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The quest for optimal water quantity in the synthesis of metal-organic framework MOF-5

(2019) *Microporous and Mesoporous Materials*, pp. 23-29.

<https://doi.org/10.1016/j.micromeso.2018.11.005>

ABSTRACT: Efficient and simple room temperature synthesis of pure phase metal-organic framework MOF-5 has been developed, based on the use of anhydrous zinc acetate, $Zn(OAc)_2$, as a precursor, instead of zinc acetate dihydrate. Crucial influence of water on a reaction pathway was revealed. In order to obtain MOF-5, different amounts of water have been added into the solutions of $Zn(OAc)_2$ in *N,N*-dimethylformamide (DMF) to prepare in situ zinc acetate hydrates with 0.25, 0.5, and 1.0 mol of water. Commercially available zinc acetate dihydrate was also used as a precursor for comparison. These solutions were mixed at room temperature with the solution of 1,4-benzenedicarboxylic acid in DMF in the absence of any base. Based on XRD, FTIR, and SEM measurements, it was shown that the optimal amount of water for the synthesis of completely pure, crystalline phase MOF-5 is 0.25-0.5 mol of water per one mole of Zn. The reaction systems with 1.0 and 2.0 mol of water per one mole of Zn also led to solids with MOF-5 as the dominant phase, but they also contain small amounts of another phase, formed due to the decomposition (hydrolysis) and/or distortion of the MOF-5 framework in the presence of excess amounts of water. The product synthesized in the system without any added water contains MOF-5 phase in a very small amount, while main phase is zinc 1,4-benzenedicarboxylate and/or zinc hydrogen 1,4-benzenedicarboxylate. Regular cubic submicro/microcrystal morphology exhibited the samples synthesized using 0.5 and 0.25 mol water per one mole of Zn (pure MOF-5), while for the samples synthesized at mole ratios $H_2O/Zn^{2+} = 1.0$ and 2.0 other particle shapes are also seen. By nitrogen sorption measurements it was found that the highest values of BET specific surface area ($1937 \text{ m}^2 \text{ g}^{-1}$), micropore volume ($0.83 \text{ cm}^3 \text{ g}^{-1}$), and micropore area ($1590 \text{ m}^2 \text{ g}^{-1}$) showed MOF-5 prepared at mole ratio $H_2O/Zn^{2+} = 0.5$, while the highest yield of MOF-5 is obtained with the theoretical mole ratio $H_2O/Zn^{2+} = 0.25$. Thermal stability of synthesized materials was investigated by TGA. © 2018 Elsevier Inc.

Georgijević, R., Vujković, M., Gutić, S., Aliefendić, M., Jugović, D., Mitrić, M., Đokić, V., Mentus, S.

The influence of synthesis conditions on the redox behaviour of $LiFePO_4$ in aqueous solution

(2019) *Journal of Alloys and Compounds*, 776, pp. 475-485.

<https://doi.org/10.1016/j.jallcom.2018.10.246>

ABSTRACT: To contribute to the knowledge on the influence of synthesis procedure on the intercalation kinetics of lithium ions into phospho-olivines, $LiFePO_4/C$ composite samples (LFPC) were synthesized in two ways, the first one in a sol-gel procedure (SG), and the other in a solid-state reaction (SS). The X-ray diffractograms (XRD) of both samples overlapped with that of pure $LiFePO_4$, taken from the crystallographic database. Scanning electron microscopy pictures indicated the high degree of interparticle sintering, which caused a considerable agglomerate growth. The results of potentiodynamic

measurements in aqueous LiNO₃ solution revealed that for SS sample, three times higher initial capacity from that of SG one, (amounting to 74 mAh g⁻¹ at 5 mV s⁻¹). However, capacity fade on rising scan rate is much more expressed for SS sample than for SG one. We suggest that a different degree of material utilization due to the incomplete coverage of olivine particles by carbon explains this difference. The technique of separation of diffusion and capacitance currents was applied in a kinetic analysis, but it was shown to be inappropriate. We suggest the inapplicability of classic CV theory to the intercalation system accompanied by phase transition. Instead, a model of ohmic resistance determination of process kinetics was considered. LFPC-SS sample delivers three times larger capacity in LiNO₃, amounting to 74 mAh g⁻¹ at 1 mV s⁻¹. © 2018 Elsevier B.V.

Zdolšek, N., Rocha, R.P., Krstić, J., Trtić-Petrović, T., Šljukić, B., Figueiredo, J.L., Vujković, M.J.
Electrochemical investigation of ionic liquid-derived porous carbon materials for supercapacitors: pseudocapacitance versus electrical double layer
(2019) *Electrochimica Acta*, 298, pp. 541-551.

<https://doi.org/10.1016/j.electacta.2018.12.129>

ABSTRACT: This work shows the potential application of carbon materials prepared by three different ionic liquid-based methods, using 1-butyl-3-methylimidazolium methanesulfonate [bmim][MeSO₃], for electrochemical supercapacitors. The effects of [bmim][MeSO₃] on morphology, texture and surface chemistry of prepared materials has been explored by SEM/TEM, N₂/CO₂ adsorption measurements and XPS. The results indicate the possibility of synthesis of carbon materials with tunable physicochemical properties using ionic liquid based methods. The charge storage behavior of all materials was studied in three different pH aqueous electrolytes. The pseudocapacitive and double layer contributions were estimated and discussed from the aspect of the textural changes and the changes of the chemical composition of surface functional groups containing heteroatoms. C=O type functional groups, with the contribution of COOH groups, were found to be responsible for a different amount of charge, which could be stored in alkaline and acidic electrolytic solution. The material prepared by direct carbonization of [bmim][MeSO₃], showed the best electrochemical performance in alkaline electrolyte with a capacitance of 187 F g⁻¹ at 5 mV s⁻¹ (or 148 F g⁻¹ at 1 A g⁻¹), due to the contribution of both electric-double layer capacitance and pseudocapacitance which arises from oxygen, nitrogen and sulfur functional groups. © 2018 Elsevier Ltd

Diklić, N.P., Dobrota, A.S., Pašti, I.A., Mentus, S.V., Johansson, B., Skorodumova, N.V.
Sodium storage via single epoxy group on graphene - The role of surface doping
(2019) *Electrochimica Acta*, 297, pp. 523-528.

<https://doi.org/10.1016/j.electacta.2018.11.108>

ABSTRACT: Due to its unique physical and chemical properties, graphene is being considered as a promising material for energy conversion and storage applications. Introduction of functional groups and dopants on/in graphene is a useful strategy for tuning its properties. In order

to fully exploit its potential, atomic-level understanding of its interaction with species of importance for such applications is required. We present a DFT study of the interaction of sodium atoms with epoxy-graphene and analyze how this interaction is affected upon doping with boron and nitrogen. We demonstrate how the dopants, combined with oxygen-containing groups alter the reactivity of graphene towards Na. Dopants act as attractors of epoxy groups, enhancing the sodium adsorption on doped oxygen-functionalized graphene when compared to the case of non-doped epoxy-graphene. Furthermore, by considering thermodynamics of the Na interaction with doped epoxy-graphene it has been concluded that such materials are good candidates for Na storage applications. Therefore, we suggest that controlled oxidation of doped carbon materials could lead to the development of advanced anode materials for rechargeable Na-ion batteries. © 2018 Elsevier Ltd

Karačić, D., Korać, S., Dobrota, A.S., Pašti, I.A., Skorodumova, N.V., Gutić, S.J.

When supporting electrolyte matters - Tuning capacitive response of graphene oxide via electrochemical reduction in alkali and alkaline earth metal chlorides

(2019) *Electrochimica Acta*, 297, pp. 112-117.

<https://doi.org//10.1016/j.electacta.2018.11.173>

ABSTRACT: The ability to tune charge storage properties of graphene oxide (GO) is of utmost importance for energy conversion applications. Here we show that the electrochemical reduction of GO is highly sensitive to the cations present in the solution. GO is reduced at more negative potential in alkali metal chloride solutions than in alkaline earth metal chlorides. During the reduction, the capacitance of GO increases from 10 to 70 times. The maximum capacitances of reduced GO are between 65 and 130 F g⁻¹, depending on the electrolyte and the presence of conductive additive. We propose that different interactions of cations with oxygen functional groups of GO during the reduction are responsible for the observed effect. This hypothesis has been confirmed by Density Functional Theory calculations of alkali and alkaline earth metals interactions with epoxy-functionalized graphene sheet. © 2018 Elsevier Ltd

Janković, B., Manić, N., Dodevski, V., Popović, J., Rusmirović, J.D., Tošić, M.

Characterization analysis of Poplar fluff pyrolysis products. Multi-component kinetic study

(2019) *Fuel*, 238, pp. 111-128.

<https://doi.org//10.1016/j.fuel.2018.10.064>

ABSTRACT: This paper describes the pyrolysis of Poplar fluff (from *Populus alba*) using on-line apparatus, and carbonization process at 850 °C using the fixed bed reactor. Characteristics of pyrolysis products were examined. Elemental and chemical analyses were shown that Poplar fluff has higher energy content characterized by increased content of fibrous structure (particularly cellulose). Independent parallel reactions model very well describes devolatilization process. It was found that increased amount of extractives can significantly affect on increased release of light gaseous products, but declining hydrocarbons, mostly the alkanes. Liquid product is mainly composed of

phenolics, aldehydes, acids, esters and ketones. The carbonization process produces the great abundance of polycyclic aromatic hydrocarbons (PAH's), where naphthalene is the most abundant. Mechanism for PAH's formation was suggested. This study represents the first step in a much wider and more comprehensive way in thermal conversion processes of this type of fuel. © 2018 Elsevier Ltd

Jović-Jovičić, N., Mojović, M., Stanković, D., Nedić-Vasiljević, B., Milutinović-Nikolić, A., Banković, P., Mojović, Z.
Characterization and electrochemical properties of organomodified and corresponding derived carbonized clay
(2019) *Electrochimica Acta*, 296, pp. 387-396.

<https://doi.org//10.1016/j.electacta.2018.11.031>

ABSTRACT: Series of alkylammonium modified smectites with different alkylammonium/clay ratios was synthesized (H series). The obtained organoclays were used as precursors for carbon-clay composite materials (C series). Both set of materials were characterized by X-ray diffraction (XRD), point of zero charge (pHPZC), N₂ adsorption-desorption isotherms, Raman spectroscopy and electron paramagnetic resonance (EPR) analysis. XRD analysis of organomodified clays confirmed incorporation of HDTMA⁺ into interlamellar space of smectite. Series of carbonized clays showed constant d₀₀₁ value of 1.4 nm. The pHPZC of two series differed indicating that carbonization changed the profile of pH dependent sites on the clay surface. Textural properties of the H series decreased throughout the series, while in the C series the most developed porous structure was obtained for sample where HDTMA⁺ loading was equal to cation exchange capacity. Raman spectroscopy showed that amorphous carbon was formed during carbonization process. The obtained materials were used as modifiers of carbon paste electrode and investigated using electrochemical impedance spectroscopy, cyclic voltammetry and square wave voltammetry. The comparison of electrochemical behavior of H series and C series showed the importance of interlamellar species for charge transfer process. The investigation of influence of composition of carbon paste and form of added carbon showed that performance of carbon-clay based electrodes depended on synergy of different factors. © 2018 Elsevier Ltd

Janković, B., Manić, N., Buchner, R., Płowaś-Korus, I., Pereiro, A.B., Amado-González, E.
Dielectric properties and kinetic analysis of nonisothermal decomposition of ionic liquids derived from organic acid
(2019) *Thermochimica Acta*, 672, pp. 43-52.

<https://doi.org//10.1016/j.tca.2018.12.013>

ABSTRACT: Dielectric relaxation spectra of three representatives of the class of hydroxyethylammonium carboxylate protic ionic liquids (PILs), namely 2-hydroxyethylammonium formate [2-HEAF], 2-hydroxyethylammonium propionate [2-HEAP] and 2-hydroxyethylammonium butanoate [2-HEAB], were recorded over a wide frequency range ($0.05 \leq \nu(\text{GHz}) \leq 50$) at 25 °C. The thermal decomposition kinetics of these ionic liquids derived from organic acids was studied by thermogravimetry (TG) using nonisothermal experiments. For the purpose of kinetic analysis, the thermal behavior of the samples was studied in the temperature interval from ambient temperature up to 420 °C at different heating rates (5, 10, 15 and 20

°C min⁻¹). Isoconversional kinetic analysis was performed using Friedman's (FR) differential method and the integral Kissinger-Akahira-Sunose (KAS) method. The dependence of the apparent activation energy (E) on the conversion fraction (α) for the investigated decomposition processes was analyzed. It was found that the molecular structure of the involved anion significantly influences the dielectric properties of the studied PILs. It was also established that a change in the anion structure drastically affects the shape of the thermo-analytical curves. Among the considered PILs [2-HEAF] has the highest thermal stability. However, considering kinetic properties, certain deviations were observed and referred to hydrogen bonding development and steric impediment effects. © 2018 Elsevier B.V.

Amić, A., Marković, Z., Dimitrić Marković, J.M., Milenković, D., Lučić, B.

The role of guaiacyl moiety in free radical scavenging by 3,5-dihydroxy-4-methoxybenzyl alcohol: thermodynamics of 3H⁺/3e⁻ mechanisms (2019) *Molecular Physics*, 117 (2), pp. 207-217.

<https://doi.org/10.1080/00268976.2018.1506174>

ABSTRACT: Participation of guaiacyl moiety of 3,5-dihydroxy-4-methoxybenzyl alcohol (DHMBA) in inactivation of free radicals was investigated using the DFT method. The thermodynamics of triple (3H⁺/3e⁻) free radical scavenging mechanisms was investigated. The Gibbs free energies of reactions of inactivation of selected 10 free radicals indicate DHMBA as a potent scavenger. Obtained results allow us to suggest that the contribution of guaiacyl moiety to antioxidant activity of phenolic compounds should be taken into account, what has been scarcely considered until now. © 2018, © 2018 Informa UK Limited, trading as Taylor & Francis Group.

Avdović, E.H., Dimić, D.S., Dimitrić Marković, J.M., Vuković, N., Radulović, M.Đ., Živanović, M.N., Filipović, N.D., Đorović, J.R., Trifunović, S.R., Marković, Z.S.
Spectroscopic and theoretical investigation of the potential anti-tumor and anti-microbial agent, 3-(1-((2-hydroxyphenyl)amino)ethylidene)chroman-2,4-dione (2019) *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy*, 206, pp. 421-429.

<https://doi.org/10.1016/j.saa.2018.08.034>

ABSTRACT: The coumarin-orthoaminophenol derivative was prepared under mild conditions. Based on crystallographic structure, IR and Raman, ¹H and ¹³C NMR spectra the most applicable theoretical method was determined to be B3LYP-D3BJ. The stability and reactivity parameters were calculated, in the framework of NBO, QTAIM and Fukui functions, form the optimized structure. This reactivity was then probed in biological systems. The antimicrobial activity towards four bacteria and three fungi species was examined and activity was proven. In vitro cytotoxic effects, against human epithelial colorectal carcinoma HCT-116 and human healthy lung MRC-5 cell lines, of the investigated substance are also tested. Compound showed significant cytotoxic effects on HCT-116 cells, while on MRC-5 cells showed no cytotoxic effects. The effect of hydroxy group in ortho-position on the overall

reactivity of molecule was examined through molecular docking with Glutathione-S-transferases. © 2018

Ristić, M.M., Petković, M., Milovanović, B., Belić, J., Etinski, M. New hybrid cluster-continuum model for pKa values calculations: Case study of neurotransmitters' amino group acidity (2019) *Chemical Physics*, 516, pp. 55-62.

<https://doi.org//10.1016/j.chemphys.2018.08.022>

ABSTRACT: Acid dissociation constant is a quantitative measure of chemical species ability to donate a proton to water molecule and plays important role in aqueous chemistry. Many computational strategies were conceived in order to properly address an acid dissociation equilibrium. In this work, we present new economical cluster-continuum method based on the density functional theory for the accurate calculation of pKa values. By analysing hydration properties of neutral and protonated 2-phenylethylamine sampled in the first principle molecular dynamics simulations, we were able to find key interactions between water molecules and amino group in the neutral and protonated state. This was used to design a reaction scheme, which was shown to yield excellent agreement between the computed and experimental pKa values of selected neurotransmitters. We believe that the proposed scheme can be generalized for computation of acidic properties of other primary and secondary amines. © 2018 Elsevier B.V.

Martins, M., Milikić, J., Šljukić, B., Soyly, G.S.P., Yurtcan, A.B., Bozkurt, G., Santos, D.M.F. Mn2O3-MO (MO = ZrO2, V2O5, WO3) supported PtNi nanoparticles: Designing stable and efficient electrocatalysts for oxygen reduction and borohydride oxidation (2019) *Microporous and Mesoporous Materials*, 273, pp. 286-293.

<https://doi.org//10.1016/j.micromeso.2018.07.022>

ABSTRACT: PtNi nanoparticles (NPs) are synthesised by microwave irradiation technique and anchored onto three binary metal oxide (BMO) supports, namely Mn2O3-ZrO2, Mn2O3-V2O5 and Mn2O3-WO3, prepared by solid-state dispersion method. The BMO supports are characterised using SEM, FTIR, N2-sorption and electrical conductivity measurements. XRD, XPS and TEM analysis confirm the formation of PtNi NPs on the BMO supports. Pt and Ni content over the support materials is set to 10 wt.% for each element. These electrocatalysts activity for oxygen reduction (ORR) and borohydride oxidation (BOR) reaction in alkaline media is assessed for the first time using voltammetric and chronoamperometric techniques. All three PtNi electrocatalysts revealed activity for ORR and BOR, with PtNi/(Mn2O3- ZrO2) exhibiting the highest current densities. The ORR onset potentials were observed to range from 0.84 to 0.97 V vs. RHE, with Tafel slopes ranging from 0.101 to 0.230 V dec⁻¹. BOR activation energies were found to range from 27 to 30 kJ mol⁻¹. Obtained results point out PtNi/(Mn2O3- ZrO2) as suitable electrocatalyst for fuel cell applications, particularly for BOR, with lower catalyst price due to partial replacement of the noble metal by a transition metal and improved stability achieved by introducing a binary metal oxide support. © 2018 Elsevier Inc.

