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MASTER-DB - a Relational Database for Energy Storage Materials

L. Borislavov, R. Stoyanova

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, “Acad. G. Bonchev” Str., bld. 11, 1113 Sofia, Bulgaria

In last years, the data-driven methods for discovery have gained a significant popularity in the field of materials science. These methods rely on the processing of large amounts of experimental or theoretically derived data and thus the presence of and well-structured datasets plays a crucial role for the successful application of such methods for discovery. Different data-driven methods can be utilized to enhance the process of developing energy-storage materials provided appropriate datasets exist, however a fairly small number of such datasets are available.

The main objective of the present work is to develop a strategy for construction of a relational database that is able to efficiently manage the storage, retrievement and searching of experimental data related to energy-storage materials. The database was optimized for storing both electrochemical data and material preparation and spectral characterization data. To achieve this goal a database manager software with a graphical user interface (GUI) for managing database records and a python advanced programming interface (API) have been developed.

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HYDROGEN STORAGE CHARCTERISTICS OF MgH_2 BASED MATERIALS WITH ADDITION OF Ni OR V AND ACTIVATED CARBONS DERIVED FROM DIFFERENT PRECURSORS

E. Grigorova[a], P. Markov[a], B. Tsyntsarski[b]

[a] *Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, “Acad. G. Bonchev” Str., bld. 11, 1113 Sofia, Bulgaria*

[b] *Institute of Organic Chemistry, Bulgarian Academy of Sciences, Sofia, bld. 9, Acad. G. Bonchev str., Bulgaria*

Magnesium-based materials are promising as hydrogen storage media due to their high hydrogen absorption capacity, abundance and low price. During the project MgH_2 based mixtures with addition of Ni or V and activated carbons synthesized via pyrolysis and steam activation from polyolefin wax, walnut shells and peach stones are prepared by ball milling under argon in a planetary mill and their hydrogen sorption characteristics are investigated. Structure, phase and surface composition of the starting compounds and the mixtures after ball milling and hydriding are monitored by XRD and TEM. The achieved absorption capacity of the composite with 15 wt.% Ni and 5 wt.% activated carbon derived from polyolefin wax at 573 K and after 60 min of hydriding is 5.3 wt. % H_2 and it is not the highest one, but the kinetics of absorption and desorption are remarkably improved. The presence of the metal additive- nickel or vanadium has more pronounced impact on the hydrogenation kinetics and the capacity achieved, especially in the case of Ni, because of the formation of Mg_2NiH_4. The observations from TEM characterization e. g. the polycrystalline SAED and HRTEM confirmed those from XRD about the presence of graphite, Mg and the ternary hydride Mg_2NiH_4 with monoclinic and orthorhombic structure or nonstoihiometric VHx.

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Improvement In The Thermoelectric Devices And Sodium-Ion Batteries By Means Of Reduced Graphene Oxide

S. Harizanova, T. Tushev, V. Koleva, R. Stoyanova

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, "Acad. G. Bonchev" Str., bld. 11, 1113 Sofia, Bulgaria

Nowadays, searching for materials that are able to convert and store energy in efficient and affordable way is of a primary research goal. In this regard, the most intriguing materials comprise the misfit layered oxides such as $Ca_3Co_4O_9$, and sodium iron phosphate-pyrophosphate, $Na_4Fe_3(PO_4)_2P_2O_7$ (NFPP). Because of their flexible structures accommodating cobalt and iron ions in different oxidation state, $Ca_3Co_4O_9$ exhibits good thermoelectric properties, while NFPP stores reversibly sodium in high amount at about 3 V vs. Na^+/Na. Thus, $Ca_3Co_4O_9$ and NFPP are recognized as effective thermoelectric and electrode materials, respectively. For practical applications, however, it is necessary to improve the thermoelectric efficiency of $Ca_3Co_4O_9$, especially at room temperature, as well as to enhance the cycling stability of NFPP at elevated temperatures. In this study, we propose an effective experimental way to improve their performance based on the formation of composites between reduced graphene oxide (rGO) and $Ca_3Co_4O_9$, respectively NFPP. rGO is choosen due to its relatively good electrical conductivity.

This study demonstrates the beneficial effect of the rGO additive when it is used as component in both thermoelectric material and cathode material for sodium-ion batteries. Some correlations have been established between the thermoelectric properties (electrochemical properties) of the composites and their morphology as well as the amount of individual components. These correlations could be used for further optimization in the performance of oxides and phosphates as thetmoelectric and electrode materials.

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Could bio-waste power the future of sodium-ion batteries?

S. Harizanova, M. Kalapsazova, R.Kukeva, I. Uzunov, L. Ivanova, R. Stoyanova

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, “Acad. G. Bonchev” Str., bld. 11, 1113 Sofia, Bulgaria

At the base of waste management to reduce environmental hazards is turning bio-waste into high-value materials, such as carbons with applications in many areas.

Herein, we face the waste recycling with another challenge – preparation of carbon material suitable for sodium-ion storage. Suitable host carbon structure for the sodium ion is non-graphitized and disordered and with pore size enough to host the large sodium ion reversibly, like as hard carbon (HC). The main drawbacks of bio-hard carbons are their critical dependence on the choice of the biomass precursors and the pyrolysis conditions. Recently we demonstrated that complementary to the carbon structure and texture, mineral ash phases and their distribution have an impact on the Na storage properties when the hard carbon is obtained from spent coffee grounds [1].

In the present contribution we highlighted the importance of the biomass selection, so we compared the Na-storage properties of HC derived from coffee grounds waste and walnut shell waste. The synthesis procedure of the hard carbon consists of torrefaction of the selected biomass at relatively low temperature (750 ^{o}C) and subsequent high temperature pyrolysis at 1100 and 1300 ^{o}C. To quantify the Na-storage performance of different bio-HCs, we determined four parameters: first irreversible capacity, reversible specific capacity, ratio slop/plateau capacity ratio, and cycling stability. To understand the mechanism of sodium storage and to evaluate the causes of capacity irreversibility, in addition to the specific surface area and pore-size distributions analyses, an innovative *ex-situ* EPR methodology were applied. This methodology could be applicable for evaluating of other bio-waste sources and we believe it will shorten the path to the practical application of biomass derived HCs in sodium-ion batteries.

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Advanced approaches for enhancing intercalation capacity of $Na_{2/3}Ni_{1/3}Mg_{1/6}Mn_{1/2}O_2$: insight into the mechanism

M. Kalapsazova, R.Kukeva, E. Zhecheva, R. Stoyanova

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, "Acad. G. Bonchev" Str., bld. 11, 1113 Sofia, Bulgaria

The sodium transition metal oxides with layered structure are in practical interests as positive electrode materials for sodium-ion batteries. However, these types of oxides have not yet reached their optimal electrochemical properties in terms of specific capacity and cycling stability.

Recently, we demonstrated two different approaches for further development of the electrochemical performance of $Na_{2/3}Ni_{1/3}Mn_{1/2}O_2$ oxide. Improved cycling stability is metal substitution of transition metals with electrochemically inactive ions such as Mg^{2+} [1]. Improved cycling stability is obtained via metal substitution of transition metals with electrochemically inactive ions such as Mg^{2+} [1], while the surface modification of the layered oxide with oxygen-storage material such as CeO_2 [2] and Al_2O_3 [3] leads to a drastic increase in the reversible capacity.

Herein we provide new data on the synergetic effect of both approaches – metal substitution in the structure and surface modification by coating. After partial substitution of the low-oxidized nickel ions for Mg^{2+} ions, the target $Na_{2/3}Ni_{1/3}Mg_{1/6}Mn_{1/2}O_2$ oxide was treated with electrochemically inactive oxides, such as CeO_2 and Al_2O_3. It is found that the coated oxides show improved electrochemical characteristics in terms of specific capacity and cycling stability in comparison with pristine $Na_{2/3}Ni_{1/2}Mn_{1/2}O_2$ and substituted $Na_{2/3}Ni_{1/3}Mg_{1/6}Mn_{1/2}O_2$ oxides. The combined use of *in-situ* and *ex-situ* analyses provided an opportunity to gain insight into the mechanism of the intercalation reaction. An *in-situ* XRD analysis reveals that Al_2O_3 coating leads to additional stabilization of the oxide structure during de/intercalation compared to uncoated and CeO_2 coated oxides. An EIS technique, *ex-situ* XPS and EPR analyses reveals that the CeO_2 and A_2O_3 modifier tunes the electrode–electrolyte interaction and prevent the cathode surface from hydrogen fluoride (HF) attack at upper potential limit.

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Effects of Li reduction on the surface of organic electrodes

I. Kichev[a,b], A. Tadjer[a,b], R. Stoyanova[a]

[a]*Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, "Acad. G. Bonchev" Str., bld. 11, 1113 Sofia, Bulgaria*
[b]*Faculty of Chemistry and Pharmacy, Sofia University, 1 "James Bourchier" Blvd., Sofia, Bulgaria*

Organic electrode materials present a promising alternative to the traditional Li-ion battery electrodes, offering renewability and cost reduction [1]. Understanding the effects of surface reduction on the overall properties of organic electrodes is crucial [2]. The insights gained from computer simulations of novel materials play a pivotal role in the efficient material design. However, simulating such large-scale systems poses significant challenges rendering first principles approaches usually impractical. Yet, the utilization of linear-scaling DFT codes emerges as a valuable tool. This approach enables the simulation of large systems without the cubic increase in calculation time, thereby facilitating the exploration of complex organic electrode materials. The current research leverages the ONETEP [3] code to simulate a system comprising 900 atoms, consisting of four layers of benzoquinone $(20\bar{1})$ surfaces in periodic boundary conditions (PBC). The primary objective of this study is to explore the structural modifications induced by Li reduction in quinones and the ensuing changes in local properties.

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Improvement in the electrochemical properties of sodium iron phosphate as an electrode material for sodium-ion batteries through Ce modification

V. Koleva, T. Tushev, S. Harizanova, R. Stoyanova

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, "Acad. G. Bonchev" Str., bld. 11, 1113 Sofia, Bulgaria

Sodium-ion battery (SIB) technology is one of the best promissing alternatives to the lithium-ion batteries due to the low cost and abundance of sodium which are critical issues for large-scale application. One of the challenges facing SIBs is the exploration of new cheap electrode materials with efficient electrochemical performances suitable for practical applications. Among the sodium intercalation compounds, phosphate framework materials and particularly these containing iron ($Na_xFe_y(PO_4)_z$) have attracted increasing attention due to their low cost, safety and being environmental friendly. Intercalation-based cathodes typically rely on the cationic redox activity of the transition metals. The activation of both cationic and anionic redox reactions in the electrodes has been found to increase drastically the reversible capacity of P3-$Na_{2/3}Ni_{1/2}Mn_{1/2}O_2$ by using CeO_2 as an oxygen storage material. Moreover, first principle calculations have shown that anionic (O^{2-}) redox processes in $NaFePO_4$ are also visible. Inspired by these data the main **idea** of present contribution is to study effect of Ce-modification on electrochemical properties of $NaFe_xPO_4$ as cathode material in sodium and lithium half-cells. The electrochemical properties of Ce-modified $NaFe_xPO_4$ are studied in galvanostatic and potentiostatic regimes at 20 and 40 °C. The results show that the presence of Ce has the following effects: (i) A change in the phase composition of $NaFe_xPO_4$ with formation of NASICON and alluaudite type phases; (ii) Progressive increase in the redox potentials in the two ion cells; (iii) Strong polarization of the ion cells which causes capacity decrease during the cycling. The **main conclusion** at this stage of study is that a further electrode optimization is necessary to overcome the strong polarization and to clarify the state of Ce^{n+} ions in the electrodes and their role to affect the electrochemical behavior of the $NaFe_xPO4$ electrodes.

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TEM Characterization Of Sensitive Materials Based On MgH_2

P. Markov[a], E. Grigorova[a], B. Tsyntsarski[b]

[a] *Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, "Acad. G. Bonchev" Str., bld. 11, 1113 Sofia, Bulgaria*

[b] *Institute of Organic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, bld. 9, Acad. G. Bonchev str., Bulgaria*

The development of hydrogen storage materials is an important scientific topic whose progress will contribute to the widespread application of hydrogen as an energy carrier. Characterization of these materials by transmission electron microscopy (TEM) is challenging, because of their sensitivity to oxidation and the high energy electron beam exposure, which could cause negative impact. The nanoporous carbons prepared by hydro-pyrolysis from different biomass precursors as peach stones, crushed walnut shell and a polyolefin wax a waste from polyethylene production among with Ni or V are added to MgH_2 to obtain mixtures by ball milling under argon with different composition and are analyzed by TEM (HR STEM JEOL JEM 2100 with GATAN Orius 832 SC1000 CCD Camera) at accelerating voltage of 200 kV. The samples are dispersed in acetone and the obtained suspensions are dripped on standard carbon/Cu grids. The TEM analyses of these sensitive materials especially HRTEM and SAED are obtained by low beam current values. The HRTEM of the nanoporous carbons are showed that they consist of areas with graphitic structure and contain some impurities of carbonates and oxides of Ca and Mg when the carbon is obtained from biomass precursors. The TEM characterization of these materials revealed co-existence of monoclinic and also orthorhombic Mg_2NiH_4 or non-stoichiometric VH_x. These materials are fine powders and in particular after hydriding they have an average diameter particles size of bellow 10nm. The results obtained by TEM give a more comprehensive description of the microstructures, phase composition and help in the development of improved materials for hydrogen storage.

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Influence Of Cerium (IV) Oxide For Reversible Oxygen Activity In Li_2RuO_3 And Li_3RuO_4

M. Nedyalkov, L. Alexandrov, R. Kukeva, P. Tzvetkov, R. Stoyanova

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, "Acad. G. Bonchev" Str., bld. 11, 1113 Sofia, Bulgaria

Ruthenates are group of inorganic compounds with variety of oxidation states of ruthenium ranging from plus (IV) to (VII). That rich variety of oxidation states combined with layered structure makes them highly perspective for use of battery applications. A very high specific capacity for some of these compounds has been reported [1,2]. This is possible because two different forms of active redox reaction affecting both the transition metal and the oxygen are possible. Our main objective is to activate the oxygen redox activity which can significantly enhance the specific capacity of ruthenate based electrode materials to above 300 mAh/g. Achieving such a high specific capacity poses a challenge because the oxygen activity becomes irreversible shortly after few cycles and hence oxygen gas is released into the battery enclosure and a serious decrease of specific capacity is observed. In the present work we study the influence of the irreversible oxygen activity. We hypothesize that addition of cerium (IV) oxide to ruthenate based electrode materials can influence the irreversible oxygen activity by reversibly binding during battery charging and releasing oxygen during the discharge phase. The modification of ruthenates with CeO_2 is motivated due to its exceptional capability to store oxygen reversibly.

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The Role of Carbon-black in Composite Electrodes for Lithium and Sodium Ion Batteries

S. Stanchovska , D. Marinova, M. Kalapsazova, R. Stoyanova

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, "Acad. G. Bonchev" Str., bld. 11, 1113 Sofia, Bulgaria

Sodium ion batteries (NIBs) emerge as a attractive technology for large scale energy storage, while lithium analogues (LIBs) are recognized as a exceptional technology for mobile energy storage [1]. The operation of both NIBs and LIBs relies on shuttling of Na^+ or Li^+ ions between two electrodes via non-aqueous electrolyte. The performance of NIBs and LIBs depends on the fabrication quality of their electrodes [1]. This is usually a complex procedure that includes mixing of the active material with electrochemically inactive polymer binder and carbon-based conductive additive followed by casting on metal collectors. To gain the beneficial effects of this procedure, it is of importance to understand how the conductive additives cover the particles of the active materials and what is their optimal amount. This is of a great significance when active materials has a nano-morphology and/or low electron conductivity.

Herein, we examine the formation of composites between carbon black additives and two specific electrodes for NIBs: sodium titanates with nanowire-like morphology [2] and *peri*-diselenolo-substituted 1,8-naphthalimide derivatives having lower electron conductivity [3].

We have demonstrated that carbon black forms flexible composites with sodium titanate nanowires and low-conductive organic derivatives. These composites serve as electrodes in sodium and lithium ion cells since they deliver high capacity and exhibit good cycling stability. For sodium titanate nanowires, the best performance is achieve when the amount of carbon black is of 12 wt.%, while much more carbon black is needed as an additive for the fabrication of organic electrode (i.e. the ratio of 22-to-78 wt%). These results could contribute to correct analysis of the electrochemical properties of materials with nano-morphology and low electron conductivity in both sodium and lithium-ion batteries.

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Theoretical study on the electrochemical properties of naphthalene monoimides with *peri*-anulated diselenide bridge

Y. Danchovski[a,b], H. Rasheev[a,b], Y. Zagranyarski [b], A. Tadjer[a,b], R. Stoyanova[a]

[a] Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, "Acad. G. Bonchev" Str., bld. 11, 1113 Sofia, Bulgaria
[b] Faculty of Chemistry and Pharmacy, University of Sofia, 1164 Sofia, Bulgaria

Innovative organic electrode materials have been intensively investigated during the recent years. Studies have shown that 1,8-naphthalen monoimides possess interesting characteristics - chemo- and photostability, accessibility, and relatively easy functionalisation. Furthermore, the addition of disulphide bridge between 4th and 5th position has proved to be a successful strategy for enhancing the electrochemical properties due to the ease of the two-electron Li-redox reaction for cleavage of S-S bond. The reaction is highly exergonic and completely reversible.

The purpose of the current study is to expand the idea of substituted 1,8-naphthalen monoimides replacing the disulphide bridge by a Se-Se one. The introduction of Cl and Br substituents at positions 3 and 6 gives a systematic approach towards the examination of the electrochemical properties depending on the substituent electronegativity. The computed electrode potentials are in good agreement with the experimental data and the simulations give an insight into the spatial changes that occur during the lithiation process. We have succeeded to relate some electrochemical results with the corresponding theoretically modelled processes.

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rGO decorated $NaFeVPO_4(SO_4)_2$ as a standout electrode material for sodium-ion batteries

T.Tushev, V. Koleva, S. Harizanova, R. Kukeva, M.Shipochka, P. Markov, R. Stoyanova

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, “Acad. G. Bonchev” Str., bld. 11, 1113 Sofia, Bulgaria

The anionic substitution is a successful strategy to tune the position of the redox couples in the polyanion electrode materials for lithium and sodium ion batteries and thus to increase the power density. For Fe-based NASICON type $A_xFe_2(XO_4)_3$ materials, it has been shown that the increase in the redox potentials follows the increase in the electronegativity of X in $XO4^{n-}$. Hence, the combination of PO_4 with highly electronegative SO_4 ions into NASICON framework is expected to increase considerably the operating voltage without loss of gravimetric capacity.

The present contribution is focused on the electrochemical performance of a little known mixed phosphate-sulfate compound $NaFeVPO_4(SO_4)_2$ (denoted as NFVPS) decorated with 15 % reduced graphene oxide (rGO). The simultaneous presence of the most abundant Fe and V having multiple oxidation state (2+, 3+, 4+, 5+) available for charge storage, in combination with two anions, and in addition with rGO decoration, could meet the requirements for higher capacity and working voltage, good cycling stability and rate capability. The electrochemical studies of NFVPS/rGO have been performed in sodium half-cells (electrolyte $NaPF_6$ in PC) by voltammetric (CV) and galvanostatic methods at 20 and 40 °C. It has been established that NFVPS/rGO operates *via* a mixed mechanism (both Faradaic and capacitive reactions) and exhibits good electrochemical performance at the two temperatures with a reversible capacity of 92 mAh/g after 100 cycles with capacity retention of 93 % (C/2 rate). These results show that the anion substitution opens a great perspective to design new types of electrode materials and NFVPS/rGO is a promising candidate for sodium-ion battery application.

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Redox processes in electrolytes for rechargeable batteries

G. Vassilev[a,b], H. Rasheev[a,b], A. Tadjer[a,b], R. Stoyanova[a]

[a] *Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, "Acad. G. Bonchev" Str., bld. 11, 1113 Sofia, Bulgaria*
[b] *Faculty of Chemistry and Pharmacy, University of Sofia, 1164 Sofia, Bulgaria.*

The electrolyte LP30 is composed of 1M $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with molar ratio 1:1 and is widely used in lithium-ion batteries (LIBs). On the other hand, propylene carbonate (PC) is the main solvent choice for sodium-ion batteries (SIBs) combined with $NaPF_6$ as a salt. Preliminary experimental evidence suggests that during both the oxidative and reductive stages, within the electrochemical stability window (ESW) of the LP30 solvents, stable radicals are formed. Surprisingly, they are characterized with different concentration but identical electron paramagnetic resonance (EPR) signal in both phases, which implies that the same radical is formed. The results obtained for the electrolyte suitable for SIBs are different. In this case the EPR signals during the oxidative and reductive scans do not match, suggesting the presence of different radical species. In this research we used Density Functional Theory to provide interpretation of the observed EPR spectra and outline the main differences between the behavior of EC and PC. The g-factors of various radicals were calculated and the effects of traditional additives were also examined. All cation-radicals are unstable and they would deprotonate to a neutral radical whose g-value is similar to the experimentally found one. However, the lack of hyperfine structure in the sample containing LP30 refutes this possibility which led us to the assumption that an anion-radical should be formed even in the oxidative stage, due to electron leakage at the electrode surface. Homo- and hetero-dimerization of the reduced cyclic carbonates and the complex formation, as a result of Li^+ and Na^+ solvation, were also investigated.

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