and GO/WPA to 500 °C induced twofold increase of capacitance of GO and 40% increase of GO/WPA, accompanied with significant increase of operating voltage compared to GO (for 300 mV). Above 500 °C, a decrease of capacitance of both GO and GO/WPA was observed. The results suggest that understanding of structural changes of components and their interaction is crucial for improvement of electrochemical properties of considered composite. © 2017 Elsevier B.V.

Dimitrijević, A., Ignjatović, L., Tot, A., Vraneš, M., Zec, N., Gadžurić, S., Trtić-Petrović, T.
Simultaneous extraction of pesticides of different polarity applying aqueous biphasic systems based on ionic liquids
(2017) Journal of Molecular Liquids, 243, pp. 646-653.

https://doi.org/10.1016/j.molliq.2017.08.077

ABSTRACT: In this paper we report a simultaneous one-step extraction of five pesticides (acetamiprid, imidaclopride, simazine, linuron and tebufenozide) of different polarity using aqueous biphasic system based on 1-butyl-3(methyl or ethyl) substituted imidazolium or pyrrolidinium ionic liquids with bromide or dicyanamide anion and potassium carbonate as a salting-out agent. Experimentally data obtained for the ternary system {ionic liquid + K2CO3 + H2O} were fitted and correlated by Merchuk equation with satisfactory high correlation factor. The effect of the cation alkyl chain length and the variation of anions of the ionic liquid on the aqueous biphasic system formation and the efficiency of pesticide extraction were investigated. Complete extraction of all studied pesticides was obtained applying aqueous biphasic system based on 1-butyl-3-ethyl imidazolium dicyanamide. It was shown that simultaneous extraction of the different polarity pesticides is achieved in a single-step procedure applying properly tailored ionic liquids in the aqueous biphasic system formulation. In order to explain excellent extraction of the polar pesticides in the studied aqueous biphasic systems, molecular dynamics was applied and the binding energies and non-covalent interactions were calculated. It was found that 1-butyl-3-ethyl imidazolium dicyanamide achieves the strongest interactions with the polar pesticides (acetamiprid and imidaclopride) leading to the highest partition coefficients. It was shown that combination of experimental and computational approach can be successfully applied for the selection and design of suitable ionic liquids for efficient extraction of various polarity pesticides using simple aqueous biphasic ionic liquid based systems. © 2017 Elsevier B.V.

Vraneš, M., Cvjetićanin, N., Papović, S., Šarac, B., Prislan, I., Megušar, P., Gadžurić, S., Bešter-Rogač, M.
Electrical, electrochemical and thermal properties of the ionic liquid + lactone binary mixtures as the potential electrolytes for lithium-ion batteries
(2017) Journal of Molecular Liquids, 243, pp. 52-60.

https://doi.org/10.1016/j.molliq.2017.07.129

ABSTRACT: Electrical conductivity of four binary mixtures containing 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquid, [bmim][NTf2], with selected lactones, namely: β-butyrolactone (BBL), γ-valerolactone (GVL), δ-valerolactone (DVL) and ε-caprolactone (ECL) was measured at temperatures from (293.15 to 323.15) K at atmospheric pressure (p = 0.1 MPa) over the whole composition range. The effects of the temperature and ionic liquid (IL) concentration on the electrical conductivity were correlated using Casteel-Amis and Arrhenius equations. It was found that addition of lactone does not reduce electrochemical stability of investigated solution. In order to determine the flammability of the mixtures, the electrolyte self-extinguishing time (SET) was measured and evaluated. DSC was used to determine thermophysical properties of pure compounds and mixtures such as phase transition temperatures and changes in heat capacities. Different heating rates were used to evaluate the kinetic events. Determination of these properties for investigated systems is relevant for their possible applications in the field of electrochemistry. © 2017 Elsevier B.V.

Dobrota, A.S., Pašti, I.A., Mentus, S.V., Johansson, B., Skorodumova, N.V.
Functionalized graphene for sodium battery applications: the DFT insights
(2017) Electrochimica Acta, 250, pp. 185-195.

https://doi.org/10.1016/j.electacta.2017.07.186

ABSTRACT: Considering the increasing interest in the use of graphene-based materials for energy conversion and storage applications, we have performed a DFT study of Na interaction with doped graphene, both in non-oxidized and oxidized forms. Oxidation seems to play the crucial role when it comes to the interaction of doped graphene materials with sodium. The dopants act as attractors of OH groups, making the material prone to oxidation, and therefore altering its affinity towards Na. In some cases, this can result in hydroxide or water formation – an irreversible change lethal for battery performance. Our results suggest that one should carefully control the oxidation level of doped graphene-based materials if they are to be used as sodium battery electrode materials as the optimal oxidation level depends on the dopant type. © 2017 Elsevier Ltd

Ristić, M.M., Aoneas, M.M., Vojnović, M.M., Poparić, G.B.
Excitation of Electronic States of N2 in Radio-Frequency Electric Field by Electron Impact
(2017) Plasma Chemistry and Plasma Processing, 37 (5), pp. 1431-1443.

https://doi.org/10.1007/s11090-017-9826-6

ABSTRACT: Excitation of electronic states of the N2 molecule by electron impact is recognized as an essential process in nitrogen plasmas that strongly impacts their chemical reactivity and other properties. Many surface and coating technologies are based on radio-frequency plasma discharges in nitrogen. In this paper the electron impact excitation rate coefficients for singlet and triplet electronic states of the N2 molecule have been calculated in non-equilibrium conditions in the presence of a radio-frequency electric field. A Monte Carlo simulation has been performed in order to determine non-equilibrium electron energy distribution functions within one period of the electric field. By using these distribution functions, the excitation rate coefficients have been obtained in the frequency range from 13.56 up to 500 MHz, at reduced electric field values from 200 to 700 Td. © 2017, Springer Science+Business Media, LLC.

Bajuk-Bogdanović, D., Popa, A., Uskoković-Marković, S., Holclajtner-Antunović, I.
Vibrational study of interaction between 12-tungstophosphoric acid and microporous/mesoporous supports
(2017) Vibrational Spectroscopy, 92, pp. 151-161.

https://doi.org/10.1016/j.vibspec.2017.06.007

ABSTRACT: Raman and FTIR spectroscopy are powerful techniques used to characterize or observe alterations in the structure or properties of Keggin type heteropoly acids, microporous/mesoporous materials, as well as their composites. These methods were applied in this study for investigation of 12-tungstophosphoric acid (WPA) supported as active phase on zeolites (H-BEA and NaY-zeolite) and mesoporous molecular sieves (TiO_2, MCM-41, SBA-15). It has been shown that important information on interaction of heteropoly acid and the support can be obtained by the applied vibrational spectroscopic methods. Obtained results show how interaction of WPA with different supports depends on the nature and properties of both, active phase and the support. In the case of microporous supports such as BEA or NaY zeolites, the basicity of the support, i.e., ratio of Si/Al, strongly determines interaction between WPA species and surface of the support. In the case of mesoporous silica supports, WPA is well dispersed over the support without strong interaction. However, TiO2 causes strong and complex interaction with WPA. © 2017 Elsevier B.V.

Janković, B., Marinović-Cincović, M., Janković, M.
Distribution of apparent activation energy counterparts during thermo – And thermo-oxidative degradation of Aronia melanocarpa (black chokeberry)
(2017) Food Chemistry, 230, pp. 30-39.

https://doi.org/10.1016/j.foodchem.2017.03.008

ABSTRACT: Kinetics of degradation for Aronia melanocarpa fresh fruits in argon and air atmospheres were investigated. The investigation was based on probability distributions of apparent activation energy of counterparts (εa). Isoconversional analysis results indicated that the degradation process in an inert atmosphere was governed by decomposition reactions of esterified compounds. Also, based on same kinetics approach, it was assumed that in an air atmosphere, the primary compound in degradation pathways could be anthocyanins, which undergo rapid chemical reactions. A new model of reactivity demonstrated that, under inert atmospheres, expectation values for εa occured at levels of statistical probability. These values corresponded to decomposition processes in which polyphenolic compounds might be involved. εa values obeyed laws of binomial distribution. It was established that, for thermo-oxidative degradation, Poisson distribution represented a very successful approximation for εa values where there was additional mechanistic complexity and the binomial distribution was no longer valid. © 2017 Elsevier Ltd

Vasić, M.M., Surla, R., Minić, D.M., Radović, L., Mitrović, N., Maričić, A., Minić, D.M.
Thermally Induced Microstructural Transformations of Fe72Si15B8V4Cu1 Alloy
(2017) Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science, 48 (9), pp. 4393-4402.

https://doi.org/10.1007/s11661-017-4182-y

ABSTRACT: Thermal stability, mechanism, and kinetics of thermally induced microstructural transformations and their effects on magnetic permeability of Fe72Si15B8V4Cu1 alloy with combined amorphous/nanocrystalline structure were studied. DTA curves revealed two separated thermally activated exothermic events in the temperature ranges from 740 K to 820 K (467 °C to 547 °C) and 870 K to 930 K (597 °C to 657 °C). Crystalline phases present in the as-prepared and thermally treated alloy samples were identified, and their microstructural parameters were determined using XRD, while, to gain further insight into the mechanism of microstructural transformations, AFM and SEM-EDS analyses were performed. Deconvolution of the complex DTA peak into individual steps was conducted, and, in correlation with the results of microstructural analysis, kinetic triplets corresponding to individual transformation steps were determined, allowing for the estimation of the lifetimes of the alloy at different temperatures. Magnetic permeability measurements showed that, in spite of the influence of microstructural transformations on magnetic properties of the alloy, the favorable magnetic properties are retained over relatively a wide temperature range. © 2017, The Minerals, Metals & Materials Society and ASM International.

Jovanovic, M., Selmic, M., Macura, D., Lavrnic, S., Gavrilovic, S., Dakovic, M., Radenkovic, S., Soldatovic, I., Stosic-Opincal, T., Maksimovic, R.
Structural and Metabolic Pattern Classification for Detection of Glioblastoma Recurrence and Treatment-Related Effects
(2017) Applied Magnetic Resonance, 48 (9), pp. 921-931.

https://doi.org/10.1007/s00723-017-0913-x

ABSTRACT: Artificial neuronal network (ANN) in classification of glioblastoma multiforme (GBM) recurrence from treatment effects using advanced magnetic resonance imaging techniques was evaluated. In 56 patients with treated GBM, normalised minimal and mean apparent-diffusion coefficient (ADC) values, vessels number on susceptibility-weighted images (SWI) and Cho/Cr ratio were analysed statistically and by ANN. Significant correlation exists between normalised minimal and mean ADC values, and no correlation between ADC and Cho/Cr values. Cut-off values for tumour presence were: 1.14 for normalised minimal ADC (54% sensitivity, 71% specificity), 1.13 for normalised mean ADC (51% sensitivity, 71% specificity), 1.8 for Cho/Cr ratio (92% sensitivity, 82% specificity), grade 2 for SWI (87% sensitivity, 82% specificity). An accurate prediction of ANN to classify patients into GBM progression or treatment effects group was 99% during the training and 96.8% during the testing phase. Multi-parametric ANN allows distinction between GBM recurrence and treatment effects, and can be used in clinical practice. © 2017, Springer-Verlag GmbH Austria.

Bober, P., Trchová, M., Morávková, Z., Kovářová, J., Vulić, I., Gavrilov, N., Pašti, I.A., Stejskal, J.
Phosphorus and nitrogen-containing carbons obtained by the carbonization of conducting polyaniline complex with phosphites
(2017) Electrochimica Acta, 246, pp. 443-450.

https://doi.org/10.1016/j.electacta.2017.06.036

ABSTRACT: Non-conducting polyaniline base interacts with organic phosphites to a conducting product resembling classical polyaniline salts. Polyaniline–phosphite complexes were carbonized in inert atmosphere at 650 °C to phosphorus- and nitrogen-containing carbons. The resulting materials were tested with respect to their electrochemical performance by considering their capacitive properties and electrocatalytic activity towards oxygen reduction reaction (ORR). Carbonized polyaniline–diphenyl phosphite displayed the highest capacitance among all investigated carbons, reaching the values above 100 F g−1 at 5 mV s−1 in concentrated potassium hydroxide solution, while the same material also displayed the highest ORR activity in alkaline media. Considering small specific surface area of obtained carbon materials, the synthetic procedures lead to the surface structures which are exceptionally active for charge storage and in electrocatalysis of ORR. It is proposed that further improvement of electrochemical properties can be obtained by preserving the type of the present surface functional groups with simultaneous increase of their number by the increase of the specific surface. © 2017 Elsevier Ltd

Ristić, M.M., Petković, M., Etinski, M.
Quantum chemical study on phenethylamines reveals new cation structures
(2017) Computational and Theoretical Chemistry, 1114, pp. 47-54.

https://doi.org/10.1016/j.comptc.2017.05.029

ABSTRACT: Phenethylamines are compounds known by their psychoactive and stimulant effects. Their physiological activity is strongly conformer dependent. In this work, the quantum chemical investigation of neutral and cationic phenylethylamine, amphetamine and methamphetamine was performed in order to determine the most stable physiologically relevant conformers. Calculations were performed employing density functional theory and ωB97XD functional. A previously unknown double-ring cation structure formed by cyclization of aliphatic tail was found for all three molecular species. Calculations performed on several levels of theory reveal significant stability of these double-ring cations relative to other conformers. The transition state structures and energies for the cyclization reactions have been determined. Their stability and structural properties are discussed, as well as the possibility for their experimental observation. The significance of dispersion and NH⋯π interactions between side chain and phenyl ring on stability of phenethylamines and their charged forms were pointed out. © 2017

Marković, Z.M., Matijašević, D.M., Pavlović, V.B., Jovanović, S.P., Holclajtner-Antunović, I.D., Špitalský, Z., Mičušik, M., Dramićanin, M.D., Milivojević, D.D., Nikšić, M.P., Todorović Marković, B.M.
Antibacterial potential of electrochemically exfoliated graphene sheets
(2017) Journal of Colloid and Interface Science, 500, pp. 30-43.

https://doi.org/10.1016/j.jcis.2017.03.110

ABSTRACT: Electrochemically exfoliated graphene is functionalized graphene with potential application in biomedicine. Two most relevant biological features of this material are its electrical conductivity and excellent water dispersibility. In this study we have tried to establish the correlation between graphene structure and its antibacterial properties. The exfoliation process was performed in a two electrode-highly oriented pyrolytic graphite electrochemical cell. Solution of ammonium persulfate was used as an electrolyte. Exfoliated graphene sheets were dispersed in aqueous media and characterized by atomic force microscopy, scanning electron microscopy, Raman spectroscopy, Fourier transform infrared spectroscopy, X photoelectron spectroscopy, X-ray diffraction, electron paramagnetic resonance, zeta potential, contact angle measurements and surface energy. Antibacterial assays have shown lack of the significant antibacterial activity. Major effect on bacteria was slight change of bacteria morphology. Membrane remained intact despite significant change of chemical content of membrane components. © 2017 Elsevier Inc.

Vujković, M., Matović, L., Krstić, J., Stojmenović, M., Đukić, A., Babić, B., Mentus, S.

Mechanically activated carbonized rayon fibers as an electrochemical supercapacitor in aqueous solutions
(2017) Electrochimica Acta, 245, pp. 796-806.

https://doi.org/10.1016/j.electacta.2017.06.018

ABSTRACT: The activated carbon cloth (ACC), obtained by chemical/physical activation of carbonized rayon fibers, was grinded in a ball mill and studied from the aspect of double layer capacitance. The changes in pore structure, morphology and acid/basic properties caused by ball milling were studied by means of N2 adsorption/desorption, Fourier-transformed infrared spectrometry, Boehm's titration and Scanning Electron Microscopy. Both potentiodynamic and galvanostatic cycling were used to evaluate the double layer capacitance in three alkaline, acidic and neutral aqueous solutions (KOH, H2SO4 and Na2SO4). While double layer capacitance of original ACC was found to be negligible, ball milled material (ACCm) displayed capacitance in the range of supercapacitors. In order to explain this huge capacitance improvement, we found that ball milling substantially increased the concentration of lactone, phenolic and quinone groups on the surface. We suggest that these groups, through improved hydrophilicity, enable faster ion diffusion into carbon micropores. The energy density stored by double layer was highest in neutral sodium sulphate solution. Namely, operational voltage of ~2 V and double layer capacitance of 220 F g−1 at 1A g−1, enable the energy density of ACCm/Na2SO4/ACCm capacitor of 31.7 Wh kg−1 at 2000 W kg−1, much higher than that of commercial EDLC carbon capacitors. According to the here presented literature survey in a tabular form, the energy density of the studied sample is also higher from that of numerous thus far published aqueous carbon capacitors. © 2017 Elsevier Ltd

Dimkić, I., Stanković, S., Nišavić, M., Petković, M., Ristivojević, P., Fira, D., Berić, T.
Corrigendum: The profile and antimicrobial activity of Bacillus lipopeptide extracts of five potential biocontrol strains [Front. Microbiol,(2017) (925),8] https://doi.org/10.3389/fmicb.2017.00925
(2017) Frontiers in Microbiology, 8 (AUG), art. no. 1500, .

https://doi.org/10.3389/fmicb.2017.01500

ABSTRACT: In the original article, there was an error. Due to the oversight, a technical error was made in some parts of first two sentences, in the section Bacterial Isolates Used in Bioautography Assay. The corrections include the isolates code (IZB for the Xanthomonas strains), and the origin of the collection (Institute for Plant Protection and Environment, Belgrade, Serbia instead Laboratory of Microbiology, Faculty of Biology, University of Belgrade). The corrected paragraph appears below: The antibacterial activity of the Bacillus spp. extracts was measured against phytopathogenic bacteria Pseudomonas syringae pv. aptata (P16) isolated from sugar beets, and Xanthomonas arboricola pv. juglandis (IZB 301, IZB 311, and IZB 320; hereinafter referred to: 301, 311, and 320), originating from walnut trees. The phytopathogenic strains were previously identified and belong to the collection of the Institute for Plant Protection and Environment, Belgrade, Serbia. The authors apologize for this error and state that this does not change the scientific conclusions of the article in any way. © 2017 Dimkić, Stanković, Nišavić, Petković, Ristivojević, Fira and Berić.

Stankovic, B., Jovanovic, J., Ostojic, S., Adnadjevic, B.
Kinetic analysis of non-isothermal dehydration of poly(acrylic acid)-g-gelatin hydrogel using distributed activation energy model
(2017) Journal of Thermal Analysis and Calorimetry, 129 (1), pp. 541-551.

https://doi.org/10.1007/s10973-017-6180-0

ABSTRACT: The applicability of distributed activation energy model (DAEM) for describing non-isothermal dehydration kinetics of poly(acrylic acid)-g-gelatin (PAG) hydrogel has been examined. Thermogravimetric curves were recorded at different heating rates from 5 to 20 K min−1. The activation energy dependence on dehydration degree was determined by Kissinger–Akahira–Sunose and Vyazovkin’s methods. The possibility of applying thermodynamically inhibited nucleation and growth reaction model on investigating process has been examined. Miura–Maki method was used to establish the shape of activation energy distribution function and the dependence of pre-exponential factor on dehydration degree. Non-isothermal dehydration kinetics of PAG hydrogel can be successfully described by the DAEM. Here we defined the procedure by which DAEM can be successfully connected with kinetic models commonly used for reactions in solid state. The dependences of specific rate (i.e., rate constant) and reaction model function on dehydration degree were established for all of the investigated heating rates. It has been concluded that the specific rate changes with dehydration degree and that this is the one of the reasons why non-isothermal dehydration kinetics of PAG hydrogel is complex. © 2017, Akadémiai Kiadó, Budapest, Hungary.

Stamenković, S., Pavićević, A., Mojović, M., Popović-Bijelić, A., Selaković, V., Andjus, P., Bačić, G.
In vivo EPR pharmacokinetic evaluation of the redox status and the blood brain barrier permeability in the SOD1G93A ALS rat model
(2017) Free Radical Biology and Medicine, 108, pp. 258-269.

https://doi.org/10.1016/j.freeradbiomed.2017.03.034

ABSTRACT: Amyotrophic lateral sclerosis (ALS) is a fatal neurodegenerative disorder affecting the motor pathways of the central nervous system. Although a number of pathophysiological mechanisms have been described in the disease, post mortem and animal model studies indicate blood-brain barrier (BBB) disruption and elevated production of reactive oxygen species as major contributors to disease pathology. In this study, the BBB permeability and the brain tissue redox status of the SOD1G93A ALS rat model in the presymptomatic (preALS) and symptomatic (ALS) stages of the disease were investigated by in vivo EPR spectroscopy using three aminoxyl radicals with different cell membrane and BBB permeabilities, Tempol, 3-carbamoyl proxyl (3CP), and 3-carboxy proxyl (3CxP). Additionally, the redox status of the two brain regions previously implicated in disease pathology, brainstem and hippocampus, was investigated by spectrophotometric biochemical assays. The EPR results indicated that among the three spin probes, 3CP is the most suitable for reporting the intracellular redox status changes, as

Tempol was reduced in vivo within minutes (t1/2 =2.0±0.5 min), thus preventing reliable kinetic modeling, whereas 3CxP reduction kinetics gave divergent conclusions, most probably due to its membrane impermeability. It was observed that the reduction kinetics of 3CP in vivo, in the head of preALS and ALS SOD1G93A rats was altered compared to the controls. Pharmacokinetic modeling of 3CP reduction in vivo, revealed elevated tissue distribution and tissue reduction rate constants indicating an altered brain tissue redox status, and possibly BBB disruption in these animals. The preALS and ALS brain tissue homogenates also showed increased nitrilation, superoxide production, lipid peroxidation and manganese superoxide dismutase activity, and a decreased copper-zinc superoxide dismutase activity. The present study highlights in vivo EPR spectroscopy as a reliable tool for the investigation of changes in BBB permeability and for the unprecedented in vivo monitoring of the brain tissue redox status, as early markers of ALS. © 2017 Elsevier Inc.

Zdravković, J.D., Poleti, D.D., Rogan, J.R., Blagojević, V.A., Szécsényi, K.M., Minić, D.M.
The influence of alkaline cations on the mechanism and kinetics of dehydration of polymeric phthalatocuprate(II) dihydrates
(2017) Journal of Analytical and Applied Pyrolysis, 126, pp. 323-331.

https://doi.org/10.1016/j.jaap.2017.05.014

ABSTRACT: Thermal dehydration of two heterometallic complexes containing dianion of phthalic acid, pht, $Na_2[Cu(pht)_2] \cdot 2H_2O$, 1, and $K_2[Cu(pht)_2] \cdot 2H_2O$, 2, was investigated under non-isothermal conditions. Mechanism and kinetics of dehydration were analyzed in detail using TG/DSC/MS measurements, XRPD analysis and FT-IR spectroscopy. The reversibility of dehydration processes was identified. According to XRPD, dehydrated product of 1 maintains original structure, but dehydration of 2 undergoes structural transformation giving a dehydrated product of different crystal structure. In both cases dehydration process involves more than one elementary step, which was confirmed using isoconversional methods Deconvolution of this process using Fraiser-Suzuki function yielded two single step processes for 1 and 2. Subsequent kinetic analysis was performed using Màlek algorithm, resulting in the determination of kinetic triplets (Ea, A and f(α)) for each individual step. In addition, the dehydrated complexes were investigated as possible candidates for H_2 adsorption, using molecular simulations. © 2017 Elsevier B.V.

Dodevski, V., Janković, B., Stojmenović, M., Krstić, S., Popović, J., Pagnacco, M.C., Popović, M., Pašalić, S.
Plane tree seed biomass used for preparation of activated carbons (AC) derived from pyrolysis. Modeling the activation process
(2017) Colloids and Surfaces A: Physicochemical and Engineering Aspects, 522, pp. 83-96.

https://doi.org/10.1016/j.colsurfa.2017.03.003

ABSTRACT: In this work, plane tree seed-based activated carbons (AC) were used for possible application in carbon dioxide capture and storage (CCS) technology. After carbonization process at 850 °C, resulting preliminary AC's were activated at various temperatures. The high levels of the growth in basal planes of graphite structure in carbonized sample were detected. Also, it was found that the samples activated at 750 and 850 °C have a lower graphitization degree and contained substantially disordered sections and defects, which are characteristic of typical amorphous porous carbons. Process modeling has shown that the CO2 sorption can be described by multi-parametric continuous distributed reactivity model. Analysis showed the occurrence of gas reduction process, involving gibberellic acid and coenzymes which can produce the methane gas. The highly ordered arrangement of the gas molecules on the carbons was assumed. © 2017 Elsevier B.V.

Pašti, I.A., Gavrilov, N.M., Mentus, S.V.
Electrocatalytic behavior of Pt/WO3 composite layers formed potentiodynamically on tungsten surfaces
(2017) International Journal of Electrochemical Science, 12 (6), pp. 5772-5791.

https://doi.org/10.20964/2017.06.80

ABSTRACT: The Pt/WO3 composites, in a form of thin layer on W support, were prepared by potentiodynamic polarization of either bare or oxide covered tungsten disc in hexachloroplatinic acid solutions. Both the Pt loading and the thickness of WO3 interlayer between Pt nanoparticles and W metal surface were varied. The chemical and electrochemical stability tests in 0.1 mol dm-3 HClO4 solution were performed by cyclic voltammetry. These test revealed that the shape of cyclovoltammetric curves displayed relatively slight dependence on the number of cycles. The shape changes were attributed to a slight redistribution of WO3 over the composite surface. Tracking for the synergistic effects in the Pt/WO3 system, the influence of both WO3 thickness and Pt loading on the kinetics of both hydrogen evolution/oxidation (HER/HOR) and oxygen reduction reactions (ORR) in acidic solution were investigated. The kinetics of HER was found to be a) independent on the WO3 thickness, and b) inversely proportional to the Pt loading. For ORR we found that the onset potential, approaching thermodynamic limit of 1.23 V vs. RHE, was almost independent on oxide thickness, while the reaction kinetics was commensurable to the Pt loading. © 2017 The Authors.

Waisi, H., Janković, B., Janković, M., Nikolić, B., Dimkić, I., Lalević, B., Raičević, V.
New insights in dehydration stress behavior of two maize hybrids using advanced distributed reactivity model (DRM). Responses to the impact of 24-epibrassinolide
(2017) PLoS ONE, 12 (6), art. no. e0179650, .

https://doi.org/10.1371/journal.pone.0179650

ABSTRACT: Proposed distributed reactivity model of dehydration for seedling parts of two various maize hybrids (ZP434, ZP704) was established. Dehydration stresses were induced thermally, which is also accompanied by response of hybrids to heat stress. It was found that an increased value of activation energy counterparts within radicle dehydration of ZP434, with a high concentration of 24-epibrassinolide (24-EBL) at elevated operating temperatures, probably causes activation of diffusion mechanisms in cutin network and may increases likelihood of formation of free volumes, large enough to accommodate diffusing molecule. Many small random effects were detected and can be correlated with micro-disturbing in a space filled with water caused by thermal gradients, increasing capillary phenomena, and which can induce thermo-capillary migration. The influence of seedling content of various sugars and minerals on dehydration was also examined. Estimated distributed reactivity models indicate a dependence of reactivity on structural arrangements, due to present interactions between water molecules and chemical species within the plant. © 2017 Waisi et al. This is an open access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

Pagnacco, M.C., Mojović, M.D., Popović-Bijelić, A.D., Horváth, A.K.
Investigation of the Halogenate-Hydrogen Peroxide Reactions Using the Electron Paramagnetic Resonance Spin Trapping Technique
(2017) Journal of Physical Chemistry A, 121 (17), pp. 3207-3212.

https://doi.org/10.1021/acs.jpca.7b02035

ABSTRACT: The differences in the mechanism of the halogenate reactions with the same oxidizing/reducing agent, such as H2O2 contribute to the better understanding of versatile halogen chemistry. The reaction between iodate, bromate, and chlorate with hydrogen peroxide in acidic medium at 60 °C is investigated by using the electron paramagnetic resonance (EPR) spin trapping technique. Essential differences in the chemistry of iodate, bromate, and chlorate in their reactions with hydrogen peroxide have been evidenced by finding different radicals as governing intermediates. The reaction between KIO3 and H2O2 is supposed to be the source of IO2 • radicals. The KBrO3 and H2O2 reaction did not produce any EPR signal, whereas the KClO3-H2O2 system was found to be a source of HO• radical. Moreover, KClO3 dissolved in sulfuric acid without hydrogen peroxide produced HO• radical as well. The minimal-core models explaining the origin of obtained EPR signals are proposed. Current findings suggested the inclusion of IO2 • and HOO• radicals, and ClO2 • and HO• radicals in the particular kinetic models of iodate-hydrogen peroxide and chlorate-hydrogen peroxide systems, as well as possible exclusion of BrO2 • radical from the kinetic scheme of the bromate-hydrogen peroxide system. Obtained results may pave the way for understanding more complex, nonlinear reactions of these halogen-containing species. © 2017 American Chemical Society.

Marković, B.M., Stefanović, I.S., Hercigonja, R.V., Pergal, M.V., Marković, J.P., Onjia, A.E., Nastasović, A.B.
Novel hexamethylene diamine-functionalized macroporous copolymer for chromium removal from aqueous solutions
(2017) Polymer International, 66 (5), pp. 679-689.

https://doi.org/10.1002/pi.5306

ABSTRACT: Macroporous copolymers of poly[(glycidyl methacrylate)-co-(ethylene glycol dimethacrylate)] (PGME) with various crosslinker (ethylene glycol dimethacrylate) concentrations and porosity parameters and additionally functionalized with hexamethylene diamine (PGME-HD) were tested as potential Cr(VI) oxyanion sorbents from aqueous solutions. Kinetics of Cr(VI) sorption was investigated in the temperature range 298-343 K and the results were fitted to chemical reaction and particle diffusion models. The Cr(VI) sorption obeys the pseudo-second-order model with definite influence of pore diffusion. A temperature rise promotes chromium removal, with a maximum experimental uptake capacity of 4.21 mmol g−1 at 343 K for the sample with the highest amino group concentration. Equilibrium data were analysed with Langmuir, Freundlich and Temkin adsorption isotherm models. Thermodynamic parameters, i.e. Gibbs free energy (ΔG0), enthalpy (ΔH0) and entropy change (ΔS0) and activation energy of sorption (Ea), were calculated. The Cr(VI) adsorption onto PGME-HD was found to be spontaneous and endothermic, with increased randomness in the system. Desorption experiments show that chromium anion sorption was reversible and the PGME-HD sample GMA 60 HD was easily regenerated with 0.1 mol L−1 NaOH up to 90% recovery in the fourth sorption/desorption cycle. In the fifth cycle, a substantial sorption loss of 37% was observed. © 2016 Society of Chemical Industry. © 2016 Society of Chemical Industry

Aleksić, O.S., Vasiljević, Z.Ž., Vujković, M., Nikolić, M., Labus, N., Luković, M.D., Nikolić, M.V.
Structural and electronic properties of screen-printed Fe2O3/TiO2 thick films and their photoelectrochemical behavior
(2017) Journal of Materials Science, 52 (10), pp. 5938-5953.

https://doi.org/10.1007/s10853-017-0830-2

ABSTRACT: Nanostructured Fe2TiO5 thick films were deposited on fluorine-doped tin oxide glass substrate using screen printing technology. Starting hematite and anatase nanopowders were mixed in molar ratios 1:1 and 1:1.5 and calcined in air at 900°C for 2 h to form pseudobrookite, Fe2TiO5. Functional powders and sintered thick films were analyzed by X-ray diffraction, scanning electron microscopy, energy-dispersive spectroscopy and transmission electron microscopy. UV–Vis analysis enabled determination of the band gap. Separation and transfer efficiency of photogenerated charge carriers was confirmed by the photoluminescence and electrochemical impedance spectra. Even though a slightly high onset oxygen evolution potential of photoexcited film electrode samples in NaOH was obtained, photocurrent densities were high, especially in the presence of H2O2 (~12 mA cm−2 at 1.7 V RHE). This work shows promise for practical application due to favorable band positions of pseudobrookite and low-cost screen printing technology. © 2017, Springer Science+Business Media New York.

Abulseoud, O.A., Ho, M.C., Choi, D.-S., Stanojević, A., Cupić, Z., Kolar-Anić, L., Vukojević, V.
Corticosterone oscillations during mania induction in the lateral hypothalamic kindled rat-Experimental observations and mathematical modeling
(2017) PLoS ONE, 12 (5), art. no. e0177551, .

https://doi.org/10.1371/journal.pone.0177551

ABSTRACT: Changes in the hypothalamic-pituitary-adrenal (HPA) axis activity constitute a key component of bipolar mania, but the extent and nature of these alterations are not fully understood. We use here the lateral hypothalamic-kindled (LHK) rat model to deliberately induce an acute manic-like episode and measure serum corticosterone concentrations to assess changes in HPA axis activity. A mathematical model is developed to succinctly describe the entwined biochemical transformations that underlay the HPA axis and emulate by numerical simulations the considerable increase in serum corticosterone concentration induced by LHK. Synergistic combination of the LHK rat model and dynamical systems theory allows us to quantitatively characterize changes in HPA axis activity under controlled induction of acute manic-like states and provides a framework to study in silico how the dynamic integration of neurochemical transformations underlying the HPA axis is disrupted in these states.

Dimić, D., Milenković, D., Marković, Z., Marković, J.D.
Structural and spectral analysis of 3-metoxytyramine, an important metabolite of dopamine
(2017) Journal of Molecular Structure, 1134, pp. 226-236.

https://doi.org/10.1016/j.molstruc.2016.12.082
ABSTRACT: Density functional theory calculations, with B3LYP functional and 6-311++G(d,p) basis set are performed with the aim to support the molecular structure and the spectroscopic characteristics of 3-methoxytyramine, the major extracellular metabolite of dopamine. Natural Bond Orbital (NBO) and Quantum Theory of Atoms in Molecules (QTAIM) analysis were used to explain the specific interactions in the most stable conformations in vacuum and water. The conformer resembling the crystallographic structure was compared to the experimentally available data and NMR spectra. The detailed vibrational spectral analysis and the assignments of the bands, done on the best-fit basis comparison of the experimentally obtained and theoretically calculated IR and Raman spectra, match quite well indicating DFT calculations as very accurate source of normal mode assignments. The obtained results demonstrate the applicability and performance of DFT calculations in conformational analysis of 3-methoxytyramine at the state of the isolated molecule. The molecular docking showed that the most stable conformation in vacuum was not the most stable one when docked in protein, proving that only the weak interactions stabilize the gaseous phase conformations. © 2016

Luginbühl, S., Milojević-Rakić, M., Junker, K., Bajuk-Bogdanović, D., Pašti, I., Kissner, R., Ćirić-Marjanović, G., Walde, P.
The influence of anionic vesicles on the oligomerization of p-aminodiphenylamine catalyzed by horseradish peroxidase and hydrogen peroxide
(2017) Synthetic Metals, 226, pp. 89-103.

https://doi.org/10.1016/j.synthmet.2017.01.011

ABSTRACT: The aniline dimer N-phenyl-1,4-phenylenediamine (=p-aminodiphenylamine, PADPA) was oxidized with horseradish peroxidase isoenzyme C (HRPC) and hydrogen peroxide (H_2O_2) to oligo(PADPA) in an aqueous suspension of 80–100 nm-sized anionic vesicles at pH = 4.3 and at T ≈ 25 °C. The vesicles were formed from AOT (=sodium bis(2-ethylhexyl) sulfosuccinate) and served as templates for obtaining oligo(PADPA) as emeraldine salt form of polyaniline (PANI-ES) in the polaron form. The optimal reaction conditions for obtaining a stable oligo(PADPA)-AOT vesicle suspension with a high conversion and low amounts of HRPC were elaborated by using UV/vis/NIR spectroscopy. The formation of PANI-ES type products was confirmed by in situ UV/vis/NIR, Raman and EPR spectroscopy measurements. However, HPLC–MS analyses indicated that the oligo(PADPA) products obtained are not only of PANI-

ES type, but that a number of other products formed as well. Some of these were identified and shown to contain oxygen atoms (as a result of hydrolysis), others most likely containing phenazine (or phenoxazine) moieties. The latter is also supported by Raman and UV/vis/NIR spectroscopy measurements. The as-obtained oligo(PADPA)-AOT vesicle suspension was also analyzed by cyclic voltammetry, which showed redox activity of oligo(PADPA) up to pH = 6.0, a property which is beneficial for various applications. Overall, the work demonstrates the successful use of different complementary and sensitive in situ spectroscopic methods for following the progress of a complex enzyme-triggered reaction. In addition, the good solubility of the deprotonated and reduced reaction products in organic solvents allowed us to use a HPLC-MS analysis for a direct comparison of the product distribution with the previously studied oxidation and oligomerization of PADPA with Trametes versicolor laccase at pH = 3.5. One of the template effects of AOT vesicles takes into account possible interactions between AOT and oligo(PADPA). © 2017 Elsevier B.V.

Jović-Jovičić, N., Mojović, Z., Mojović, M., Banković, P., Ajduković, M., Milutinović-Nikolić, A., Jovanović, D.
Electrochemical behavior of immobilized hemoglobin in alkaline solution
(2017) Applied Surface Science, 400, pp. 347-354.

https://doi.org/10.1016/j.apsusc.2016.12.151

ABSTRACT: Glassy carbon electrode was modified with different synthesized hybrid clay-based materials and tested in alkaline solution with and without H2O2. The hybrid materials were obtained by immobilizing hemoglobin (Hb) on acid activated (AA) clay, or on AA clay modified with different sodium dodecyl sulfate (SDS) loadings. The obtained materials were characterized using DR UV-vis and ESR spectroscopy, elemental analysis, and SEM. The characterization confirmed higher degree of hemoglobin incorporation in the presence of SDS. The presence of SDS on the surface of clay particles resulted in the partial oxidation/denaturation of hemoglobin and formation of hemichrome. Cyclic voltammetry was used for the investigation of the electrochemical behavior of immobilized hemoglobin in alkaline solution. Two cathodic peaks at −0.45 V and −0.70 V were recorded and ascribed to the reduction of heme Fe(III)/Fe(II), and formation of HbFe(I) – highly reduced form of hemoglobin – respectively. The latter peak reflects hemoglobin denaturation. The presence of H2O2 in the alkaline solution increased current intensities corresponding to both peaks (−0.45 V and −0.7 V). Linear response of peak current intensity vs. H2O2 concentration was monitored for all investigated samples within different H2O2 concentration ranges. The AA-SDS1.0-Hb electrode exhibited the highest current response with linear regression equation in the following form: I(μA) = 7.99 + 1.056 × [H2O2] (mM) (R = 0.996). The limit of detection of 28 μM was estimated using the 3 sigma method. Different modified electrodes exhibited different degrees of denaturation resistance. The obtained values of Michaelis-Menten constant indicated that prolonged cycling in the presence of SDS increases protein denaturation. © 2016 Elsevier B.V.

Prekodravac, J.R., Marković, Z.M., Jovanović, S.P., Holclajtner-Antunović, I.D., Kepić, D.P., Budimir, M.D., Todorović-Marković, B.M.
Graphene quantum dots and fullerenol as new carbon sources for single-layer and bi-layer graphene synthesis by rapid thermal annealing method

(2017) Materials Research Bulletin, 88, pp. 114-120.

https://doi.org/10.1016/j.materresbull.2016.12.018

ABSTRACT: Graphene as a new material is in the spotlight due to its extraordinary properties and wide range of potential applications. Chemical vapour deposition, as a method for graphene synthesis from gaseous hydrocarbon sources has great promises for large-scale graphene synthesis. However, for such grow high temperatures of 800–1000 °C are typically required. Here we demonstrate synthesis of single-layer and bi-layer graphene thin films of approximately 10 μm in size by rapid thermal annealing process at low annealing temperature such as 600 °C. Synthesis was performed on copper foil from graphene quantum dots and fullerenol as solid carbon sources at different concentrations. Raman spectroscopy study has shown that the number of grown graphene layers depends on the carbon source concentration. The quality of formed graphene layers withal depends on the carbon source and its concentration, whereby graphene from graphene quantum dots had better quality. © 2016 Elsevier Ltd

Dimitrić Marković, J.M., Pejin, B., Milenković, D., Amić, D., Begović, N., Mojović, M., Marković, Z.S.
Antiradical activity of delphinidin, pelargonidin and malvin towards hydroxyl and nitric oxide radicals: The energy requirements calculations as a prediction of the possible antiradical mechanisms
(2017) Food Chemistry, 218, pp. 440-446.

https://doi.org/10.1016/j.foodchem.2016.09.106

ABSTRACT: Naturally occurring flavonoids, delphinidin, pelargonidin and malvin, were investigated experimentally and theoretically for their ability to scavenge hydroxyl and nitric oxide radicals. Electron spin resonance (ESR) spectroscopy was used to determine antiradical activity of the selected compounds and M05-2X/6-311+G(d,p) level of theory for the calculation of reaction enthalpies related to three possible mechanisms of free radical scavenging activity, namely HAT, SET-PT and SPLET. The results obtained show that the molecules investigated reacted with hydroxyl radical via both HAT and SPLET in the solvents investigated. These results point to HAT as implausible for the reaction with nitric oxide radical in all the solvents investigated. SET-PT also proved to be thermodynamically unfavourable for all three molecules in the solvents considered. © 2016

Amić, A., Lučić, B., Stepanić, V., Marković, Z., Marković, S., Dimitrić Marković, J.M., Amić, D.
Free radical scavenging potency of quercetin catecholic colonic metabolites: Thermodynamics of 2H+/2e- processes
(2017) Food Chemistry, 218, pp. 144-151.

https://doi.org/10.1016/j.foodchem.2016.09.018

ABSTRACT: Reaction energetics of the double (2H+/2e-), i.e., the first 1H+/1e- (catechol → phenoxyl radical) and the second 1H+/1e- (phenoxyl radical → quinone) free radical scavenging mechanisms of quercetin and its six colonic catecholic metabolites (caffeic acid, hydrocaffeic acid, homoprotocatechuic acid, protocatechuic acid, 4-methylcatechol, and catechol) were computationally studied using density functional theory, with the aim to estimate the antiradical potency of these molecules. We found that second hydrogen atom transfer (HAT) and second sequential proton loss electron transfer (SPLET) mechanisms are less energy demanding than the first ones indicating 2H+/2e− processes as inherent to catechol moiety. The Gibbs free energy change for reactions of inactivation of selected free radicals indicate that catecholic colonic metabolites constitute an efficient group of more potent scavengers than quercetin itself, able to deactivate various free radicals, under different biological conditions. They could be responsible for the health benefits associated with regular intake of flavonoid-rich diet. © 2016 Elsevier Ltd

Nikolić, V.N., Tadić, M., Panjan, M., Kopanja, L., Cvjetićanin, N., Spasojević, V.
Influence of annealing treatment on magnetic properties of Fe2O3/SiO2 and formation of ε-Fe2O3 phase
(2017) Ceramics International, 43 (3), pp. 3147-3155.

https://doi.org/10.1016/j.ceramint.2016.11.132

ABSTRACT: Magnetic properties of Fe2O3/SiO2 samples were studied after being produced by sol-gel synthesis and formation of ε-Fe2O3 polymorph. Samples were thermally treated, using different annealing temperatures and annealing times. The size and morphological characteristics of the iron oxide nanoparticles were examined using a TEM microscope. We used the “ellipticity of shapes”, which is a measure of how much the shape of a nanoparticle differs from a perfect ellipse, in order to quantitatively describe morphological properties of nanoparticles. Coercivity measurements were used to identify and monitor the formation of the epsilon-iron oxide phase during the thermal treatments (annealing). Coercivity values were in the range from 1.2 to 15.4 kOe, which is in accordance with previous experience regarding the existence of ε-Fe2O3. We have determined the optimal formation conditions for the ε-Fe2O3 polymorph (t=1050 °C for 7 h, HC=15.4 kOe), as well as the narrow temperature interval (1050–1060 °C) in which the polymorph abruptly vanished (HC=2300 Oe), on the basis of results of the magnetic properties. The threshold temperature for the ε-Fe2O3 phase transformation was measured as 1060 °C. We found that different annealing temperatures and annealing times significantly affected magnetic properties of the examined samples. © 2016 Elsevier Ltd and Techna Group S.r.l.

Jugović, D., Mitrić, M., Milović, M., Cvjetićanin, N., Jokić, B., Umićević, A., Uskoković, D.
The influence of fluorine doping on the structural and electrical properties of the LiFePO4 powder
(2017) Ceramics International, 43 (3), pp. 3224-3230.

https://doi.org/10.1016/j.ceramint.2016.11.149

ABSTRACT: Low intrinsic electronic conductivity is the main disadvantage of LiFePO4 when used as a cathode material in lithium ion batteries. The paper offers experimental proofs of the theoretical prediction that fluorine doping of LiFePO4 can enhance its electrical conductivity. The LiFePO4 and fluorine-doped LiFePO4 olivine type, carbon-free powders are synthesized and examined. The crystal structure refinements in the Pnma space group reveal that doping with fluorine ions preserves the olivine structure, while reducing both the lattice parameters and the antisite defect, and increasing the crystallite size. A small amount of incorporated fluorine enhances the electrical conductivity from 4.6×10−7 S cm−1 to 2.3×10−6 S cm−1 and has a positive impact on the electrochemical performance. Several spectroscopy techniques (Mössbauer, FTIR, and Raman) reveal differences between the two powders and additionally support the findings of both the Rietveld refinement and the conductivity measurements. © 2016 Elsevier Ltd and Techna Group S.r.l.

Aoneas, M.M., Vojnović, M.M., Ristić, M.M., Vićić, M.D., Poparić, G.B.
Ionization of CO in radio-frequency electric field
(2017) Physics of Plasmas, 24 (2), art. no. 023502, .
https://www.scopus.com/inward/record.uri?eid=2-s2.0-85011715792&doi=10.1063%2f1.4975312&partnerID=40&md5=fba7bfb79a1ebc12b84e827a02cb8a18

https://doi.org/10.1063/1.4975312

ABSTRACT: The rate coefficients for the electron impact ionization of the CO molecule have been calculated in the presence of the radio-frequency (RF) electric field. The non-equilibrium electron energy distribution functions, used for the rate coefficient calculations, were generated by using a Monte Carlo simulation. The rate coefficients were obtained, time resolved within one period, in the frequency range from 13.56 up to 500 MHz, at effective reduced electric field values up to 700 Td. A temporal behavior of the rate coefficients under the influence of magnitude and frequency of the fields has been studied. The total ionization rate coefficients and the rate coefficients for the production of different ion fragments have been period averaged and presented in the order to be of use for practical implementation in the RF discharges in CO. Also, the temporal characteristics of the electron energy distribution functions and the diffusion coefficients have been studied separately revealing some interesting features in their time dependence within the period of electric field oscillations. © 2017 Author(s).

Ćirić-Marjanović, G., Milojević-Rakić, M., Janošević-Ležaić, A., Luginbühl, S., Walde, P.
Enzymatic oligomerization and polymerization of arylamines: State of the art and perspectives
(2017) Chemical Papers, 71 (2), pp. 199-242.

https://doi.org/10.1007/s11696-016-0094-3

ABSTRACT: The literature concerning the oxidative oligomerization and polymerization of various arylamines, e.g., aniline, substituted anilines, aminonaphthalene and its derivatives, catalyzed by oxidoreductases, such as laccases and peroxidases, in aqueous, organic, and mixed aqueous organic monophasic or biphasic media, is reviewed. An overview of template-free as well as template-assisted enzymatic syntheses of oligomers and polymers of arylamines is given. Special attention is paid to mechanistic aspects of these biocatalytic processes. Because of the nontoxicity of oxidoreductases and their high catalytic efficiency, as well as high selectivity of enzymatic oligomerizations/polymerizations under mild conditions - using mainly water as a solvent and often resulting in minimal byproduct formation - enzymatic oligomerizations and polymerizations of arylamines are environmentally friendly and significantly contribute to a "green" chemistry of conducting and redox-active oligomers and polymers. Current and potential future applications of enzymatic polymerization processes and enzymatically synthesized oligo/polyarylamines are discussed. © Institute of Chemistry, Slovak Academy of Sciences 2016.

Jović, A., Bajuk-Bogdanović, D., Nedić Vasiljević, B., Milojević-Rakić, M., Krajišnik, D., Dondur, V., Popa, A., Usković-Marković, S., Holclajtner-Antunović, I.
Synthesis and characterization of 12-phosphotungstic acid supported on BEA zeolite
(2017) Materials Chemistry and Physics, 186, pp. 430-437.

https://doi.org/10.1016/j.matchemphys.2016.11.015

ABSTRACT: An optimized synthetic route for obtaining heteropoly acid (HPA) species supported on BEA zeolite was applied, and different samples, comprising 20 to 50 wt% of 12-phosphotungstic acid (HPW) were prepared. The as-synthesized supported HPW were subjected to different post-synthesis routes, which involved calcination and ultrasound treatment. Characterization of these materials was performed by means of Scanning Electron Microscopy, zeta potential measurements, Infrared Spectroscopy and X-ray Powder Diffraction analysis. Results suggest strong interaction of HPW with the support and revealed that ultrasound treatment resulted in better dispersion of active phase and thus homogeneous morphology of the samples. The zeta potential was found to be dependent on the preparation procedure and HPW content in these materials, while higher HPW loadings induced its agglomeration. Catalytic activity of the synthesized materials was investigated in an ethanol dehydration reaction, where lower HPW loadings induced higher ethanol conversion. Acid sites distribution and accessibility for ethanol molecules were found to be more essential for catalytic activity than HPW loadings, i.e., amount of active sites present in these hybrid materials. © 2016 Elsevier B.V.

Jovanovic, J., Stankovic, B., Adnadjevic, B.
Kinetics of isothermal dehydration of equilibrium swollen PAAG hydrogel under the microwave heating conditions
(2017) Journal of Thermal Analysis and Calorimetry, 127 (1), pp. 655-662.

https://doi.org/10.1007/s10973-016-5440-8

ABSTRACT: The isothermal dehydration kinetics under microwave heating (MWH) of the equilibrium swollen poly(acrylic acid)-g-gelatin hydrogel (PAAG) was investigated. Dehydration kinetics curves have been measured for this recently synthesized and structurally defined hydrogel using a microwave thermogravimetric analyzer, within the temperature range from 323 to 353 K. It was found that the isothermal dehydration of the PAAG hydrogel was 15–17 times faster under the MWH than under the conventional heating (CH). We have established that the investigated dehydration is an elementary kinetics process. By applying the model-fitting method, it was found that the kinetics of isothermal dehydration under the microwave heating is mathematically best described by the Polanyi–Winger's equation. The model rate constant values of the PAAG hydrogel isothermal microwave dehydration have been calculated. In accordance with the Arrhenius equation, the values of kinetics parameters have been obtained: Ea = 52.0 kJ mol−1 and ln(A/min−1) = 12.1. The higher values of dehydration rate under MWH, than under CH, are a consequence of the increase in the preexponential factor value caused by the change in the activated-state entropy of water molecules. © 2016, Akadémiai Kiadó, Budapest, Hungary.

Stevanović, K.Z., Bubanja, I.N.M., Stanisavljev, D.R.
Domination of thermodynamically demanding oxidative processes in reaction of iodine with hydrogen peroxide
(2017) Chemical Physics Letters, 684, pp. 257-261.

https://doi.org/10.1016/j.cplett.2017.06.061

ABSTRACT: We investigated the degree of isothermal iodine conversion to iodate as one of the most intriguing steps of the Bray-Liebhafsky oscillator. The amount of the produced iodate, in the presence of hydrogen peroxide, was determined by the stopped-flow titration with iodide ions. From five different experiments, high degree of iodine conversion to iodate (95.4 ± 0.6)% is obtained. It confirmed that, after the induction period of spontaneous hydrogen peroxide catalytic decomposition, reaction dynamics is dominated by thermodynamically demanding oxidative processes. Isothermal change of the reaction dynamics introduces some specific energy redistribution as a possible initiator of oxidizing radicals. © 2017 Elsevier B.V.

Marinović, S.R., Ajduković, M.J., Jović-Jovičić, N.P., Mudrinić, T.M., Nedić-Vasiljević, B.M., Banković, P.T., Milutinović-nikolić, A.D.
Adsorption of strontium on different sodium-enriched bentonites
(2017) Journal of the Serbian Chemical Society, 82 (4), pp. 449-463.

https://doi.org/10.2298/JSC161010008M

ABSTRACT: Bentonites from three different deposits (Wyoming, TX, USA and Bogovina, Serbia) with similar cation exchange capacities were sodium enriched and tested as adsorbents for Sr2+ in aqueous solutions. X-Ray diffraction analysis confirmed successful Na-exchange. The textural properties of the bentonite samples were determined using low-temperature the nitrogen physisorption method. Significant differences in the textural properties between the different sodium enriched bentonites were found. Adsorption was investigated with respect to adsorbent dosage, pH, contact time and the initial concentration of Sr2+. The adsorption capacity increased with pH. In the pH range from 4.0-8.5, the amount of adsorbed Sr2+ was almost constant but 2-3 times smaller than at pH ≈11. Further experiments were performed at the unadjusted pH since extreme alkaline conditions are environmentally hostile and inapplicable in real systems. The adsorption capacity of all the investigated adsorbents toward Sr2+ was similar under the investigated conditions, regardless of significant differences in the specific surface areas. It was shown and confirmed by the Dubinin-Radushkevich model that the cation exchange mechanism was the dominant mechanism of Sr2+ adsorption. Their developed microporous structures contributed to the Sr2+ adsorption process. The adsorption kinetics obeyed the pseudo-second-order model. The isotherm data were best fitted with the Langmuir isotherm model.

Adnadjević, B., Gigov, M., Jovanović, J.
Comparative analyses on isothermal kinetics of water evaporation and PAAG hydrogel dehydration under the microwave heating conditions
(2017) Chemical Engineering Research and Design, 122, pp. 113-120.

https://doi.org/10.1016/j.cherd.2017.04.009

ABSTRACT: The isothermal kinetic of water evaporation and poly(acrylic-g-gelatin) hydrogel (PAAG) dehydration in temperature range from 333 K to 363 K was investigated under microwave heating conditions (MWH). The isothermal kinetic curves of water evaporation and hydrogel dehydration could be entirely mathematically described by the Polanyi–Winger equation. The values of the rate constant for water evaporation and hydrogel dehydration and their kinetics parameters were calculated. Both the value of activation energy (Ea) and pre-exponential factor (lnA) for hydrogel dehydration under MWH is higher than those for water evaporation. The existence of a linear correlation relationship — compensation effect was established between the values of kinetics parameters for water evaporation and hydrogel dehydration. The values of thermodynamic parameters of activated complex formation for water evaporation and hydrogel dehydration (standard enthalpy of activation (ΔH*), standard entropy activation (ΔS*), and standard free Gibbs energy of activation (ΔG*)) were calculated. The mechanism of water molecules activation, both for evaporation and dehydration, by the resonant transfer of certain energy amount from the reaction system to the libration vibration of molecules of water is suggested. © 2017 Institution of Chemical Engineers

Milikić, J., Stoševski, I., Krstić, J., Kačarević-Popović, Z., Miljanić, Š., Šljukić, B.
Electroanalytical Sensing of Bromides Using Radiolytically Synthesized Silver Nanoparticle Electrocatalysts
(2017) Journal of Analytical Methods in Chemistry, 2017, art. no. 2028417, .

https://doi.org/10.1155/2017/2028417

ABSTRACT: Monitoring bromides (Br-) is of crucial importance since bromates, potential human carcinogens, are formed during ozonation of water containing bromides in concentrations >100 μg L-1. Within this study, silver (Ag) and four carbon-supported Ag catalysts were synthesized by the γ-radiation method and their morphology and structure examined using transmission electron microscopy, X-ray diffraction, and UV-Vis analysis. The nanocatalysts were tested for Br-sensing in aqueous media using cyclic voltammetry. All five Ag materials exhibited electroactivity for sensing of Br- ions, with pure Ag catalyst giving the best response to Br- ions presence in terms of the lowest limit of detection. Sensing of bromides was also explored in tap water after addition of bromides suggesting that herein prepared catalysts could be used for bromides detection in real samples. Furthermore, sensing of other halogen ions, namely, chlorides and iodides, was examined, and response due to chloride presence was recorded. © 2017 Jadranka Milikić et al.

Milovanović, M., Veličković, S., Veljković, F., Jerosimić, S.
Structure and stability of small lithium-chloride Li:NClm(0,1+) (n ≥ m, n = 1-6, m = 1-3) clusters
(2017) Physical Chemistry Chemical Physics, 19 (45), pp. 30481-30497.

https://doi.org/10.1039/c7cp04181k

ABSTRACT: In the present study, we report the results of a detailed theoretical investigation along with the experimental observations of chlorine-doped small lithium clusters. The cluster ions of the type LinClm+ (n ≥ m, n = 1-6, m = 1-3) were obtained by the evaporation of LiCl from a Knudsen cell as a chemical reactor in the temperature range between 1800 and 2700 K. Heterogeneous clusters with more than one Cl atom are produced and detected for the first time, and the experimental conditions for formation and stability are examined. The structural characteristics and stabilities of neutral and positively charged LinClm species are analyzed by using quantum chemistry methods. Doping lithium clusters with chlorine increases their stability, although there is a typical closed-shell-open-shell alternation in stability. Calculated dissociation energies are the best indicator of cluster stability of experimentally detected clusters. Heterogeneous lithium-chloride clusters can be viewed as species consisting of m negative Cl- ions and a positively charged Lin(1+,2+) "cage"; upon ionization, an electron departs from the lithium cage. An important reason for the higher stability of closed-shell clusters is the delocalization of electrons over the lithium cage, which is more energetically favored than localization of electrons between two lithium atoms. According to their ionization energies, the titled clusters can be classified as "superalkalis". © 2017 the Owner Societies.

Barudžija, T., Cvjetićanin, N., Bajuk-Bogdanović, D., Mojović, M., Mitrić, M.
Vibrational and electron paramagnetic resonance spectroscopic studies of β-MnO2 and α-KxMnO2 nanorods
(2017) Journal of Alloys and Compounds, 728, pp. 259-270.

https://doi.org/10.1016/j.jallcom.2017.09.015

ABSTRACT: Raman scattering (RS), Fourier transform infrared (FTIR) and electron paramagnetic resonance (EPR) spectroscopic measurements on β-MnO2 and α-KxMnO2 nanorods were performed. The infrared spectrum of β-MnO2 is sensitive towards the particle sizes, while the Raman spectrum is sensitive towards the presence of nonstoichiometric and disordered MnO2-δ on the surface of nanorods. EPR measurements show the appearance of two types of Mn4+ ions having different local environment: (i) Mn4+ ions in Mn4+-rich environment and (ii) Mn4+ ions in mixed-valence Mn4+/Mn3+ environment that match up with region of nonstoichiometric MnO2-δ. Observed bands in vibrational spectra of tetragonal hollandite-type α-KxMnO2 are considered to be mainly due to the vibration modes of Mn[sbnd]O frameworks. The EPR spectra of α-KxMnO2 nanorods contain two signals that can be attributed to Mn4+ ions in Mn4+-rich environment and Mn4+ ions in mixed-valence Mn4+/Mn3+ environment close to K+ ions. © 2017 Elsevier B.V.

Savović, J.J., Živković, S.M., Momčilović, M., Trtica, M., Stoiljković, M., Kuzmanović, M.

Determination of low alloying elements concentrations in cast iron by laser induced breakdown spectroscopy based on TEA CO2 laser system
(2017) Journal of the Serbian Chemical Society, 82 (10), pp. 1135-1145.

https://doi.org/10.2298/JSC170303073S

ABSTRACT: The analytical capability of laser-produced plasma for the analysis of low alloying elements in cast iron samples has been investigated. The plasma was induced by irradiation of a sample in air at atmospheric pressure using an infrared CO2 laser. Emission spectra were recorded by time-integrated spatially-resolved measurement technique. A set of ten cast iron samples in a powder or particulate form were provided by BAM (Bundesanstalt für Material Forschung und Prüfung, Deutschland), seven of which were used for calibration, and three were treated as unknowns. Linear calibration curves were obtained for copper, chromium, and nickel, with correlation coefficients above 0.99. Precision and accuracy of the LIBS method was evaluated and compared to those obtained by the inductively coupled plasma (ICP) analysis of the same samples. Detection limits for Cu, Cr and Ni were close to those reported in the literature for other comparable iron-based alloys obtained using different LIBS systems. Analytical figures of merit of the studied LIBS system may be considered as satisfying, especially in the light of other advantages of the method, like cost effective and fast analysis with no sample preparation, and with a possibility for real-time on-site analysis.

Stanisavljev, D., Gojgić-Cvijović, G., Bubanja, I.N.
Scrutinizing microwave effects on glucose uptake in yeast cells
(2017) European Biophysics Journal, 46 (1), pp. 25-31.

https://doi.org/10.1007/s00249-016-1131-4

ABSTRACT: Taking into account different literature reports on microwave (MW) effects on living organisms, we thoroughly investigated the influence of constant 2.45 GHz MW irradiation on glucose uptake in yeast cells. A Saccharomyces cerevisiae suspension of 2.9 × 108 cells/ml was used in all experiments. A large specific absorption rate of 0.55 W/g of suspension is compensated by efficient external cooling of the reaction vessel, which established a strong non-equilibrium flow of energy through the solution and enabled a constant bulk temperature of 30 °C to within 1 °C during glucose uptake. Comparison of MW effects with control experiments revealed insignificant changes of glucose uptake during the initial stages of the experiment (up to the 10th min). Statistically “notable” differences during the next 20 min of the irradiation were detected corresponding to thermal overheating of 2 °C. Possible specific thermal MW effects may be related to local temperature increase and a large flow of energy throughout the system. The obtained effects show that environmental MW pollution (fortunately) is of too low intensity to provoke metabolic changes in living cells. At the same time, a longer exposure of cells to electromagnetic irradiation may have impacts on biochemical applications and production of valuable biotechnological products. © 2016, European Biophysical Societies' Association.

Radusinović, S., Jelenković, R., Pačevski, A., Simić, V., Božović, D., Holclajtner-Antunović, I., Životić, D.

Content and mode of occurrences of rare earth elements in the Zagrad karstic bauxite deposit (Nikšić area, Montenegro)
(2017) Ore Geology Reviews, 80, pp. 406-428.

https://doi.org/10.1016/j.oregeorev.2016.05.026

ABSTRACT: Three vertical sections through the Zagrad deposit of Jurassic karst bauxite in central Montenegro have provided knowledge of the vertical distribution of major and some selected trace elements, including rare earth elements (REE). Variations in the mineralogy, particularly those hosting REE, have been studied. This has revealed the presence of authigenic mineral phases such as xenotime, mottramite and monazite (best proved using Raman microprobe analysis) as well as residual phases such as zircon, titanite and monazite. The mobility of the elements during bauxitization processes has been studied to show that the REE minerals ensure progressive concentration of these elements during removal of major elements through weathering. The similarity of normalized REE in the bauxite to the typical Post-Archean Australian Shales (PAAS) and Upper Continental Crust (UCC) profile, and the preserved Eu anomaly, are evidence that the bauxite was not derived from carbonates and represents alteration of shale, marly limestone and volcanogenic or proximal igneous sourced detritus that accumulated in the original karst landform. Mass change during bauxitization, using Ti as "index" element and compared to PAAS composition, revealed almost 100% depletion of Si and weak enrichment in Al. Deeper parts of the deposit with authigenic minerals exhibit very strong enrichment in all REE. The bauxite ores have high ΣREE contents (693.5–6953.4 ppm), especially ΣLREE contents (582.8–4882.9 ppm), while ΣHREE contents (106.6–2070.5 ppm) are much lower. © 2016 Elsevier B.V.

Senćanski, J.V., Vujković, M.J., Stojković, I.B., Majstorović, D.M., Bajuk-Bogdanović, D.V., Pastor, F.T., Mentus, S.V.
Recycling of LiCo0.59MN0.26NI0.15O2 cathodic material from spent li-ion batteries by the method of the citrate gel combustion [Reciklaža katodnog materijala LiCo0,59MN0,26NI0,15O2 iz istrošenih litijum-jonskih baterija metodom sagorevanja citratnog gela]
(2017) Hemijska Industrija, 71 (3), pp. 211-220.

https://doi.org/10.2298/HEMIND160418031S

ABSTRACT: The Li-ion batteries are the main power source for the high technology devices, such as mobile phones and electric vehicles. Because of that, the number of spent Li-ion batteries significantly increases. Today, the number of active mobile phones crossed 7.19 billion. It is estimated that the mass of the spent lithium ion batteries in China will exceed 500,000 t by 2020. The trouble is in the ingredients of these batteries. They contain Li, Co, Mn, Ni, Cu, Al and toxic and flammable electrolytes which have a harmful affection to the environment. Because of that, the recycling procedure attracts raising attention of researches. Several commercial spent Li-ion batteries were recycled by the relatively fast, economic and simple procedure. The three ways of separating the cathode material from Al collector were examined after the manual dismantling of the components of batteries with the Li(Co-Mn-Ni)O2 as cathode material. These were: 1. dissolution of the Al collector in the alkali medium, 2. peeling off with N-methylpyrrolidone and 3. thermal decomposition of the adhesive at 700

°C. The procedure with the highest yield was the one with the dissolution in alkali medium. The chemical analysis of the single batteries' components (the crust, Al/Cu collector, cathode material) were done by the atomic absorption spectrometry. The components, before the analysis, were dissolved. The re-synthesis of the cathode material by the method of the citrate gel combustion was done after the separating the cathode material and dissolving it in the nitric acid. The obtained product was, after annealing, characterized by the methods of X-ray diffraction and Raman spectroscopy. The recycled product was LiCo0.59Mn0.26Ni0.15O2 stoichiometry, with the hexagonal layered structure α-NaFeO2 type. The functionalization of the resynthesized material was examined in the 1 M solution LiClO4 in the propylene carbonate, by galvanostatic charging, with the current density of 0.7C. The recycled material showed relatively good capacities of charging and discharging which are 94.9 i 64.8 mA h g−1, respectively. © 2017, Association of Chemists and Chemical Engineers of Serbia. All rights reserved.

Adnadjevic, B., Koturevic, B., Jovanovic, J.
Comparative kinetic analysis of isothermal extraction of caffeine from guarana seed under conventional and microwave heating
(2017) Chemical Engineering Research and Design, 118, pp. 61-70.

https://doi.org/10.1016/j.cherd.2016.12.006

ABSTRACT: The kinetics of the isothermal extraction of caffeine from the guarana seed powder with water under conventional (CH) and microwave heating (MWH) were investigated. By applying the isoconversional method, it was established that the kinetics of the caffeine extraction under CH and also under MWH is an elementary kinetic process. The model fitting method was used to determine the kinetics model of caffeine extraction. It was found that the kinetics of the caffeine extraction for both heating modes can be described by the Jander's equation. The rate of the extraction of caffeine under MWH is ~2 times higher than under CH. The values of kinetics parameters (Eaand lnA) of the extraction process under MWH are lower than for CH. The established influence of MWH on the kinetics of caffeine extraction is explained with a specific activation mechanism of water molecules and with an increase in the energy of the ground vibration level of resonant oscillator of N3–CH3band of caffeine molecule (ν = 317 cm−1) which is caused by the absorption of microwave energy. © 2016 Institution of Chemical Engineers

Koturevic, B., Adnadjevic, B., Jovanovic, J.
Isothermal green microwave-assisted extraction of caffeine from guarana: A kinetic study
(2017) Green Processing and Synthesis, 6 (6), pp. 555-563.

https://doi.org/10.1515/gps-2016-0135

ABSTRACT: The kinetics of isothermal green microwaveassisted extraction of caffeine from guarana seed powder with water at a temperature range from 40°C to 60°C was investigated. The caffeine concentration in the water extract was determined by UV-Vis spectrophotometry. By applying the isoconversional method, it was established that the kinetics of the caffeine extraction from the guarana seed powder with microwave heating is an elementary kinetic process. The model fitting method was used to determine the kinetic model of the caffeine extraction under microwave heating. It was found that the kinetics of the caffeine extraction can, under microwave heating, be modeled by the Jander's model of three dimensional diffusion. The kinetic parameters, activation energy and pre-exponential factor of the caffeine extraction were determined.

Senćanski, J., Bajuk-Bogdanović, D., Majstorović, D., Tchernychova, E., Papan, J., Vujković, M.
The synthesis of Li(Co[sbnd]Mn[sbnd]Ni)O2 cathode material from spent-Li ion batteries and the proof of its functionality in aqueous lithium and sodium electrolytic solutions
(2017) Journal of Power Sources, 342, pp. 690-703.

https://doi.org/10.1016/j.jpowsour.2016.12.115

ABSTRACT: Several spent Li-ion batteries were manually dismantled and their components were uncurled and separated. The chemical composition of each battery's component was determined by atomic absorption spectroscopy. Among several ways to separate cathode material from the collector, the alkali dissolution treatment was selected as the most effective one. After both complete separation and acid leaching steps, the co-precipitation method, followed by a thermal treatment (700 °C or 850 °C), was used to resynthesize cathode material LiCo0.415Mn0.435Ni0.15O2. Its structure and morphology were characterized by XRD, Raman spectroscopy and SEM-EDS methods. The electrochemical behavior of recycled cathode materials was examined by cyclic voltammetry and chronopotentiometry in both LiNO3and NaNO3aqueous solutions. High sodium storage capacity, amounting to 93 mAh g−1, was measured galvanostatically at a relatively high current of ~100 mA g−1. Initial lithium intercalation capacity of ~64 mAh g−1, was determined potentiodynamically at very high scan rate of 20 mV s−1(~40 C). Somewhat lower initial capacity of ~30 mAh g−1, but much lower capacity fade on cycling, was found for sodium intercalation at the same scan rate. The differences in the Li and Na charge storage capability were explained in terms of ion rearrangement during charging/discharging processes. © 2017 Elsevier B.V.

Marković, Z.M., Kepić, D.P., Matijašević, D.M., Pavlović, V.B., Jovanović, S.P., Stanković, N.K., Milivojević, D.D., Spitalsky, Z., Holclajtner-Antunović, I.D., Bajuk-Bogdanović, D.V., Nikšić, M.P., Todorović Marković, B.M.
Ambient light induced antibacterial action of curcumin/graphene nanomesh hybrids
(2017) RSC Advances, 7 (57), pp. 36081-36092.

https://doi.org/10.1039/c7ra05027e

ABSTRACT: Curcumin and its derivates are well-known for their different biological activities including antibacterial. On the other hand there are controversial reports concerning the antibacterial potential of graphene and, in particular, graphene oxide. In this study we have reported for the first time the antibacterial activity of curcumin/graphene nanomesh hybrids under ambient light conditions. The graphene nanomesh was synthesized by electrochemical exfoliation of highly oriented pyrolytic graphite in 1 M solution of ammonium persulfate and further functionalized by curcumin. Identical values of minimum inhibitory concentration (1 mg mL-1) were determined for pure curcumin and curcumin/graphene nanomesh hybrids toward Staphylococcus aureus. All tested samples had more pronounced antibacterial activity against Gram positive bacteria, Staphylococcus aureus compared to Escherichia coli as a representative of Gram negative strains. The poor antibacterial potential of exfoliated graphene improves significantly by the functionalization with curcumin, which allows for its usage as a antibacterial coating. © 2017 The Royal Society of Chemistry.

Jović-Jovičić, N., Banković, P., Mojović, Z., Nedić-Vasiljević, B., Marinović, S., Mudrinić, T., Milutinović-Nikolić, A.
Ecologically friendly chitosan-montmorillonite bio-nanocomposite as adsorbent for textile dyes from aqueous solutions
(2017) Science of Sintering, 49 (4), pp. 419-429.

https://doi.org/10.2298/SOS1704419J

ABSTRACT: The bio-nanocomposite of montmorillonite and natural biopolymer chitosan (C-MM) was synthesized. Intercalation of chitosan in form of monolayer into the interlamellar space of montmorillonite was confirmed by XRD and IR analysis. The adsorption of textile dyes: Acid Yellow 99 (AY99), Acid Orange 10 (AO10) and Reactive Black 5 (RB5) onto C-MM was investigated. The adsorption was performed with the respect to adsorption time, pH and initial dye concentration. The kinetics of adsorption obeyed pseudo-second-order of kinetics and was the most efficient in acidic pH. Langmuir model best described the adsorption of AY99 and AO10, while RB5 adsorption isotherm was best fitted with Freundlich model. © 2016 Authors.

Etinski, M., Marian, C.M.
A theoretical study of low-lying singlet and triplet excited states of quinazoline, quinoxaline and phthalazine: Insight into triplet formation
(2017) Physical Chemistry Chemical Physics, 19 (21), pp. 13828-13837.

https://doi.org/10.1039/c7cp02022h

ABSTRACT: Quinazoline, quinoxaline and phthalazine are nitrogen containing heterocyclic aromatic molecules which belong to the class diazanaphthalenes. These isomers have low-lying nπ* and naphthalene-like ππ* states that interact via spin-orbit coupling. In this contribution, we study their structure and electronic states by means of a coupled-cluster method. The computed properties are compared to those of cinnoline which were obtained in our previous study [Etinski et al., Phys. Chem. Chem. Phys., 2014, 16, 4740]. The excited state features of these isomers are dependent on the position of the nitrogen atoms. We find that quinazoline and quinoxaline exhibit similarities in the ordering and character of the excited states. In contrast, a marked difference in the electronic and geometric structures of the lowest excited triplet states of cinnoline and phthalazine is noticed, although both are orthodiazanaphthalenes. Our findings suggest that the S1 T1 channel is responsible for the rapid intersystem crossing in quinazoline and quinoxaline, whereas the S1 T2 pathway is active in phthalazine. © the Owner Societies 2017.

Labus, N., Vasiljević, Z., Aleksić, O., Luković, M., Marković, S., Pavlović, V., Mentus, S., Nikolić, M.V.
Characterisation of Mn0.63Zn0.37Fe2o4 powders after intensive milling and subsequent thermal treatment
(2017) Science of Sintering, 49 (4), pp. 455-467.

https://doi.org/10.2298/SOS1704455L

ABSTRACT: Commercial Mn-Zn powder (Mn0.63Zn0.37Fe2O4, 93 wt. % and Fe2O3 7 wt. %) was milled 0.5, 1, 2 and 4 hours in a planetary ball mill. The goal was to observe intensive milling influences on oxidation and reduction processes that will happen during subsequent heating. Powders were characterized with XRD, SEM and particle seizer. Subsequent heating was monitored on TGA/DTA in an air atmosphere. After compaction of the milled powders, sintering was also performed in a dilatometric device. Sintered specimens were characterized micro structurally with SEM on a fresh breakage. Obtained differential TGA diagrams suggest intensive changes during prolonged milling of the oxidation kinetics on heating. Ferrite powders changed with milling as well as with second run heating were characterized to enable determination of the potentially best ratio of milling and heating to be applied to obtain the desired microstructure. © 2016 Authors.

Waisi, H.K., Petković, A.Z., Nikolić, B.R., Janković, B.Ž., Raičević, V.B., Lalević, B.T., Giba, Z.S.
Influence of 24-epibrassinolide on seedling growth and distribution of mineral elements in two maize hybrids [Uticaj 24-epibrasinolida na rastenje klijanaca i distribuciju mineralnih elemenata kod dva hibrida kukuruza]
(2017) Hemijska Industrija, 71 (3), pp. 201-209.

https://doi.org/10.2298/HEMIND160318030W

ABSTRACT: In this study, influence of wide range of 24-epibrassinolide (24-EBL) on early growth potential of two maize hybrids (ZP 434 and ZP 704) was examined. Paper concerns germination, seedling biomass, important chlorophylls content, and redistribution of elements (heavy metals and microelements), in a seedlings of the maize hybrids, as influenced by different 24-EBL concentrations. It was found that hybrids react differently to exogenously applied hormone. The biggest differences between two examined maize hybrids considering the germination level were reached with the lowest values at 86% for ZP 704 and 72% for ZP 434, gained at the highest applied concentration of 24-EBL. Seedlings of hybrid ZP 434 reacted positively moderately in the case of shoot length and biomass under the influence of 24-EBL, but seedlings of hybrid ZP 704 had lower values of these parameters under the influence of the phytohormone. Chlorophyll a/b ratios showed that photosynthetic apparatus of seedlings of the hybrids is not active in this stage of development. It was established that 24-EBL affects seedling growth and re-allocation of naturally present mineral elements in early growth stages and that could be one of the reason for poorer growth of ZP 704 treated with various concentrations of 24-EBL, comparing to control. When applied in lower concentrations, 24-EBL is blocking toxic elements such as chromium and nickel to relocate to vital parts of plant, what was case in hybrid ZP704. In case of ZP 434, lower concentrations of 24-EBL are affecting re-allocation of Cu and Cr and these findings suggest that maize hybrid seedlings treated with lower concentrations of 24-EBL could survive and be successful in polluted areas. © 2017, Association of Chemists and Chemical Engineers of Serbia. All rights reserved.

Papović, S., Cvjetićanin, N., Gadžurić, S., Bešter-Rogač, M., Vraneš, M.
Physicochemical and electrochemical characterisation of imidazolium based IL + GBL mixtures as electrolytes for lithium-ion batteries
(2017) Physical Chemistry Chemical Physics, 19 (41), pp. 28139-28152.

https://doi.org/10.1039/c7cp04478j

ABSTRACT: Ionic liquid/organic solvent mixtures are investigated as potential optimal electrolytes for lithium-ion batteries (LIBs) that can combine low flammability, good thermal stability and high electrical conductivity. In this work the standard ionic association constants of different 1-alkyl-3-methylimidazolium ([Cnmim]+, n is the number of C in the alkyl side chain-2, 4, 6 or 8) TFSI- based ionic liquids (ILs) in γ-butyrolactone (GBL) are determined using the low concentration Chemical Model (lcCM). Based on the values of for ILs in GBL and earlier physicochemical systematic investigations in that solvent, the system with the lowest was selected for the preparation of the LiTFSI/C2mimTFSI/GBL electrolyte for testing TiO2 nanotube arrays as anode material for LIBs. In an attempt to realize LIBs with enhanced safety, we report herein a comparative study of the electrochemical properties of LiTFSI/C2mimTFSI/GBL and an electrolyte containing an IL without acidic C(2)H on the imidazolium cation, namely, LiTFSI/C2mmimTFSI/GBL. The presence of GBL can improve the reduction stability of imidazolium-based ILs and GBL in LiTFSI/IL/GBL-based electrolytes. It was shown that TiO2 nanotube structures display stable galvanostatic cycling in the LiTFSI/C2mimTFSI/GBL electrolyte after 350 full (dis-)charge cycles and after cell exposure to T = 328.15 K. © the Owner Societies 2017.

Bratić, M., Jugović, D., Mitrić, M., Cvjetićanin, N.
Insertion of lithium ion in anatase TiO2 nanotube arrays of different morphology
(2017) Journal of Alloys and Compounds, 712, pp. 90-96.

https://doi.org/10.1016/j.jallcom.2017.04.065

ABSTRACT: Anatase TiO2 nanotube arrays of different morphology were prepared by a two-step process: anodic oxidation at voltages 20–60 V and subsequent annealing at 400 °C. By amplifying anodization voltage the inner diameter of nanotubes increased. At 60 V nanotubes changed the shape from cylindrical tube to truncated cone with elliptical opening. Electrochemical insertion of Li-ion in nanotubes was studied by cyclic voltammetry and galvanostatic charge-discharge experiments. The cyclovoltammetric response was fast for all nanotube arrays. The galvanostatic areal charge/discharge capacity of nanotube arrays increased with increasing anodizaton voltage. Although the mass of nanotubes prepared at 45 V was larger, the gravimetrical capacity was much higher for nanotubes prepared at 60 V because of the larger surface area exposed to the electrolyte. Gravimetrical capacity values exceed theoretical bulk capacity of anatase due to the surface storage of Li-ion. Diffusion coefficient of Li-ion was calculated to be between 5.9·10−16 and 5.9·10−15 cm2 s−1. © 2017 Elsevier B.V.

Janković, B.Ž., Waisi, H.
The thermodynamic properties of dehydration of two maize hybrids under the influence of 24-epibrassinolide: The impact of the mutual interaction of bioactive compounds and water molecules during this process
(2017) Bioactive Compounds: Sources, Properties and Applications, pp. 179-234.

ABSTRACT: Thermodynamic analysis of the dehydration process of seedlings of two maize hybrids (ZP434 (drought tolerant) and ZP704 (older generation hybrid, drought sensitive)) was performed. Thermodynamic quantities during the dehydration process of the seedlings treated with the different concentrations of 24-epibrassinolide (24-EBL) (a brassinosteroid originally isolated from Aegle marmelos L. Correa (Rutaceae), also known as golden apple) was examined. Comparison of results was carried out in the case of control samples with those which were treated with 24-EBL. In this work, the influence of various bioactive compounds present in plant systems on the dehydration process under thermal stress was investigated. It was found that trehalose has an impact on the level of resistance to thermal activation of dehydration process, and it was assumed that it may have an impact on the possible change in the reaction mechanismin toward stress protection. Based on the enthalpy-entropy compensation theory, it has been found that water desorption mechanism in hybrids is controlled by entropy, where results demonstrated that the molecular rearrangements are at high levels. Based on the BET (Brunauer-Emmett-Teller) and modified BET approaches, it has been found that response of ZP704 to 24-EBLs is more acceptable than in the case of ZP434. Based on the performed glass transition temperature analysis of control samples, it was assumed that presence of LEA proteins probably increases the glass transition temperature (where this is checked by means of theoretical analysis) of a glassy matrix made of sucrose and strengthens hydrogen-bonding network. Results showed that this phenomenon is favored in the case of ZP434 control sample. It was found that 24-EBL affects both germination and growth of the maize hybrids ZP704 and ZP434 at the lower and higher concentrations of applied phytohormone. The hybrids reacted divergently to the exogenous application of 24-EBL. Lower concentration has a stimulating effect on growth and germination, while high concentration of 24-EBL has an inhibitory effect on these processes. © 2017 by Nova Science Publishers, Inc. All rights reserved.

Radoičić, M., Ćirić-Marjanović, G., Spasojević, V., Ahrenkiel, P., Mitrić, M., Novaković, T., Šaponjić, Z.
Superior photocatalytic properties of carbonized PANI/TiO2 nanocomposites
(2017) Applied Catalysis B: Environmental, 213, pp. 155-166.

https://doi.org/10.1016/j.apcatb.2017.05.023

ABSTRACT: A simple bottom-up method for the preparation of novel and very efficient photocatalytic nanocomposite system based on carbonized form of polyaniline (PANI) and colloidal TiO2 nanocrystals has been developed. The carbonized PANI/TiO2 nanocomposites were synthesized in a two-step procedure. Firstly, non-carbonized PANI/TiO2 nanocomposites were synthesized by the chemical oxidative polymerization of aniline (ANI) with ammonium peroxydisulfate, in the presence of colloidal TiO2 nanoparticles (TiO2 NPs) (d ~ 4.5 nm). Initial [TiO2]/[ANI] mole ratios were 20, 50, and 80. In the second step, following the polymerization process, the carbonization of PANI/TiO2 nanocomposites was performed by thermal treatment in an inert atmosphere at 650 °C. The morphological and structural properties of the carbonized nanocomposites were studied using transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray powder diffraction (XRD) and Raman spectroscopy. The accomplishment of complete carbonization of PANI in PANI/TiO2 nanocomposites was confirmed by Raman spectroscopy. The appearance of anatase and rutile crystal forms in TiO2 NPs upon carbonization, with mass ratio depending on the initial molar ratio of ANI and TiO2 NPs was revealed by XRD measurements, TEM, SEM and Raman spectroscopy. The photocatalytic activities of carbonized PANI/TiO2 nanocomposites were evaluated following the photocatalytic degradation processes of Rhodamine B and Methylene blue. Carbonized PANI/TiO2 nanocomposites showed higher photocatalytic efficacy compared to bare TiO2 NPs and non-carbonized PANI/TiO2 nanocomposites. The porosity and surface structure of carbonized PANI/TiO2 nanocomposites, as well as crystalline structure of TiO2, affect photocatalytic activity of nanocomposites. © 2017 Elsevier B.V.

Pejin, B., Ciric, A., Dimitric Markovic, J., Glamoclija, J., Nikolic, M., Sokovic, M.
An insight into anti-biofilm and anti-quorum sensing activities of the selected anthocyanidins: the case study of Pseudomonas aeruginosa PAO1
(2017) Natural Product Research, 31 (10), pp. 1177-1180.

https://doi.org/10.1080/14786419.2016.1222386

ABSTRACT: Anti-biofilm activity of three anthocyanidins (pelargonidin, cyanidin and delphinidin) was evaluated for the first time at in vitro conditions. All the compounds reduced the formation of Pseudomonas aeruginosa PAO1 biofilm at low sub-MIC (0.125 MIC) with delphinidin (c 56.25 μg/mL) being the most active (43%). In comparison, ampicillin (c 93.75 μg/mL) and streptomycin (c 21.25 μg/mL) (used as positive controls) were considerably less effective at the same sub-MIC (8 and 12%, respectively). Furthermore, at 0.5 MIC (c 225 μg/mL) this anthocyanidin molecule partly reduced the bacterial protrusions. However, no any of the aforementioned compounds inhibited the production of pyocyanin by the bacterial strain P. aeruginosa PAO1. Taken all together, the delphinidin scaffold could be taken into consideration for the design of the novel and more effective anti-biofilm agents inspired by the anthocyanidins. © 2016 Informa UK Limited, trading as Taylor & Francis Group.

Glumac, M., Pejin, B., Karaman, M., Mojović, M., Matavulj, M.
Lignicolous fungi hydrodistilled extracts may represent a promising source of natural phenolics
(2017) Natural Product Research, 31 (1), pp. 104-107.

https://doi.org/10.1080/14786419.2016.1212036

ABSTRACT: In vitro evaluation of total phenolic contents and antiradical activities of the lignicolous fungi Fomes fomentarius and Schizophyllum commune hydrodistilled extracts was the subject of this study. This preliminary screening included four free radical species evaluated by UV-vis (DPPH•, ABTS•and•NO) and EPR (Asc•), respectively. According to the experimental data obtained, both F. fomentarius and S. commune hydrodistilled extracts may be considered as promising sources of phenolic natural products (157 and 138 mg GAE/g d.e., respectively) and other bioactives showing good anti-DPPH (1.31 μg/mL) and anti-Asc (70.40%) radical activities, respectively, at in vitro conditions. © 2016 Informa UK Limited, trading as Taylor & Francis Group.

Smarun, A.V., Duzhin, F., Petković, M., Vidović, D.
Alkene-assisted: Cis -to- trans isomerization of non-conjugated polyunsaturated alkenes
(2017) Dalton Transactions, 46 (41), pp. 14244-14250.

https://doi.org/10.1039/c7dt03041j

ABSTRACT: Complex [Cp*Ru(NCMe)3][PF6], 1a, has been identified as a cis-to-trans isomerization catalyst of various non-conjugated cis-polyalkenes under exceptional kinetic control as no alkene conjugation was observed. According to the experimental and theoretical data, the cis-trans isomerization occurred via an alkene-assisted mechanism in which one cis-double bond always served as an anchoring site. Using a combination of multinuclear NMR spectroscopic evidence and mathematical methods it was possible to determine the extent of trans isomerization. © 2017 The Royal Society of Chemistry.

Čebela, M., Zagorac, D., Batalović, K., Radaković, J., Stojadinović, B., Spasojević, V., Hercigonja, R.
BiFeO3 perovskites: A multidisciplinary approach to multiferroics
(2017) Ceramics International, 43 (1), pp. 1256-1264.

https://doi.org/10.1016/j.ceramint.2016.10.074

ABSTRACT: Bismuth ferrite (BiFeO3) is one of the most studied multiferroic system with a large number of published articles. This is mainly because BiFeO3 material possesses both ferromagnetic and ferroelectric properties observed at room temperature, which opens great possibility for industrial and technological applications. Well-crystallized single-crystal BiFeO3 nanopowder has been successfully synthesized with the hydrothermal method. The phase composition of the synthesized samples was determined by the x-ray diffraction (XRD) analysis, and the results showed that synthesized material crystallizes in the space group R3c as α-BiFeO3 phase, which was confirmed by the previous experiments. In addition, a structure prediction has been performed and 11 additional BiFeO3 modifications have been proposed. In the next phase, an ab initio optimization of predicted structures has been performed and the structure of the γ-form has been elucidated. Furthermore, electronic and magnetic properties of BiFeO3 were investigated using combination of experimental and theoretical methods. Spectroscopic Ellipsometry has been used to study electronic properties of BiFeO3, while magnetic behavior of synthesized material was investigated by SQUID. Finally, theoretical studies were performed using a full potential linearized augmented plane-waves plus local orbital (FP(L)APW+lo) method, based on density functional theory (DFT). © 2016 Elsevier Ltd and Techna Group S.r.l.

Zec, N., Cvjetićanin, N., Bešter-Rogač, M., Vraneš, M., Gadžurića, S.
Electrochemical performance of anatase TiO2 nanotube arrays electrode in ionic liquid based electrolyte for lithium ion batteries
(2017) Journal of the Electrochemical Society, 164 (8), pp. H5100-H5107.

https://doi.org/10.1149/2.0051708jes

ABSTRACT: Ternary electrolyte composed of 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ionic liquid (PYR14TFSI), γ-butyrolactone (GBL) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and anatase TiO2 nanotube arrays (NTAs) electrode are investigated for the application in new generation of lithium-ion batteries (LIBs). The electrical conductivity and viscosity are measured in the whole composition range at several temperatures. Also, cyclic voltammetry experiments are performed at different temperatures and scan rates. At all scan rates, up to 100 mV · s−1 Ti4+/Ti3+ redox peaks appear designating exceptionally fast intercalation/deintercalation reaction. At the end of cycling the intercalation/deintercalation capacity was 144.8/140.7 mAh · g−1 at current rate 3 C. The diffusion coefficient for Li+ extraction from TiO2 nanotubes (NTs) have been calculated for temperatures from (25 to 55) ◦C. Activation energy for diffusion was found to be 54.7 kJ/mol (0.57 eV). © The Author(s) 2017. Published by ECS. All rights reserved.

Milenković, D., Dorović, J., Jeremić, S., Dimitrić Marković, J.M., Avdović, E.H., Marković, Z.
Free Radical Scavenging Potency of Dihydroxybenzoic Acids
(2017) Journal of Chemistry, 2017, art. no. 5936239, .

https://doi.org/10.1155/2017/5936239

ABSTRACT: In order to evaluate the free radical scavenging potency of dihydroxybenzoic acids (DHBAs) the Density Functional Theory (DFT) was used. The M05-2X/6-311++G(d,p) and B3LYP-D2/6-311++G(d,p) theoretical models were applied. Three possible antioxidant mechanisms were examined: hydrogen atom transfer (HAT), single-electron transfer followed by proton transfer (SET-PT), and sequential proton loss electron transfer (SPLET) mechanisms. All of these mechanisms have been studied in nonpolar (benzene and pentylethanoate) and polar solvents (water) using an implicit solvation model (SMD). The following thermodynamic quantities related to these mechanisms were calculated: bond dissociation enthalpy (BDE), ionization potential (IP), and proton affinity (PA). The obtained results indicated the HAT mechanism as the most favourable reaction pathway for antioxidative action of DHBAs in benzene. On the other hand, SPLET is indicated as predominant reaction mechanism in polar solvent. The SET-PT mechanism was not favourable reaction path for antioxidative action in any of the solvents under investigation. © 2017 Dejan Milenković et al.

Dimić, D., Milenković, D., Dimitrić Marković, J., Marković, Z.

Antiradical activity of catecholamines and metabolites of dopamine: Theoretical and experimental study
(2017) Physical Chemistry Chemical Physics, 19 (20), pp. 12970-12980.

https://doi.org/10.1039/c7cp01716b

ABSTRACT: The importance of molecules with antiradical potency that are produced in the human body has significantly increased. Among others, neurotransmitters and their metabolites act as the first line of defense against oxidative stress in the peripheral endocrine and the central nervous systems. Dopamine (DO), epinephrine (EP), norepinephrine (NE), l-DOPA, catechol, and three metabolites of dopamine (3-methoxytyramine (3-MT), homovanillic acid (HO), and 3,4-dihydrophenylacetic acid (DOPAC)) were investigated for their antiradical potency via computational methods and DPPH assay. Density functional theory calculations were used to determine the most probable reaction mechanism based on the thermodynamic parameters. These results suggested that hydrogen atom transfer (HAT)/proton-coupled electron transfer (PCET) and sequential proton loss electron transfer (SPLET) mechanisms are preferable in polar solvents. Several techniques were employed to differentiate between HAT and PCET mechanisms via examination of the transition state structures. Kinetic studies of HAT/PCET and electron transfer (ET) reactions, the second step of SPLET, have proven that ET is much faster for an order of 105-106. Based on this, it was concluded that SPLET was the dominant mechanism for the antiradical activity towards DPPH radicals in polar solvents. The findings suggest that all the investigated molecules can be classified as excellent antiradical scavengers, except for 3-MT and homovanillic acid. © 2017 the Owner Societies.

Savovic, J., Momcilovic, M., Zivkovic, S., Stancalie, A., Trtica, M., Kuzmanovic, M.
LIBS Analysis of Geomaterials: Comparative Study of Basalt Plasma Induced by TEA CO2 and Nd:YAG Laser in Air at Atmospheric Pressure
(2017) Journal of Chemistry, 2017, art. no. 9513438, .

https://doi.org/10.1155/2017/9513438

ABSTRACT: We present a study of the plasma generated by transversely excited atmospheric (TEA) CO2 laser irradiation of a basalt sample. The plasma was induced in air at atmospheric pressure. The same sample was also analyzed using a commercial LIBS system based on Nd:YAG laser and time-gated detection. The main plasma parameters, temperature, and electron number density were determined and analytical capabilities of the two systems compared. Despite differences in laser wavelength, pulse duration, applied fluence, and signal detection scheme, the two systems are comparable in terms of element detectability and limits of detection. In both cases, all elements usually present in geological samples were identified. The estimated limits of detection for most elements were below 100 ppm, while for Cu, Cr, and Sr they were around or below 10 ppm. The obtained results led to the conclusion that simple, cost-effective TEA CO2 LIBS system can find applications for geological explorations. © 2017 Jelena Savovic et al.

Gutić, S.J., Dobrota, A.S., Leetmaa, M., Skorodumova, N.V., Mentus, S.V., Pašti, I.A.

Improved catalysts for hydrogen evolution reaction in alkaline solutions through the electrochemical formation of nickel-reduced graphene oxide interface
(2017) Physical Chemistry Chemical Physics, 19 (20), pp. 13281-13293.

https://doi.org/10.1039/c7cp01237c

ABSTRACT: H2 production via water electrolysis plays an important role in hydrogen economy. Hence, novel cheap electrocatalysts for the hydrogen evolution reaction (HER) are constantly needed. Here, we describe a simple method for the preparation of composite catalysts for H2 evolution, consisting in simultaneous reduction of the graphene oxide film, and electrochemical deposition of Ni on its surface. The obtained composites (Ni@rGO), compared to pure electrodeposited Ni, show an improved electrocatalytic activity towards HER in alkaline media. We found that the activity of the Ni@rGO catalysts depends on the surface composition (Ni vs. C mole ratio) and on the level of structural disorder of the rGO support. We suggest that HER activity is improved via Hads spillover from the Ni particles to the rGO support, where quick recombination to molecular hydrogen is favored. A deeper insight into such a mechanism of H2 production was achieved by kinetic Monte-Carlo simulations. These simulations enabled the reproduction of experimentally observed trends under the assumption that the support can act as a Hads acceptor. We expect that the proposed procedure for the production of novel HER catalysts could be generalized and lead to the development of a new generation of HER catalysts by tailoring the catalyst/support interface. © the Owner Societies 2017.

Dobrota, A.S., Pašti, I.A., Mentus, S.V., Skorodumova, N.V.
A DFT study of the interplay between dopants and oxygen functional groups over the graphene basal plane - Implications in energy-related applications
(2017) Physical Chemistry Chemical Physics, 19 (12), pp. 8530-8540.

https://doi.org/10.1039/c7cp00344g

ABSTRACT: Understanding the ways graphene can be functionalized is of great importance for many contemporary technologies. Using density functional theory calculations we investigate how vacancy formation and substitutional doping by B, N, P and S affect the oxidizability and reactivity of the graphene basal plane. We find that the presence of these defects enhances the reactivity of graphene. In particular, these sites act as strong attractors for OH groups, suggesting that the oxidation of graphene could start at these sites or that these sites are the most difficult to reduce. Scaling between the OH and H adsorption energies is found on both reduced and oxidized doped graphene surfaces. Using the O2 molecule as a probe we show that a proper modelling of doped graphene materials has to take into account the presence of oxygen functional groups. © the Owner Societies 2017.

Xu, X., Spasojević-De Biré, A., Ghermani, N.E., Wei, Y., Novaković, S., Bošnjaković-Pavlović, N., Wu, P.
Experimental evidence of charge transfer in a functionalized hexavanadate: A high resolution X-ray diffraction study
(2017) Physical Chemistry Chemical Physics, 19 (28), pp. 18162-18166.

https://doi.org/10.1039/c7cp01840a

ABSTRACT: A high resolution X-ray diffraction study has been carried out on [(C4H9)4N]2 [V6O13{(OCH2)3CCH2OCCH2CH3}2] (V6-C3) at 100 K. The V6 core possesses a negative charge, leading to a strong polarization of the anion. A nucleophilic region localized near the organic moiety and an electrophilic region in the vicinity of the V6 core provide an overall description of charge-transfer behavior. © 2017 the Owner Societies.