



COIN2022

CONTEMPORARY BATTERIES AND SUPERCAPACITORS

INTERNATIONAL SYMPOSIUM
BELGRADE 2022

PROGRAM AND BOOK OF ABSTRACTS

June 1-2, 2022,
Serbian Academy of Sciences and Arts
Belgrade, Serbia

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**CONTEMPORARY BATTERIES AND
SUPERCAPACITORS**

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Program and Book of Abstracts

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SCOPE

Serbian Academy of Sciences and Arts will host world-renowned professors and their collaborators to share their activities and achievements in the energy storage and conversion field, thus shedding light on future opportunities. Besides, Alumni of University of Belgrade will present their ongoing research activities.

The conference will cover different research and industrial perspectives in Europe and also educational activities within the prestigious MESC+ study program. Students will get acquainted with possibilities of upgrading their skills and knowledge through postgraduate studies in the best European and world institutions.

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- Advances and challenges of contemporary batteries and supercapacitors
- Interactive opportunities for students within MESC+ activities.
<https://mesc-plus.eu>
- Future perspectives on battery research within Battery 2030+ initiative.
<https://battery2030.eu>
- Future industrial battery developments in Serbia
- Activities within research projects in Europe and especially those in Serbia and Montenegro funded by Science Fund of the Republic of Serbia and NATO Science for Peace and Security Programme

RESEARCH TOPICS

- Battery and supercapacitor systems
- Metal-ion (Li-, Na-...) batteries
- Metal-air batteries
- Multivalent charge storage systems
- Materials for energy storage and conversion

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Agenda

Wednesday, June 1, 2022

| | |
|-------------|---|
| 13.00-18.45 | Registration |
| 14.00-14.20 | Symposium opening and welcome speeches Main Hall of Serbian Academy of Sciences and Arts <i>Academicians Zoran Popović, Slavko Mentus, Dr. Milica Vujković, Prof. Dr. Robert Dominko</i> |

| | |
|------------------|---|
| Session 1 | Chair: Dragana Jugović |
| 14.20-14.55 | Christian Masquelier , Sunkyu Park, Jean-Noël Chotard, Dany Carlier, Laurence Croguennec, François Fauth, Pieremanuele Canepa Crystal Chemistry of Advanced Polyanionic Positive Electrodes for Na-Ion Batteries |
| 14.55-15.30 | Patrice Simon Electrochemistry At the Nanoscale: Application to Materials for Energy Storage |
| 15.30-16.05 | Robert Dominko From Lithium Sulfur to Multivalent Sulfur Batteries |

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16.05 - 17.25 coffee break/catering & poster sessions

| | |
|-----------------|---|
| Session2 | Chair: Dragana Jugović |
| 17.25-17.45 | Milica J. Vujković , Aleksandra Gezović, Danica Bajuk-Bogdanović, Veselinka Grudić, Slavko Mentus Towards alternative Li-free Electrode Materials: Synthesis and Phase Compositon Interrelation |
| 17.45-18.05 | Jana Mišurović , Gordana Ćirić-Marjanović Comparison of Charge Storage Ability of Polyaniline and Poly(p-aminodiphenylamine) |
| 18.05-18.25 | Zoran Jovanović , Danica Bajuk-Bogdanović, Milica Vujković, Željko Mravik, Sonja Jovanović, Smilja Marković, Milica Pejčić, Ivanka Holclajtner-Antunović The Role of Surface Chemistry, Structure and Interactions in the Electrochemical Charge Storage Properties of Graphene Oxide and 12-tungstophosphoric Acid Nanocomposites |
| 18.25-18.45 | Nemanja Mikać ElevenEs - The First LFP Gigafactory in Europe |

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19.30 *Dinner (Restaurant "Dva Jelena" in Skadarlija)*

Thursday, June 2, 2022

08.00-13.25 **Registration**

Session 1

Chair: Robert Dominko

9.00-09.35 **Kristina Edström**
How BATTERY 2030+ Could Animate the Research Efforts in Europe

09.35-10.10 **Isidora Cekić-Lasković**
(Multi)-Functional Electrolytes for Lithium-Based Batteries:
From Synthesis to Interfacial Electrochemistry

10.10-10.45 **Nagore Ortiz Vitoriano**
Electrochemical Storage at CIC energiGUNE: Across Energy Storage
Value Chain

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10.45 - 12.05 coffee break/catering & poster sessions

Session 2

Chair: Robert Dominko

12.05-12.25 Aleksandra S. Popović, **Branimir Grgur**
Polypyrrole-silver Chloride Composite as Energy Storage Materials

12.25-12.45 **Zoran Mandić**
Importance of the Simultaneous Testing of Positive and Negative
Electrodes in Batteries and Supercapacitors

12.45-13.05 **Olivera Lužanin**, Jože Moškon, Jan Bitenc, Robert Dominko
Organic Cathodes for Multivalent Metal Batteries – Prospects and
Challenges

13.05-13.25 **Daniel M. Mijailović**, Uroš Č. Lačnjevac, Vladimir D. Jović, Dušica B.
Stojanović, Vuk V. Radmilović, Velimir R. Radmilović and Petar S.
Uskoković
Mesoporous Electrodes Based on Carbon Nanofibers and Transition
Metal Oxides for High-performance Supercapacitors

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13.25-13.30 *Closing remarks*

13.30 *Catering/refreshment*

Posters Agenda

| Poster session I, June 1, 2022 | |
|--------------------------------|---|
| I.1. | Electrochemical Formation and Behavior of Silver and Lead Chlorides as Potential Cathodes for Rechargeable Magnesium Seawater Battery Aleksandra S. Popović , Branimir N. Grgur |
| I.2. | Synthesis and Characterization of Cathode Material $\text{MgCr}_{0.15}\text{Mn}_{1.85}\text{O}_4$ for Magnesium Ion Batteries Nikolina Jokić , Ivana Stojković-Simatović |
| I.3. | Comparative Study of Li-ion Intercalation into $\text{LiCr}_{0.15}\text{Mn}_{1.85}\text{O}_4$ from Aqueous and Organic Electrolyte Latas Nemanja , Cvjetičanin Nikola |
| I.4. | Catalysts Toward Highly Efficient Rechargeable Metal-air Batteries: Polyoxometalates with Reduced Graphene Oxide Teodora Đurić , Filipe M. B. Gusmão, Jadranka Milikić, Sara Knežević, Dalibor Stanković, Kristina Radinović, Diogo M. F. Santos, Nemanja Gavrilov and Biljana Šljukić |
| I.5. | Carbon encapsulated Fe-species as Anodes in Alkaline Batteries Jelena Rugar , Nemanja Gavrilov, Maja Milojević-Rakić and Aleksandra Janošević Ležaić |
| I.6. | Challenges in Sustainable Use of Lithium for Highly Innovative Final Products Created and Made in Serbia with EU Environmental Standards Ilija Batas Bjelić , Uros Andjelkovic, Boban Stojanović and Milosav Georgijević |
| I.7. | Layered CaV_2O_6 as Promising Electrode Material for Aqueous Calcium-ion Batteries Tamara Petrović , Danica Bajuk-Bogdanović and Milica Vujković |
| I.8. | Synthesis of Zinc Doped Phosphate Tungsten Bronzes and its Redox Activity in Aqueous Solution of LiNO_3 Jovana Acković , Zoran Nedić, Tamara Petrović and Ružica Micić |
| I.9. | Cyclic Stability of Sodium-pillared Vanadium Oxides-carbon Composite in Aqueous Electrolytes Dušan Mladenović , Tamara Petrović, Danica Bajuk-Bogdanović, Biljana Šljukić Paunković, Slavko Mentus and Milica J. Vujković |
| I.10. | Electrochemical Properties of Active Carbon Materials Obtained from Biowaste Vladimir Dodevski , Milan Kragović, Milena Rosić, Sanja Krstić, Maria Čebela, Marija Stojmenović and Jelena Gulicovski |
| I.11. | Characterization and Application of Activated Carbon Materials Obtained from Sucrose by Chemical Activation Process Sanja Krstić , Branka Kaluđerović, Vladimir Dodevski, Maria Čebela, Milica Košević, Aleksandar Devečerski, Đorđe Petrović |

| | |
|-------|---|
| I.12. | Enhancement of Supercapacitors Energy Density Using Manganese Modified Carbon Electrode and Mixture of Multivalent Ions Electrolyte Nikola Zdolšek , Ivana Perović, Snežana Brković, Mina Seović, Slavko Dimović and Milica Vujković |
| I.13. | Al-ion Charge Storage Ability of Vine Shoots-derived Carbon Aleksandra Gezović , Jana Mišurović, Jugoslav Krstić, Nikola Simović, Veselinka Grudić, Robert Dominko, Slavko Mentus, Milica J. Vujković |
| I.14. | Al-ions Charge Storage Ability of the Conductive Polyaniline Emeraldine Salt Bojana Kuzmanović , Katarina Batalović, Bojana Paskaš Mamula, Mirjana Medić Ilić, Milica Vujković |

Poster session II, June 2, 2022

| | |
|-------|--|
| II.1. | The Influence of Reduced Graphene Oxide on the Pseudocapacitive Properties of a Conductive Polymer Layer for Supercapacitor Applications Gabrijela Ljubek and Marijana Kraljić Roković |
| II.2. | Preparation of flexible free-standing reduced graphene oxide paper containing Zn and V ₂ O ₅ for battery and hybrid supercapacitor application Dora Lovrenčić, Josipa Romić, Željka Petrović, Ivana Stojković-Simatović, Marijana Kraljić Roković |
| II.3. | Thermally Treated and Ion Beam Irradiated Graphene Oxide for Supercapacitor Application Željko Mravik , Milica Pejčić, Danica Bajuk-Bogdanović, Jelena Rmuš, Marko Jelić, Marija Grujić, Maria Vesna Nikolić, Nemanja Gavrilov and Zoran Jovanović |
| II.4. | The Effect of Chemical Titration and Thermal Treatment on Oxygen Functional Groups of GO and GO/WPA Nanocomposites Milica Pejčić , Željko Mravik, Danica Bajuk-Bogdanović, Snežana Uskoković-Marković, Bojana Nedić Vasiljević, Sonja Jovanović, Zoran Jovanović |
| II.5. | The Synthesis and Characterization of Yb ³⁺ and Ho ³⁺ Doped SrGd ₂ O ₄ Tijana Stamenković, Maria Čebela, Vesna Lojpur |
| II.6. | Synthesis, Structural and Morphological Properties of Multiferroics Maria Čebela , Milena Rosić, Vesna Lojpur, Vladimir Dodevski, Sanja Krstić |
| II.7. | Complex Metal Oxide Oxidation State Changes Monitoring by TGA and Dilatometric Means Nebojša Labus , Milena Rosić, Maria Čebela |
| II.8. | Experimental Investigation of Octahedral Tilting and Related Effects of Ca _{1-x} Gd _x MnO ₃ (x = 0.05, 0.1, 0.15, 0.2) Compound Milena Rosić , Maria Čebela, Nebojša Labus |

| | |
|--------|---|
| II.9. | A Series of Magnesium Vanadium Oxide Materials Potentially Applicable for Aqueous RMBs Milica M. Vasić , Milica Vujković |
| II.10. | A Comparison of the Capacities of ZnMn_2O_4 and $\text{ZnCr}_{0.15}\text{Mn}_{1.85}\text{O}_4$ in Aqueous Media Jelena Senćanski , Nenad Nikolić and Ivana Stojković-Simatović |
| II.11. | Mixed Ni-Mg Spinel Ferrites Used as Materials for Charge Storage Electrodes Milena Dojcinovic , Zorka Z. Vasiljevic, Vera P. Pavlovic, Jelena Vujancevic, Nenad B. Tadic, Maria Vesna Nikolic |
| II.12. | Al^{3+} Cation Interaction with Pristine and Defective Graphene Using Microsolvated Cluster Model: DFT Study Branislav Milovanović , Milica J. Vujković and Mihajlo Etinski |
| II.13. | Data-driven Design of New Mg-based Hydride Materials – A Synergy of Experiments and DFT Katarina Batalović , Jana Radaković, Bojana Kuzmanović, Mirjana Medić Ilić, Bojana Paskaš Mamula |
| II.14. | Electron Trapping and Energy Density in Polymers at Low Electric Field Duško Dudić |

Plenary Lectures

Crystal Chemistry of Advanced Polyanionic Positive Electrodes for Na-Ion Batteries

Christian Masquelier¹, Sunkyu Park^{1,2,3}, Jean-Noël Chotard¹, Dany Carlier²,

Laurence Croguennec², François Fauth⁴ and Pieremanuele Canepa

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Polyanionic materials (phosphates in particular) are of special interest as positive electrodes for Li-Ion or Na-ion batteries since they offer competitive electro-chemical performances compared to sodiated or lithiated transition metal oxides. [1,2] They are based upon stable 3D frameworks, which provide long-term structural stability and demonstrate a unique variety of atomic arrangements in their crystal structures. Recent electrochemical and structural investigations of vanadium-based phosphate compounds (LiVPO₄O-LiVPO₄F, Na₃V₂(PO₄)₂F₃, Na₃V₂(PO₄)₃ ...) revealed promising perspectives. [3-5]

The NASICON structural family with its large panel of compositions, Na_xMM'(PO₄)₃ (0 < x < 4 ; M, M' = Ti, Fe, V, Cr, Mn) is among the most widely investigated due to its specific three-dimensional framework structure, stable long-term cycling ability and high Na⁺ mobility. [1-2, 5-6] Among them, the vanadium phosphate Na₃V₂(PO₄)₃ [7] is of particular interest. We will present several new structures that we determined, from pristine powders or for intermediate compositions spotted by operando X-Ray diffraction.

Recently, we succeeded in synthesizing Fe-substituted Na₄FeV(PO₄)₃ that allows the reversible extraction of close to 3 Na⁺ (for two transition metals) and we will report on its crystal structure and on that of Na₃FeV(PO₄)₃ for which new Na⁺ order-disorder phenomena have been spotted. [8] Even more recently, we reported on the existence of an intriguing definite phase of composition Na₂V₂(PO₄)₃ through computational methods [9] and operando X-ray diffraction during battery operation. [10]

References:

- [1] C. Masquelier, L. Croguennec, *Chemical Reviews*, 113(8), 6552-6591 (2013).
- [2] P. Adelhelm, M. Casas-Cabanas, L. Croguennec, I. Hasa, A. Kopusov, S. Mariyappan, C. Masquelier, D. Saurel, *J. Power Sources*, 482, 228872 (2021).
- [3] E. Boivin, J. N. Chotard, C. Masquelier, L. Croguennec, *Molecules*, 26(5), 1428 (2021).
- [4] T. Broux, F. Fauth, N. Hall, M. Bianchini, T. Bamine, J.-B. Leriche, E. Suard, D. Carlier, L. Simonin, C. Masquelier & L. Croguennec, *Small Methods*, 3, 1800215 (2019).
- [5] F. Chen, V. Kovrugin, R. David, J. N. Chotard, O. Mentré, F. Fauth & C. Masquelier, *Small Methods*, 3, 1800218 (2019).
- [6] B. Singh, Z. Wang, S. Park, G. Sai Gautam, J.N. Chotard, L. Croguennec, D. Carlier, A. K. Cheetham, C. Masquelier & P. Canepa, *J. Mater. Chem. A*, 9(1), 281-292 (2021).
- [7] J.N. Chotard, G. Rousse, R. David, O. Mentré, C. Masquelier, *Chem. Mater.*, 27(17), 5982-5987 (2015).
- [8] S. Park, J. N. Chotard, D. Carlier, I. Moog, M. Courty, M. Duttine, F. Fauth, A. Iadecola, L. Croguennec, C. Masquelier, *Chem. Mater.*, submitted (2021) .
- [9] Z. Wang, S. Park, Z. Deng, F. Fauth, D. Carlier, L. Croguennec, C. Masquelier, J. N. Chotard, P. Canepa, *J. Mater. Chem. A.*, 10, 209-217 (2022).
- [10] S. Park, Z. Wang, Z. Deng, I. Moog, P. Canepa, F. Fauth, D. Carlier, L. Croguennec, C. Masquelier & J. N. Chotard, *Chemistry of Materials*, 34, 451-462 (2021).

Electrochemistry At the Nanoscale: Application to Materials for Energy Storage

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Growing demand for fast charging electrochemical energy storage devices with long cycle lifetimes for portable electronics has led to a desire for alternatives to current battery systems, which store energy via slow, diffusion-limited faradaic reactions. The closest devices that fit these demands are electrochemical capacitors (ECs), also called supercapacitors, which can be fully charged within minutes, with almost unlimited cyclability. However, the main challenge ECs are facing is the improvement of their energy density and this is why high-rate redox materials are also currently intensively investigated.

This presentation will give an overview of the research work achieved on capacitive (porous carbon) and high-rate redox (pseudocapacitive) materials, and show the challenges/limitations associated with the development of these materials. Starting with porous carbons [1,2], we will present the state-of-the-art of the fundamental of ion adsorption mechanism in porous carbons and its practical applications. Moving from double layer to high-rate redox materials, we will show how the control of the electrodes structure can help in preparing high capacitance electrodes using 2-Dimensional MXene materials in both aqueous and non-aqueous electrolytes [3-5].

This set of results helped in developing our basic understanding of the ion fluxes at the electrolyte/material interface as well as ion interactions in confined structures. From a practical point of view, they offer new opportunities for designing high energy density supercapacitors and high-power batteries.

References:

- [1] H. Shao, Y.-C. Wu, Z. Lin, P.-L. Taberna and P. Simon, *Chemical Society Reviews*, 2020, 49, 3005-3039.
- [2] P. Simon and Y. Gogotsi, *Nature Materials* 19 (11), (2020) 1151-11633.
- [3] I. Wu et al., *Angew. Chem.* (2021), 133,2-8.
- [3] B. Anasori et al., *Nature Reviews Materials*, vol. 2, no. 2, 2017, pp. 17.
- [4] X. Wang, et al., *Nature Energy* 4, 241-248 (2019).
- [5] Y. Li et al., *Nature Materials* (2020), 19, (2020) 894-899.

From Lithium Sulfur to Multivalent Sulfur Batteries

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Sulfur batteries are attractive high energy storage system, and they are considered as cheap and more sustainable devices compared to Li-ion batteries. Unfortunately, their performance is not yet suitable for large-scale commercialization. Polysulfide shuttle problem, electrolyte consumption for metal passivation, and redistribution of sulfur during battery operation are among the most critical problem that need to be solved. Polysulfide shuttle can be mitigated by a proper encapsulation of sulfur in the porous matrix which surface is protected for direct exchange of polysulfides with electrolyte. [1]

Sulfur conversion into sulfide, is similar when coupled with lithium, magnesium, or calcium metal anode. [2-4] The differences between the lithium and divalent anodes are related to the passivation phenomena of metal electrodes and the properties of electrolytes used in the full cell configuration. Soluble polysulfide act as redox reaction mediators and enable the growth of the surface films in 3D structures, however, their presence in the electrolyte is responsible for several changes of the electrolyte properties. [5,6] While an increase of viscosity and decrease of conductivity can be foreseen in Li-S batteries, the use of electrolytes for divalent batteries shows a much more complex behavior of dissolved polysulfides. [7,8]

References:

- [1] R. Dominko, et al., Polysulfides formation in different electrolytes from the perspective of X-ray absorption spectroscopy. *J. Electrochem. Soc.*, 165 (2018), A5014-A5019.
- [2] R Dominko et al., Analytical detection of polysulfides in the presence of adsorption additives by operando X-ray absorption spectroscopy. *J. Phys. Chem. C*, 119, (2015), p. 19001-19010.
- [3] A. Robba, et al., Mechanistic study of magnesium-sulfur batteries. *Chem. Mater.*, 29 (2017), 9555-9564.
- [4] A. Scafuri, et al., Spectroscopic insights into the electrochemical mechanism of rechargeable calcium/sulfur batteries, *Chem. Mater.*, 32 (2020), p. 8266-8275.
- [5] S. Drvarič Talian, et al., Which process limits the operation of a Li-S system? *Chem.mater.* 31 (2019), 9012-9023.
- [6] S. Drvarič Talian, et al., Impedance response of porous carbon cathodes in polysulfide redox system. *Electrochimica Acta*, 302 (2019) 169-179.
- [7] A. Robba, et al. Role of Cu current collector on electrochemical mechanism of Mg-S battery. *J. Power Sources*, 450 (2020), 227672-1-227672-7.
- [8] S. Drvarič Talian, et al., Magnesium Polysulfides: Synthesis, Disproportionation, and Impedance Response in Symmetrical Carbon Electrode Cells, *Chemelectrochem*, 8 (2021), 1062-1069.

How BATTERY 2030+ Could Animate the Research Efforts in Europe

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BATTERY 2030+ is a large-scale research initiative in Europe implementing the research described in our long-term research roadmap (www.battery2030.eu). Just now six projects and a coordination and support action are forming this large environment. The results from our efforts are now starting to appear and one of our goals is to share our knowledge, our methods and our ideas for use and inspiration to all battery scientists in Europe. This presentation will describe our work on standards for data sharing, battery ontologies, and how we will bring smart functionalities into the battery. The presentation will take examples from our projects: BIG-MAP, Bat4Ever, HIDDEN, INSTABAT, SENSIBAT, and SPARTACUS.

(Multi)-Functional Electrolytes for Lithium-Based Batteries: From Synthesis to Interfacial Electrochemistry

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In all types of current and future lithium-based batteries, electrolyte plays a central key role in terms of design and control of the electrode processes as well as regarding material interactions, performance, long-term stability, safety and last but not least the cost. Being the only component connecting all other active and inactive parts, electrolyte has a significant impact on many chemical and technological aspects of a battery. Although its role is often considered trivial, the right choice based on criteria that differ depending on the battery chemistry and application, is rather crucial. [1] Chemistry of liquid electrolytes and their interaction with anode and cathode materials is complex and yet not fully understood, thus representing a delicate balance of various properties. The development of new and improvement of existing electrolytes is strongly impacted by the complexity of interactions between electrolyte components with each other and with other battery components. Straightforward approaches for the optimization of existing electrolyte systems often lead to situations where specific properties can only be improved at the expense of other relevant properties. This implies that current electrolytes are already close to their optimum performance and that major gains can only be achieved with moving to substantially altered electrolyte systems.

Despite our limited knowledge, modern needs for battery electrolytes require the development of sophisticated electrolyte solutions with multifunctional components, able to simultaneously fulfill several duties. [2,3] Typical requirements include combined roles as conducting salt dissolution enhancers, viscosity deceasers, flame-retardants or effective electrolyte interphase formers at the electrodes. The introduction of these modern components can be regarded as a paradigm shift in order to increase the efficiency and safety of lithium-based and post-lithium-based batteries, when compared with nowadays technologies. The objective of advanced battery research and development relates to obtaining the best compromise among the determined goals, followed by a decision whether the balanced system should be implemented instead of a competing technology. To avoid a time-consuming traditional, trial and error approach, automated high throughput experimentation formulation-characterization-evaluation chain based on a set of previously established requirements and orchestrated by data-driven analysis is utilized for the effective optimization in electrolyte formulation and performance. [4]

This talk is an invitation to a journey of the scientific development, technology as well as engineering of selected classes of advanced liquid electrolytes for lithium-based batteries under systematic approach that allows to understand the structure-property-performance relationships of the selected compounds/formulations, their impact on the overall battery chemistry, performance and safety, thus helping to further tailor relevant properties of electrolyte components/formulations for considered cell chemistries and targeted applications.

References:

- [1] I. Cekić-Laskovic, C. Wölke, K. Xu, M. Winter, Electrolytes: From a Thorn Comes a Rose, and from a Rose, a Thorn *Isr. J. Chem.*, 61 (2021) 85-91.
- [2] I. Cekić-Laskovic *et al* Synergistic Effect of Blended Components in Nonaqueous Electrolytes for Lithium Ion Batteries (2017) 375:37.
- [3] N von Aspern, G.-V. Roeschenthaler, M. Winter, I. Cekić-Laskovic Fluorine and Lithium: Ideal Partners for High-Performance Rechargeable Battery Electrolytes, *Angew. Chem. Int. Ed.* 58 (2019).
- [4] I. Cekić-Laskovic *et al*, High-throughput experimentation and computational freeway lanes for accelerated battery electrolyte & interface development research, *Advanced Energy Materials*, (2021) 2102678.

Electrochemical Storage at CIC energiGUNE: Across Energy Storage Value Chain

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Energy storage plays, undoubtedly, a fundamental role in the process of total decarbonization of the global economy that is expected to take place in the coming decades. The energy transition to a renewable and sustainable generation will be the solution to reduce greenhouse gas emissions and thus achieve the European Commission's goal of becoming the world's first decarbonized economy.

At CIC energiGUNE, our mission is therefore aligned with this goal to contribute to the improvement of industry competitiveness and sustainable development, from a benchmark position in energy research, generating disruptive knowledge in materials and high-tech solutions. Within the electrochemical storage area, we work from the atom to the device, covering both initial and last stages of energy storage value chain. The Centre focuses on strategic knowledge areas such as technologies and applications associated with electrochemical storage. From lithium-ion batteries, that have already transformed our society by enabling the wireless revolution, to beyond-li ion technologies that promise higher energy density, safety and lower cost, among others. Not to mention supercapacitors, high power systems with outstanding stabilities, exceeding in most of the cases one million of cycles without significant decay of their pristine capacity. All this research is oriented towards the development of valuable electrochemical applications that can be transferred to industry and is boosted by the state-of-the-art platforms and facilities available within the Centre. At CIC energiGUNE we are also committed to providing a collaborative and dynamic learning environment through mentorship of master's and PhD students, teaching at Erasmus Mundus Master of Materials for Energy Storage and Conversion (MESc+) and other courses and seminars where we actively participate.

In this talk, a general overview of electrochemical storage area at CIC energiGUNE will be given along with specific research devoted to metal-air batteries. These batteries have been considered as the holy grail of battery research due to their high theoretical energy densities; however, several challenges remain to be solved before commercialization. Among metal-air batteries, rechargeable sodium oxygen batteries are receiving a great deal of interest due to their high gravimetric energy densities (1605 or 1108 Wh/kg based on Na₂O₂ or NaO₂ discharge products, respectively) resulting from the use of an oxygen-based phase-change reaction (potentially reducing the weight and freeing up space for other components). The main challenges remaining in this field will be highlighted, along with the future steps required to advance Na-O₂ batteries.

Invited Lectures

Towards Alternative Li-free Electrode Materials: Synthesis and Phase Composition Interrelation

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Design of cathode materials, in terms of tailoring phase composition, particle size and electronic conductivity, plays an important role for battery applications. In that context, a myriad synthesis routes [1] have been developed to optimize various Li-ion intercalation structures. Numerous challenges, aimed at their improving electronic and ionic wiring, have been addressed over the years, which finally resulted in the digital revolution of Li-ion batteries. Similar hurdles have to be overcome for Li-free materials (based on Na, Mg, Al, Ca etc.) on their path to becoming competitive with Li-ion technology. On one side, a rich experience with Li-ion batteries helps overcome certain barriers faster and prompt development of alternative technologies. On the other side, the specificity of electrode/electrolyte interface brings novel chemistries with their own shortcomings and challenges.

Polyanionic structures have attracted much scientific and technological interests for development of alkaline-ion batteries [1]. Herein, an overview on the research of specific family of novel, sodium mixed-polyanion phases (combining phosphate and pyrophosphate units in anionic sublattice) will express some unclarified issues and discrepancies appearing in literature [2]. The special attention will be paid to interrelation between the synthesis conditions and phase composition in light of tailoring sodium storage properties. The following key questions will be addressed: i) How to adjust synthesis conditions towards formation of mixed polyanion phase and what parameters are determining; ii) Does the pure phase show the best performance or whether its synergy with secondary polyanionic phases is a more appropriate solution. The results provide future directions towards the design of alternative Li-free polyanionic compositions.

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References:

- [1] C. Masquelier, L. Croguennec, Polyanionic (Phosphates, Silicates, Sulfates) Frameworks as Electrode Materials for Rechargeable Li (or Na) Batteries, *Chem. Rev.* 113 (2013) 6552.
- [2] A. Gezović[#], M. J. Vujković[#], Miloš Milović, V. Grudić, R. Dominko, S. Mentus, Recent developments of Na₄M₃(PO₄)₂(P₂O₇) as the cathode material for alkaline-ion rechargeable batteries: challenges and outlook, *Energy Storage Materials* 37 (2021) 243.

Comparison of Charge Storage Ability of Polyaniline and Poly(p-aminodiphenylamine)

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Conducting polymers are very diverse and interesting group of materials widely investigated for energy related applications since their discovery in 1970s. Nonetheless, thanks to their favorable properties and simple synthesis conducting polymers are still of great relevance for modern energy storage science. Polyaniline (PANI) is one of the most employed conducting polymers in supercapacitors [1] due to its high stability, low price, unique electronic, optical, structural and morphological characteristics that can be easily controlled by simple modification of synthetic route and by protonation and deprotonation processes [2]. Nowadays researchers are investigating the effect of different physicochemical properties of conducting polymers on their electrochemical behavior.

In this work we present capacitive properties of the two polymers, PANI and poly(p-PADPA), synthesized by the oxidative polymerization of aniline and p-aminodiphenylamine (p-ADPA), respectively, with the use of H₂O₂/Fe₃O₄ nanoparticles as the oxidant/catalyst system [3,4]. Although both synthesized polymers are predominately in the conductive PANI emeraldine salt form and show very close electrical conductivities, the charge storage ability of PANI was much higher than that of poly(p-PADPA). This difference is explained in light of the molecular structure and morphology of the two polymers, as revealed by FTIR and Raman spectroscopies and scanning electron microscopy.

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References:

- [1] A. Eftekhari, L. Li, Y. Yang, Polyaniline supercapacitors, *J. Power Sources*. 347 (2017) 86–107.
- [2] G. Ćirić-Marjanović, Recent advances in polyaniline research: Polymerization mechanisms, structural aspects, properties and applications, *Synth. Met.* 177 (2013) 1–47.
- [3] J. Mišurović, M. Mojović, B. Marjanović, P. Vulić, G. Ćirić-Marjanović, Magnetite nanoparticles-catalysed synthesis of conductive polyaniline, *Synth. Met.* 257 (2019).
- [4] J. Mišurović, M. Mojović, B. Marjanović, P. Vulić, G. Ćirić-Marjanović, Magnetite nanoparticles-catalyzed synthesis of conductive poly(p-aminodiphenylamine), *Synth. Met.* 269 (2020) 116577.

The Role of Surface Chemistry, Structure and Interactions in the Electrochemical Charge Storage Properties of Graphene Oxide and 12-tungstophosphoric Acid Nanocomposites

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Gaining a momentum from newly emerging properties of nanomaterials the further enhancement and integration of various functionalities have been made possible. Also, it became apparent that interaction between nano-objects can provide additional synergy capable of yielding new or significantly improved properties. This particularly applies to the surfaces and interfaces of nanomaterials where the intimate contact between components amplifies possible contributions of interfacial interactions. Since this aspect of interaction-property relation in many nanocomposites is still insufficiently explored, it is of interest to identify to what extent the properties emerge as a result of interaction-based synergy or a co-action of individual components. To address these aspects, we have investigated a nanocomposite of graphene oxide (GO) and 12-tungstophosphoric acid (WPA) – a combination of materials that are known for the rich “portfolio” of properties. In the talk the novel findings will be presented that contribute to better the understanding of interactions between nano-objects and how they contribute to novel properties. The results are showing how simple temperature treatment and weight ratio of components is influencing the evolution of surface, structural properties and charge storage properties – all closely connected to interactions between components. Finally, the implications on synthetic approaches and fine-tuning of the functionality of GO/WPA nanocomposites will be discussed from the perspective of the obtained results.

ElevenEs - The First LFP Gigafactory in Europe

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The EU targets 30 million electric vehicles (EVs) on the road by 2030. Furthermore, the share of renewable energy will rise to 40% of final consumption by 2030, up from roughly 20% in 2019. This transition will require massive battery storage systems. Global demand for lithium-ion batteries (LIB) will have increased 9-fold in the period of 2020-2030, whereas Europe will experience an even larger growth of 13x. The current market outlook is that at least an additional 2,600 GWh of production capacity will be needed by 2030, so the market size could reach €250 billion+ depending on pricing scenarios. When it comes to cathode active material used in LIBs, lithium iron phosphate (LFP) is predicted to outperform the market with 28x growth vs 11x for ternary chemistries from 2020-2030^[1].

LFP cathode chemistry was invented in 1996 by a battery pioneer and a Nobel Prize laureate John Goodenough at the University of Texas. The patents are held by a Swiss-based consortium, whose members are Hydro-Québec(Canada), Johnson Matthey (UK), University of Montreal (Canada) and National Center for Scientific Research (France). The patents' restrictions over LFP will start to expire in 2022. On the other hand, nickel and cobalt based ternary technologies, thanks to the higher gravimetric and volumetric energy density of NMC and NCA battery cells, have enabled a quicker achievement of performance and range in electric vehicles with a respectively higher material cost. Meanwhile, LFP was perceived as an unpromising technology with no real potential to increase the energy density on a chemistry level. However, Chinese developments in the past decade have proven LFP technology to be crucial for the mass adoption of EVs and data from 2021 shows LFP took over the Chinese EV market. In the only country in the world that has the know-how, resources, and mass production of all modern battery technologies, out of every three EV produced in January 2022 – two had an LFP battery^[2]. The developments are based not only on chemistry, but also engineering level. Cell-to-pack technology (CTP) has enabled LFP batteries, starting with a lower energy density of a single cell, to achieve ternary battery performance at the level of a complete battery pack of an EV. This is achieved by eliminating redundant (for LFP only) fireproofing material, modules' housings and structural battery parts. While in a ternary battery almost 40% of energy density is lost during cell-to-module-to-pack integration, in LFP the CTP approach allows for only 15% of cell's energy density to be lost. In turn, this has enabled the competitiveness of the LFP in a mid-size EV segment too, with models now offering over 600 km range^[3], similar to representative NCM622 EV products.

ElevenEs is the first LFP LIB Gigafactory project being developed in Europe. The existing R&D laboratory and offices are located in Subotica, northern Serbia. The brownfield of cca. 18ha planned for the Gigafactory has been acquired at the same location. ElevenEs is a spin-off from Al Pack Group, a multinational industry leader in aluminum processing with operations in 3 countries and 20,000 m² of production space. Al Pack Group has more than 25 years of experience and knowledge in high precision processing of aluminum including mixing, coating, calendering, and deep drawing - all closely related to electrode manufacturing in LIB production process. The vision was demonstrated in July 2020, when after a year of analysis, it was decided that the company would focus exclusively on the development of LFP technology. The R&D center is fully operational from July 2021 and will be expanded to 1,500 m² of total space in 2022. The Megafactory with a planned 300 MWh large pilot capacity will commence initial production by 2023. With planned Gigafactory two-phase expansion, the company will reach 8 GWh of annual production by 2025 and the full capacity of 16 GWh by 2027/28, achieving the economies of scale. So far, ElevenEs has on boarded people with experience of working in BYD, SVOLT, Volvo, EIT InnoEnergy, Lazard, Mubadala, etc. ElevenEs is backed by EIT InnoEnergy, a leading pan European new energy technologies and battery development investment firm. The European Institute of Innovation & Technology (EIT) is an independent body of the European Union set up in 2008 to deliver innovation across Europe.

References:

- [1] [International Energy Agency \(IEA\) Global EV Outlook 2020](#)
- [2] [Cleantechnica Chinese EV market 2022](#)
- [3] [The New Future: Upcoming EVs in 2022](#)

Polypyrrole-silver Chloride Composite as Energy Storage Materials

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Over the last decades we are witnesses of astonishing development of different electrode materials for alkali-ion and metal-air batteries [1] supercapacitors [2] and supercapattery [3]. Even so, some rather old electrochemical systems have still space for further improvement. Seawater-activated primary battery, as another example of the old systems, discovered in 1878 [4] and developed by Bell Telephone Laboratories in 1945 as the power source for electric torpedoes, are used for a wide range of applications. [5]. Among many different cathode materials, silver chloride (AgCl) and lead chloride (PbCl₂) are most widely applied [5]. An improvement of AgCl synthesis is reported in our previous work [6] in which the fast and low-cost modified process of successive ion layer adsorption and reaction (SILAR) is effectively applied to form carbon felt-silver chloride cathode materials for primary cell.

In this work we investigated electrochemical synthesis of polypyrrole on a carbon felt (CF/PPy) electrode. Further, the CF/PPy electrode is modified by AgCl by applying modified SILAR method. Using the cyclic voltammetry and charge discharge techniques, it is shown superior behavior of composite CF/PPy-AgCl electrode. For the possible rechargeable aqueous based magnesium alloy AZ63 | 3.5% NaCl | CF/PPy-AgCl cell in the current range of 135 to 1350 A g⁻¹ the specific capacity in the range of 35-25 Ah kg⁻¹, energy of 45-25 Wh kg⁻¹ and power of 100 to 1600 W kg⁻¹ are obtained. Also the cyclic stability is determined, and concluded that such a simple cell using small photovoltaic cell could be charged at least 100 times, depending of Mg-alloy mass. The possibilities of further improvement of the system is considered.

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References:

- [1] E. Pargoletti, S. Arnaboldi, G. Cappelletti, M. Longhi, D. Meroni, A. Minguzzi, P. Mussini, S. Rondinini, A. Vertova, Smart interfaces in Li-ion batteries: near-future key challenges, *Electrochimica Acta*, 415 (2022), 140258.
- [2] Y. Wang, J. Guo, T. Wang, J. Shao, D. Wang, Y.-W. Yang, Mesoporous transition metal oxides for supercapacitors, *Nanomaterials*. 5 (2015) 1667.
- [3] L. Guan, L. Yu, G.Z. Chen, Capacitive and non-capacitive faradaic charge storage, *Electrochimica Acta*, 206 (2016) 464.
- [4] W. de la Rue, H.W. Muller, Experimental researches on the electric discharge with the chloride of silver battery, *Phil. Trans. Roy. Soc. Lond.*, 169 (1878)55.
- [5] H. Kobashi, M. Oshitani, PRIMARY BATTERIES – RESERVE SYSTEMS, Seawater Activated Batteries: Magnesium, Ed.: J. Garche, in: *Encyclopedia of Electrochemical Power Sources*, Elsevier B.V., 2009, Pages 156-163.
- [6] B.N. Grgur, J. Gojgić, M. Petrović, A novel method of preparing the silver chloride cathode for the magnesium seawater activated primary cell, *Journal of Power Sources*, 490 (2021) 229549.

Importance of the Simultaneous Testing of Positive and Negative Electrodes in Batteries and Supercapacitors

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The testing of electrochemical power sources is routinely done by electrochemical methods in a two-electrode system. With such methods, the overall properties of devices are obtained. However, in order to make further improvements to their performance, it is of key importance to separate the processes occurring at both electrodes during charging/discharging reactions. Such measurements would reveal electrodes of limiting capacitances, rate-determining step, various polarizations and the potential distribution through the devices as well as the occurrence of various resistances within different parts of the cell.

In this presentation, the studies of simultaneous testing of both electrodes will be presented with a particular focus on symmetrical carbon/carbon supercapacitors.

Organic Cathodes for Multivalent Metal Batteries – Prospects and Challenges

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The transition from fossil fuels to more sustainable energy alternatives necessitates significant advances in our ability to store energy on a global scale. Safe and inexpensive batteries are crucial for this purpose. Rechargeable batteries based on the use of metal anodes coupled with multivalent charge carriers, such as magnesium and calcium, hold a promise of high energy densities. By combining energy-dense metal anodes with environmentally friendly and high-capacity organic cathodes, the full potential of multivalent battery technology might be achieved. Despite research efforts, multivalent-metal-organic batteries still fall behind their monovalent counterparts, mainly in terms of capacity utilization. This talk will give an outline of the recent developments in organic-multivalent batteries, with the focus on specific issues hindering the performance of the systems in question. Comprehensive electrochemical impedance spectroscopy study of multivalent-organic batteries will be presented.

Mesoporous electrodes based on carbon nanofibers and transition metal spinel oxides for energy storage applications

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Driven by the search for more efficient energy storage technologies, supercapacitors have attracted worldwide attention in recent years due to their unique properties of fast charging/discharging, very high-power density, and environmental friendliness. However, the energy density is less than expected and it is crucial to develop novel high-performance electrode materials. Herein, mesoporous composite materials made of carbon nanofibers (CNFs) coupled with cobalt/manganese spinel oxides have been produced by a facile two-step process. The first step involved electrospinning of phase-separated polymer solutions and cobalt/manganese acetate precursors. In the second step, these hybrid nanofibers were converted into composite nanostructures. The phase composition of spinel nanocrystals, with an estimated diameter in the range between 13 and 60 nm, has been successfully controlled by varying the ratio of metallic precursors in the electrospinning process. The unique structural and surface properties of composite materials, tested by advanced characterization methods, significantly affect the electrochemical performance. Self-standing electrodes in alkaline electrolyte behave as battery-like materials and have high values of specific capacity up to 68.5 mAh g⁻¹. By testing electrodes in devices with symmetrical configuration, high capacitance values up to 384 F g⁻¹ were obtained. Excellent stability was achieved with over 95% of all tested electrodes. Very high energy density of 11.5 Wh kg⁻¹ at low potential sweep rates, and the superior power density of 2.6 kW kg⁻¹, indicate that these composites are attractive for high-performance electrodes in supercapacitors.

Poster Sessions

Electrochemical Formation and Behavior of Silver and Lead Chlorides as Potential Cathodes for Rechargeable Magnesium Seawater Battery

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The rapid increase in global energy consumption, along with the depletion of fossil fuels and ongoing climate change require higher efficiency and more reliable electrochemical power sources based on the current rechargeable batteries and supercapacitors. [1] Among the state-of-the-art lithium-ion, secondary cells are the most widely used electrochemical energy storage devices in various fields, due to the high energy density of the cell. [2] However, the cost-ineffectiveness and time-consuming extraction process of Li systems are the main reasons why researchers are looking for alternatives. Even rather old, the seawater-activated primary battery that has been discovered in 1978. [3], is becoming a hot topic among the scientific community. Magnesium seawater activated batteries rely on magnesium alloy as the anode material, while among different cathode materials, silver chloride (AgCl) and lead chloride (PbCl₂) are most widely applied. [4]

In this work, we presented a novel method of electrochemical synthesis of silver chloride (AgCl) and lead chloride (PbCl₂) electrodes using the galvanostatic charge/discharge techniques and we investigated the characteristics of possible rechargeable magnesium seawater-activated cells.

For the possible rechargeable aqueous-based magnesium alloy AZ63 [3.5% NaCl | Ag|AgCl cell in the current range of 0.4-2.9 A g⁻¹ the specific capacity in the range of 192-140 Ah kg⁻¹, the energy of 285-199 Wh kg⁻¹, and power of 575 to 4135 W kg⁻¹, and for AZ63 [3.5% NaCl | Pb|PbCl₂ in the current range of to 0.4-3.44 A g⁻¹ the specific capacity in the range of 127-83.6 Ah kg⁻¹, the energy of 130-84 Wh kg⁻¹ and power of 481 to 3463 W kg⁻¹ are obtained.

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References:

- [1] L. Guan, L. Yu, G.Z. Chen, Capacitive and non-capacitive faradaic charge storage, *Electrochimica Acta*, 206 (2016) 464.
- [2] E. Pargoletti, S. Arnaboldi, G. Cappelletti, M. Longhi, D. Meroni, A. Minguzzi, P. Mussini, S. Rondinini, A. Vertova, Smart interfaces in Li-ion batteries: near-future key challenges, *Electrochimica Acta*, 415 (2022) 140258.
- [3] W. de la Rue, H.W. Muller, Experimental researches on the electric discharge with the chloride of silver battery, *Phil. Trans. Roy. Soc. Lond.*, 169 (1878) 55.
- [4] H. Kobashi, M. Oshitani, PRIMARY BATTERIES – RESERVE SYSTEMS, Seawater Activated Batteries: Magnesium, Editor: Jürgen Garche, *Encyclopedia of Electrochemical Power Sources*, Elsevier B.V., 2009, Pages 156-163, ISBN 9780444527455.

Synthesis and Characterization of Cathode Material $\text{MgCr}_{0.15}\text{Mn}_{1.85}\text{O}_4$ for Magnesium Ion Batteries

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Electrochemical energy storage systems, primarily lithium-ion batteries, have experienced a huge expansion in the last couple of decades, but as they are very expensive to manufacture a lot of effort is being put into finding a more affordable replacement. For this purpose, multivalent cation compounds whose crystal structure is similar to the crystal structures of lithium compounds used in lithium-ion batteries are often studied. Magnesium cation is particularly interesting due to its high availability, significantly lower cost and high theoretical capacity. [1] As it is known that the addition of chromium ions to the lithium form of this compound increases the stability of capacity during cycling, in this study one part of manganese ions in MgMn_2O_4 was replaced by chromium ions. $\text{MgCr}_{0.15}\text{Mn}_{1.85}\text{O}_4$ was synthesized to investigate the effect of MgMn_2O_4 doping with Cr^{3+} ions.

The synthesis of $\text{MgCr}_{0.15}\text{Mn}_{1.85}\text{O}_4$ was performed by glycine-nitrate process, then part of the synthesized material was annealed at 700 °C, and the other part at 800 °C, and the obtained materials were tested in parallel. Structural analysis of the material was performed by X-ray diffraction, morphology was determined by scanning electron microscopy, and particle size by laser light diffraction, while thermal stability was tested by differential thermal analysis. It was confirmed that two phases are present in the samples - tetragonal, which is characteristic of MgMn_2O_4 , and cubic, which is characteristic of MgCr_2O_4 . From the data on the morphology of the material, it was concluded that the material is formed by agglomerates in the form of a three-dimensional network, and that the material annealed at 700 °C has larger and more adherent particles due to which it has a smaller active surface, in comparison to material annealed at 800 °C which has less cohesive particles that form agglomerates of smaller average size. Also, it was shown that there is a difference in the particle shape of the two materials - $\text{MgCr}_{0.15}\text{Mn}_{1.85}\text{O}_4$ particles annealed at 800 °C show mostly tetragonal shape, while those annealed at 700 °C show predominantly larger cubic particles. To study the electrochemical behavior of the material the following methods were used: cyclic voltammetry, galvanostatic cycling and chronopotentiometry. It has been shown that the material annealed at 700 °C has poor electrochemical behavior, while the material annealed at 800 °C has better electrochemical behavior. Both materials are electrochemically stable at different cycling current densities, and the charge and discharge capacities increase with increasing number of cycles due to the repositioning of particles of the material in a way that allows better ion passage until the maximum value of capacity is reached, after which its value starts to decrease due to permanent incorporation of magnesium ions into the structure. The tested materials show lower capacities compared to MgMn_2O_4 [2] due to the lower content of manganese ions, but the material annealed at 800 °C also shows significantly higher stability of capacities during cycling. From this it can be seen that the cation doping had the desired, expected effect of stabilizing the discharge capacity.

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References:

- [1] Priyono, S., Ginting, N. R., Humaidi, S., Subhan, A., & Prihandoko, B. Synthesis of lithium manganese dioxide (LiMn_2O_4) for lithium-ion battery cathode from various lithium sources. *Journal of Physics: Conference Series*, 2018.
- [2] Jokić N, Karakterizacija katodnog materijala MgMn_2O_4 , diplomski rad, Fakultet za fizičku hemiju, 2019.

Comparative Study of Li-ion Intercalation into $\text{LiCr}_{0.15}\text{Mn}_{1.85}\text{O}_4$ from Aqueous and Organic Electrolyte

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Electric vehicles using rechargeable Li-ion batteries (LIBs) are one of the most efficient ways to solve modern problems of industrialization – environment pollution and shortage of oil sources. Spinel LiMn_2O_4 is one of the most common cathode materials used for this purpose due to its safety and ultra-fast charging capabilities [1]. Previous research showed that chromium doped spinel $\text{LiCr}_{0.15}\text{Mn}_{1.85}\text{O}_4$ gives smaller capacities, but better capacity retention [2]. The objective of the experimental work conducted here was to compare electrochemical capabilities of chromium doped spinel, synthesized by the same method, as cathode for LIBs in aqueous and organic electrolyte. $\text{LiCr}_{0.15}\text{Mn}_{1.85}\text{O}_4$ was prepared by the glycine-nitrate method and characterized by XRPD and SEM. Its electrochemical behavior, as a cathode material for LIBs, was studied in saturated aqueous solution of LiNO_3 and 1M solution of LiClO_4 in propylene carbonate by means of cyclic voltammetry (CV) and galvanostatic (GS) cycling, at room temperature. GS cycling in aqueous electrolyte was performed in a 3-electrode regime. The CV curves at a scan rate of $5 \text{ mV}\cdot\text{s}^{-1}$ of the material in the water electrolyte show two pairs of clearly separated sharp redox peaks, while in the case of the organic electrolyte these peaks are clearly present, but overlapped. GS cycling of $\text{LiCr}_{0.15}\text{Mn}_{1.85}\text{O}_4$ cathode, in both electrolytes, was performed at current rates 1C, 2C and 5C for 50 cycles, and then again at 1C for 25 cycles. The initial discharge capacity of $\text{LiCr}_{0.15}\text{Mn}_{1.85}\text{O}_4$ in aqueous electrolyte is 108.1 , 107.2 , $101.5 \text{ mAh}\cdot\text{g}^{-1}$ at 1C, 2C and 5C with capacity retention of 97.1%, 93.5% and 91.5%, respectively, after 50 cycles. After returning to 1C, capacity increases to $118.1 \text{ mAh}\cdot\text{g}^{-1}$, but after 25 cycles capacity retention is lower and amounts 87.4%. For the organic electrolyte, initial discharge capacities stand at 109.0 , 99.2 , 76.9 and $100.6 \text{ mAh}\cdot\text{g}^{-1}$ at 1C, 2C, 5C and 1C, with capacity retention of 93.9%, 98.7%, 85.9% and 98.2%, respectively, after 50 cycles for the first three current rates, and after 25 cycles for the final current rate of 1 C. The Coulombic efficiency is found to be better in organic electrolyte.

References:

- [1] W. Tang, S. Tian, L. L. Liu, L. Li, H. P. Zhang, Y. B. Yue, Y. Bai, Y. P. Wu., K. Zhu, Nanochain LiMn_2O_4 as ultra-fast cathode material for aqueous rechargeable lithium batteries. *Electrochemistry Communications*, 13 (2011) 205-208.
- [2] N. Cvjetičanin, I. Stojković, M. Mitrić, S. Mentus, Cyclic voltammetry of $\text{LiCr}_{0.15}\text{Mn}_{1.85}\text{O}_4$ in an aqueous LiNO_3 solution. *Journal of Power Sources*, 174 (2007) 1117-1120.

Catalysts Toward Highly Efficient Rechargeable Metal-air Batteries: Polyoxometalates with Reduced Graphene Oxide

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Due to the economic problems related to using platinum-group metal (PGM) electrocatalysts in rechargeable metal-air batteries (RMAB), there is developing technology focusing on polyatomic ions as catalysts. These ions are known as polyoxometalates (POMs), usually Keggin type, and consist of one tetrahedron unit with a central heteroatom (P, Si), four oxygen atoms, and twelve octahedral MO₆ units (M = Mo, W, V) that are linked to one another by shared oxygen atoms. POMs containing transition metals and layered on carbonate or silica frameworks could be promising for rechargeable metal-air batteries use, overcoming the problems of POMs' high solubility and low surface area and leading to improved electrocatalytic activity. [1]

This study introduces composite materials based on POMs containing transition metals: Co, Mn, Fe, Cu and Ni, and reduced graphene oxide (rGO). XRD and FTIR analysis confirmed the formation of POM/rGO composites. In the search for materials with the best activity for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) occurring at the positive electrode of RMABs, materials' performance was observed via cyclic voltammetry with a rotating disc electrode. All materials showed activity for ORR as evidenced by a clear peak at 0 rpm corresponding to O₂ reduction. Tafel analysis revealed Tafel slopes ranging from -0.154 to -0.180 V dec⁻¹. The number of transferred electrons during ORR was calculated using the Koutecký Levich equation and found to be close to 2, indicating the two-electron pathway. When it comes to OER, Ni-containing POM/rGO composite showed the highest current density and the lowest Tafel slope value.

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References:

[1] Y. Kim and S. Shanmugam, Polyoxometalate–reduced graphene oxide hybrid catalyst: synthesis, structure, and electrochemical properties, ACS Appl. Mater. Interfaces 2013, 5, 22, 12197–12204.

Carbon Encapsulated Fe-species as Anodes in Alkaline Batteries

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Modern, high energy density electrochemical devices are based around the use of organic electrolytes. Push towards more environmentally friendly, cost effective, renewable/reusable, and overall green approaches has shifted some of the attention towards aqueous battery systems [1]. Material design and tailored synthesis procedures of new nano-architectures have significantly increased capacitance of materials used in aqueous systems [2]. Among them, Fe-species, with their main $\text{Fe}^{2+}/\text{Fe}^{3+}$ pair, have attracted considerable attention due to remarkable redox stability and iron availability/non-toxicity. Herein we propose a new approach to Fe-based materials architecture by electrochemical iron mono-dispersion inside alginate scaffold. Subsequent chemical and/or thermal treatments of the prepared gel allowed us to prepare different nano/micro-sized iron oxide, iron carbide and iron sulfide particles imbedded inside carbon support. Amount of this carbon support can be adjusted by thermal treatment to the optimal amount where it provides sufficient conductivity but does not decrease gravimetric capacitance. Cyclic voltammetry measurements of these materials in 4M KOH show prominent peaks related to $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox pair, possibly Fe^{2+}/Fe reduction and even H_2 evolution at the most negative potentials. Initial cycles of Fe-oxide/C sample are characterized by at least three oxidation peaks, probably due to transformation of various Fe-oxide species (@ -1.05V , -0.97V , -0.78V vs. SCE), which merge into one (@ -0.78V vs. SCE) corresponding to $\text{Fe}(\text{OH})_2$ transformation into Fe_3O_4 and/or FeOOH [2]. Significant peak separation is evidenced for this sample, decreasing its efficiency; however, it possesses remarkable stability with no capacitance loss after 200 cycles. Sample with different Fe-sulfide species and possibly some Fe_3C initially displays two oxidation peaks (@ -0.96 and -0.78V vs. SCE) with the second one diminishing with every cycle and eventually disappearing after 20 cycles. First peak is much more stable with significantly lower peak separation. Characterization is underway to identify phase related to this transition and towards gearing synthesis condition which could produce a material predominant in this crystal structure.

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References:

- [1] R. Bu, Y. Deng, Y. Wang, Y. Zhao, Q. Shi, Q. Zhang, Z. Xiao, Y. Li, W. Sun, and L. Wang, Bucket Effect: A Metal–Organic Framework Derived High-Performance $\text{FeS}_2/\text{Fe}_2\text{O}_3@S\text{-rGO}$ Negative Material for Enhanced Overall Supercapacitor Capacitance ACS Appl. Energy Mater., 4 (2021) 11004.
- [2] B. T. Hang and T. T. Anh, Controlled synthesis of various Fe_2O_3 morphologies as energy storage materials, Scientific Reports, 11 (2021) 5185.

Challenges in Sustainable Use of Lithium for Highly Innovative Final Products Created and Made in Serbia with EU Environmental Standards

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Energy systems of the future should enable transition to clean energy and reduction of CO₂ emission. Various options are under consideration and research. One direction of development are photovoltaic, and rechargeable batteries used to store the electricity needed for vehicles and stationary systems (1,2). At the current technological level and market attractiveness among rechargeable batteries significant group are those based on lithium. EU production of raw materials for all batteries is about 1%. Growing demand for lithium are expected in 2050 to be 10-50 times higher than 2018. A lithium deficit in the market is expected (3,4). The companies are searching new locations for lithium mining and production facilities in order to compensate for the deficit.

The mineral named Jadarit found in Serbia, contains lithium, sodium, boron and silica. Estimated reserves of Jadarit are of low significance for World production of lithium, but may be significant at EU level and for Serbian economy. Certain companies are interested to enter the production chain from Jadarit. These companies present the possibility for future industrial battery development in Serbia, which may lead innovative final products. They claim optimistic 3-15% increase of GDP (5).

Public debate provided argued shortcomings of currently proposed technology for lithium extraction from Jadarit (6). Major concerns are regarding permanent devastation of lush ecosystem, fertile soil, drinking water, air pollution. These non-monetary assets and their contribution to GDP should be monetized as *sine qua non* for objective cost-benefit analysis. Therefore, instead of polarization, public debate that identifies key critical points in technology of lithium extraction and its effects on human health and environment provides basis for future research that will develop new technologies capable to protect environment.

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References:

- [1] A. Pfeifer, L. Herc, I. Batas Bjelić, N. Duić, Flexibility index and decreasing the costs in energy systems with high share of renewable energy. *Energy Convers. Manag.* 240, 114258 (2021).
- [2] N. Kittner, F. Lill, D. M. Kammen, Energy storage deployment and innovation for the clean energy transition. *Nat. Energy.* 2, 17125 (2017).
- [3] GROW.R.2.DIR, "Critical Raw Materials for Strategic Technologies and Sectors in the EU - A Foresight Study" (2020), (available at <https://ec.europa.eu/docsroom/documents/42881>).
- [4] P. Greim, A. A. Solomon, C. Breyer, Assessment of lithium criticality in the global energy transition and addressing policy gaps in transportation. *Nat. Commun.* 11, 4570 (2020).
- [5] Jadar Project – What is known? Serbian Academy of Sciences and Art, March 1st 2022. Belgrade, ISBN: 978-86-7025-924-9.

Layered CaV_2O_6 as Promising Electrode Material for Aqueous Calcium-ion Batteries

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Lithium-ion batteries are the state-of-the-art electrochemical energy storage technology for portable electronic devices and electric vehicles owing to their exceptional energy and power density, cyclic stability, and high cell voltage. However, Li-ion large-scale applications are seriously limited by the low lithium abundance associated with the high price. Other crucial drawbacks of Li-ion batteries are their toxicity and safety concerns. Therefore, mentioned burning issues led to the search for alternative batteries, which will be a good choice in terms of energy and power, low cost, and eco-friendliness. Alternative earth-abundant and non-toxic metals and their ions, such as Ca, are potential candidates for rechargeable batteries to reduce the cost and impact on the environment. Also, Ca^{2+} ions could transfer two electrons per redox process, which theoretically positively affects battery performance. The only obstacle is the difficulty of finding materials upon which multivalent ions will intercalate with a fast diffusion rate. Layered metavanadate ($\text{M}^{\text{II}}\text{V}_2\text{O}_6$) materials became promising host materials for rechargeable batteries, especially for the multivalent-ion battery. So herein, CaV_2O_6 layered precursor was prepared by a standard sol-gel combustion route. Two samples were synthesized, the first when the precursor was heated at 400 °C (CaVO) and the second when CaVO was integrated with ten wt % of sucrose under thermal treatment at 400 °C in an Ar atmosphere (CaVO/C). Obtained CaVO and CaVO/C powders were thoroughly characterized by XRD, TG-DTA, SEM, FTIR, and Raman spectroscopy. The electrochemical performance of the obtained samples was evaluated for multivalent-ion storage in saturated aqueous electrolytic solutions of $\text{Ca}(\text{NO}_3)_2$ (5 M) by cyclic voltammetry and chronopotentiometry. For comparison, measurements were also done in saturated LiNO_3 (6 M). Results indicated that both samples in LiNO_3 show a substantial loss of capacity upon cycling, which is not observed in the case of $\text{Ca}(\text{NO}_3)_2$. CaVO/C composite showed a significant improvement in Ca storage capacity compared to the Ca storage capacity of CaVO, and also, its value exceeded the capacity storage of Li^+ ions. The high and stable discharge capacity of CaVO/C acquired in $\text{Ca}(\text{NO}_3)_2$ amounts to 89.3 mA h g^{-1} at 0.5 A g^{-1} . This work provides CaV_2O_6 as a compelling electrode material and promising results for Ca-ion batteries.

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Synthesis of Zinc Doped Phosphate Tungsten Bronzes and its Redox Activity in Aqueous Solution of LiNO_3

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Phosphate tungsten bronzes (WPB) have been intensively investigated for many applications due to their interesting chemical, optical, electrical, and mechanical properties. Their most known usages are as a pigment in traditional ceramics, a chemical sensor in different electric and electrochromic devices, and an electrocatalyst in fuel cells. Phosphate tungsten bronzes have a specific layered structure formed by the collapse of the Keggin anion at a temperature around 602 °C. Its three-dimensional network structure consists of interconnected PO_4 tetrahedra and WO_6 octahedra. In such a structure, pentagonal and hexagonal openings (cavities, channels) are formed, allowing diffusion of small ions like Li^+ . Due to WPB's metallic properties, the high oxidation state of tungsten, and the existence of different channels for the accommodation of Li^+ ions, make this material suitable as electrode material in Li-ion batteries. The redox activity of these materials has already been tested, and the obtained results have encouraged further research of these compounds as potential electrode materials. According to the literature, WPB materials are defined by electrochemical instability and decrease of columbic capacity upon intercalation/deintercalation processes. In order to try to stabilize the structure of WPB upon intercalation/deintercalation processes, WPB materials were doped with divalent cations. In this work, synthesized 12-tungstenphosphoric acid ($\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$, WPA) was further ionically exchanged with Zn^{2+} ions, which gave 12-tungsten phosphoric acids of the transition metal ($\text{ZnPW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$, ZnWPA). ZnWPA was then subjected to thermal analysis, which determined the phase transition temperature (when the Keggin anion collapses). The temperature of collapsing the Keggin anion is about 600 °C, and at this temperature, ZnWPA was heated for 10 minutes to obtain phosphate tungsten bronzes doped with zinc ($\text{ZnPW}_8\text{O}_{26}$, ZnWPB). Obtained ZnWPB was further characterized by XRD and FTIR, which confirmed the formation of the desired structure. The initial electrochemical measurements were done in the aqueous solution of LiNO_3 (6 M) by cyclic voltammetry. Initial cycling at a scan rate of 20 mV s^{-1} shows good electrochemical stability of ZnWPB. Obtained results open new directions toward further research of ZnWPB as potential electrode material for rechargeable batteries.

Cyclic Stability of Sodium-pillared Vanadium Oxides-carbon Composite in Aqueous Electrolytes

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Adaptable interlayer distance and a multivalent state of vanadium make layered vanadium oxides suitable electrode materials for different types of batteries, including both those containing aqueous and nonaqueous electrolytes. [1] Herein, composite of sodium vanadate and commercial carbon powder was prepared by one-pot hydrothermal synthesis. XRD analysis of the composite revealed presence of two vanadate phases: $\text{NaV}_6\text{O}_{15}$ and $\text{Na}_2\text{V}_6\text{O}_{16}$, while SEM and TEM analysis revealed presence of two morphologies: nanowires and nanospheres. The observed diverseness of the composite's phases and morphology results from the presence of carbon nanoparticles acting as a nucleation seed during the synthesis process. The synthesized heterostructured composite was next used as anode in an aqueous Li-ion battery, exhibiting enhanced charge storage upon dc charging compared to $\text{NaV}_6\text{O}_{15}$ or $\text{Na}_2\text{V}_6\text{O}_{16}$ nanowire anodes under the same conditions. Subsequently, insertion capability of the composite towards several mono (Li^+ , Na^+) and multivalent (Ca^{2+} , Mg^{2+} , Al^{3+}) ions in aqueous electrolytes was probed using cyclic voltammetry. The capacity stability was found to be dependent on the type of cation, increasing in the following order $\text{Al}^{3+} < \text{Li}^+ < \text{Mg}^{2+} < \text{Ca}^{2+}$ (capacitance retention of 64% of the initial value upon 100 potentiodynamic charging/discharging cycles). This higher capacity retention in case of Ca-containing electrolyte was attributed to the coinsertion of H_2O and OH^- species, resulting in less strained and less soluble vanadium ions. Cyclic behavior of the synthesized vanadate composite in the electrolyte containing Ca^{2+} ions was further observed to be dependent on the electrolyte's composition (type of anion), its concentration and pH value. The herein obtained results open a new perspective in the development of batteries involving vanadate towards more sustainable and cheaper electrochemical energy storage.

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References:

[1] M. Vujković, B.S. Paunković, I.S. Simatović, M. Mitrić, C.A.C. Sequeira, S. Mentus, Versatile insertion capability of $\text{Na}_1.2\text{V}_3\text{O}_8$ nanobelts in aqueous electrolyte solutions, *Electrochim. Acta.* 147 (2014) 167–175. <https://doi.org/10.1016/j.electacta.2014.08.137>.

Electrochemical Properties of Active Carbon Materials Obtained from Biowaste

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Activated carbons were successfully prepared using biowaste as a cheap and renewable raw material. Carbonization was performed on biomass first under nitrogen N₂ atmosphere at 850°C, and then were physical activated at different temperatures and different times of activation in atmosphere of carbon dioxide CO₂. The influence of temperature and time of activation on physical, structural and morphological properties was studied by XRD, Raman spectroscopy, FTIR, BET, SEM analysis. The increase of temperature and activation time leads to the increase of specific surface area of carbon material. The charge storage ability was evaluated and systematically studied by means of Cyclic Voltammetry and Impedance method. The specific discharge capacitance of activate carbon materials in different pH–aqueous electrolytes (KOH, Na₂SO₄ and H₂SO₄), increases with the surface area, indicating that the double layer charging is controlled primarily by the development of surface porosity. The active carbon material with the most developed porosity maintained a high capacitance of 110.06 Fg⁻¹ in KOH, 80.62 Fg⁻¹ in Na₂SO₄ and 126.9 Fg⁻¹ in H₂SO₄, at a very high scan rate of 300 mVs⁻¹. The micro/mesoporosity, depending on the type of aqueous electrolyte, was found to control not only the specific capacitance of materials, but also the hydrogen storage, C–H bonding and the relaxation time of adsorption.

Characterization and Application of Activated Carbon Materials Obtained from Sucrose by Chemical Activation Process

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In presented work, influence of temperature, starting material concentration and different activation agents (hydroxides) on properties and morphology of activated carbon materials obtained from sucrose were investigated. [1] The samples were prepared by hydrothermal treatment and activated using KOH, NaOH and LiOH. Two saccharose concentrations (0.5, 1.0 mol/dm³) and three different temperatures (180, 220, 260 °C) were changed in hydrothermal treatment. Activation processes were performed at 800 °C under inert atmosphere. Obtained samples were characterized by X-ray powder diffractometry, elemental analysis, N₂ adsorption-desorption measurements, Fourier-transform infrared spectrometry, scanning electron microscopy and thermal analysis. [2] The obtained samples were tested for potential application for cyclic voltammetry and electrochemical impedance spectroscopy and correlated to physicochemical properties.

References:

- [1] B. Hu, K. Wang, L. Wu, S. H. Yu, M. Antonietti, M. Titirici, Engineering Carbon materials from the hydrothermal carbonization process of biomass, *Adv. Mater.*, 22 (2010) 813.
[2] Harry Marsh Francisco Rodríguez Reinoso, *Activated Carbon*, Elsevier, 2006.

Enhancement of Supercapacitors Energy Density Using Manganese Modified Carbon Electrode and Mixture of Multivalent Ions Electrolyte

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Application of electrochemical supercapacitors (ES), important energy storage devices, has widely attracted scientific attention. According to mentioned, in the present work, we designed new strategy to improve electrochemical performance of supercapacitors. This strategy is based on the use of manganese doped carbon material as electrode material for ES and multivalent electrolyte ions ($\text{Ca}(\text{NO}_3)_2$ and $\text{Al}(\text{NO}_3)_3$). Mn-doped carbon electrode provides larger operating voltage in $\text{Ca}(\text{NO}_3)_2$, but lower capacitance value when compared to $\text{Al}(\text{NO}_3)_3$ electrolyte. In order to increase operating voltage and keep the same high value of specific capacitance obtained for $\text{Al}(\text{NO}_3)_3$, the mixture of multivalent Ca^{2+} and Al^{3+} ions as supporting electrolyte was used. Investigated carbon electrode in the mixture of multivalent ions electrolyte allows broadening of workable voltage when compared to the $\text{Al}(\text{NO}_3)_3$ electrolyte, keeping the same high value of specific capacitance as observed in aluminum nitrate. This strategy has opened up new perspectives for development of new supercapacitors technologies.

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Al-ion Charge Storage Ability of Vine Shoots-derived Carbon

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The problems emerging from the production of large amounts of biomass waste demand urgent action for their neutralization. The most promising path is utilization of this waste for the production of high value products. Especially, biomass is valuable alternative source of activated carbon (AC), one of the most common materials in energy storage and conversion devices.

In this research vine shoots, by-products of the wine industry, were used to synthesize high surface area AC through a simple two-step carbonization/activation process. [1] Physicochemical characterization revealed high quality and developed micro- and mesoporosity of thus prepared carbon. Detailed electrochemical characterization confirmed that vine shoots-derived AC (AC_{vs}) is a good candidate as electrode material in supercapacitors. Herein, a new way for widening operating voltage in aqueous medium was introduced by applying non-conventional aluminum sulfate electrolyte. Assembled symmetrical AC_{vs} -based supercapacitor based on Al-ions reached 216 F g^{-1} at 1 A g^{-1} and high operating voltage of 1.8 V. The measured capacitance of $AC_{vs}700/Al_2(SO_4)_3/AC_{vs}700$ cell overpasses the values obtained in typical acidic and neutral electrolytes (187 F g^{-1} and 141 F g^{-1} at 1 A g^{-1} , respectively). High capacitance and high operating voltage of AC_{vs} supercapacitor in Al-based electrolyte enabled higher energy density (24 Wh kg^{-1} at 1 A g^{-1}) than in the case of typical Na_2SO_4 (16 Wh kg^{-1} at 1 A g^{-1}) or H_2SO_4 (11 Wh kg^{-1} at 1 A g^{-1}) electrolytes. [1] The floating test of $AC_{vs}700//AC_{vs}700$ capacitor performed at 1.5 V in Argon- prepurged $Al_2(SO_4)_3$ shows the stable capacitance over 100 h. Such concept opens new directions for improving carbon electrochemistry towards multivalent ion charge storage.

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References:

[1] A. Gezović, J. Mišurović, B. Milovanović, M. Etinski, J. Krstić, V. Grudić, R. Dominko, S. Mentus, M. J. Vujković, High Al-ion storage of vine shoots-derived activated carbon: New concept for affordable and sustainable supercapacitors, *Journal of Power Sources*, 538 (2022) 231561.

Al-ions Charge Storage Ability of the Conductive Polyaniline Emeraldine Salt

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Development of new and attractive generation of polymer devices for application in the field of energy storage that meets the requirements of safety and environmental sustainability is an ongoing challenge. The majority of previous scientific results reported that polyaniline-based supercapacitors use only aqueous acid solutions as electrolyte. [1] The aim of this work is to examine the redox activity of polyaniline emeraldine salt (PANI-ES) in an aqueous electrolyte of aluminum salt, that have been studied to a lesser extent and lacking the characterization of charge storage behavior. The advantage of employing aluminum among various post-lithium rechargeable systems has the advantage in the fact that it is the most abundant metal element in the Earth's crust with one of the highest gravimetric and volumetric energy densities. By combining experimental (cyclic voltammetry, chronopotentiometry, galvanic charge/discharge, AFM - Atomic Force Microscopy) and theoretical approaches (density functional theory - DFT), the redox mechanism of polyaniline in the aqueous Al-salt solution is explained. [2] Polyaniline has been shown to have higher Coulombic capacitance at the same charge and discharge current in aqueous aluminum nitrate solution (1M Al(NO₃)₃) than in hydrogen chloride electrolyte solution (1M HCl), which makes it a suitable electrode for supercapacitors. From a practical point of view, a supercapacitor based on polyaniline and an aqueous solution of Al(NO₃)₃ was constructed and tested in terms of capacitance, cycle time, and self-discharge. The capacitor shows high charge and discharge capacity ($\approx 269 \text{ F g}^{-1}$ at a current density of 10 A g^{-1}) and relatively good capacity retention after 1000 charge and discharge cycles.

References:

- [1] B. Kuzmanović, M.J. Vujković, N. Tomić, D. Bajuk-Bogdanović, V. Lazović, B. Sljukić, N. Ivanović, S. Mentus, The influence of oxygen vacancy concentration in nanodispersed non-stoichiometric CeO_{2- δ} oxides on the physico-chemical properties of conducting polyaniline/CeO₂ composites, *Electrochim. Acta* 306 (2019) 506–515.
- [2] M. J. Vujković, M. Etinski, B. Vasić, B. Kuzmanović, D. Bajuk-Bogdanović, R. Dominko, S. Mentus, Polyaniline as a charge storage material in an aqueous aluminum-based electrolyte: Can aluminum ions play the role of protons? *Journal of Power Sources* 482 (2020) 228937.

The Influence of Reduced Graphene Oxide on the Pseudocapacitive Properties of a Conductive Polymer Layer for Supercapacitor Applications

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With the rapidly expanding energy storage market there has been an increasing and urgent need for efficient and sustainable sources of energy. Supercapacitors are considered a promising candidate and an alternative to batteries because of their higher power density and longer cycle life. However, one of the major disadvantages of supercapacitors is the insufficient energy density, which has been the main drawback for the wide application expected. Today, supercapacitors development is focused on active materials that are required to provide both high power and high energy density. [1] Conductive polymers, such as poly(3,4-ethylenedioxythiophene) (PEDOT) and polypyrrole (PPy) are attractive materials in terms of practical applications, especially in energy conversion and storage. They have excellent properties, including low cost, flexibility, and good electrical conductivity which results in a fast electrochemical redox reaction. However, due to their poor mechanical strength they have low cycling stability. To improve these properties different composites of conductive polymers and graphene have been synthesized by chemical or electrochemical polymerization. [2]

In this work, a facile electrochemical method is introduced for incorporating graphene oxide (GO) into PEDOT and PPy layers in the presents of sodium dodecyl sulfate (SDS) as a supporting electrolyte. The presence of SDS can enhance not only the polymerization step but also the morphology and microstructure of the conductive polymer layer. The obtained composite layers were polarised at the potential of -1.4 V in 0.1 mol dm⁻³ KCl solution to reduce GO (rGO) within the polymer. rGO could significantly increase cycling stability and improve pseudocapacitive properties suitable for supercapacitors application. Morphological and structural properties of the obtained layers were characterized by means of scanning electron microscopy and UV/Vis spectroscopy. The obtained nanocomposite materials were used to assemble symmetric supercapacitors that were tested by cyclic voltammetry and electrochemical impedance spectroscopy methods. The stability of the supercapacitors was determined by their charging/discharging at a constant current during 1000 cycles, and the specific capacitance, energy, and power were calculated. The obtained results revealed that PEDOT/rGO and PPy/rGO composites have better pseudocapacitive properties than pure PEDOT and PPy, or the unreduced composite layer.

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References:

- [1] M. Kraljić Roković, G. Ljubek, M. Žic, J. Popović, Electrochemical characterisation of sol-gel derived SnO₂ for supercapacitor application, *Croatica Chemica Acta* 90 (2017) 289-295.
- [2] X. Cai, K. Sun, Y. Qiu, X. Jiao, Recent advances in graphene and conductive polymer composites for supercapacitor electrodes: A review, *Crystals* 11 (2021) 947.

Preparation of Flexible Free-standing Reduced Graphene Oxide Paper Containing Zn and V₂O₅ for Battery and Hybrid Supercapacitor Application

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Rechargeable batteries are one of the most important issues in the present time. Among the batteries, Li-ion rechargeable batteries are considered to be the most significant due to high available energy density. However, disadvantage of Li-ion batteries is usage of organic electrolytes and therefore there are continuous efforts to develop less expensive and green battery device. One of these batteries is zinc-ion aqueous battery. [1] Although the energy density of this battery is lower, compared to Li-ion battery, it has higher power density, which enables it to bridge the gap between supercapacitors and conventional batteries.

The aim of this work was to prepared flexible free-standing rGO paper decorated with Zn or V₂O₅ and to apply it as active material in water-based hybrid supercapacitor and battery devices. rGO paper was prepared by vacuum filtration of graphene oxide (GO) dispersion and electrochemical reduction of GO in 0.1 mol dm⁻³ KCl solution. The reduction process was accomplished by connecting GO paper and Ti-rod working electrode. This procedure enabled formation of flexible free-standing material. rGO paper decorated with Zn was prepared by Zn electrodeposition at rGO support and the obtained material was used as anode in hybrid supercapacitors and batteries. In order to assemble hybrid supercapacitor rGO paper was used as cathode material while in order to assemble the battery rGO decorated with V₂O₅ was selected as cathode material. The electrolyte used in this investigation was 1 mol dm⁻³ ZnSO₄ solution. The obtained results indicate that it is possible to deposit Zn within porous rGO scaffolds, as well as, that V₂O₅ can be successfully intercalated within rGO paper retaining good activity for battery application.

References:

[1] J. Zhoua, L. Shan, Z. Wu, X. Guo, G. Fang, S. Liang, Investigation of V₂O₅ as a Low-cost Rechargeable Aqueous Zinc ion Battery Cathode, Chem. Commun, 54 (2018) 4457-4460.

Thermally Treated and Ion Beam Irradiated Graphene Oxide for Supercapacitor Application

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Interesting surface chemistry and two-dimensional nature have distinguished graphene oxide among other novel carbon nanomaterials. Type and quantity of oxygen groups are closely related to number and type of defects, which both dictates the characteristics of material. In the case of pristine GO the alkoxy and epoxy basal plane groups disturb the π conjugation of graphene layer thus decreasing the conductivity of material. On the other hand, surface oxygen groups of higher thermal stability (e.g., phenol, quinone, etc.) have beneficial influence on the charge storage properties of graphene oxide. [1] Because of this, modification of surface chemistry can be used to improve charge storage of graphene oxide. In this work thermal treatment in inert atmosphere and low energy ion beam irradiation with hydrogen (15 keV) and nitrogen (75 keV) ions was used to modify free-standing papers of graphene oxide. Electric properties of the irradiated samples were probed with solid state electrochemical impedance spectroscopy. The pristine GO showed high resistivity while samples irradiated with hydrogen ions showed minimal resistivity at 1×10^{16} ions/cm². With higher fluences, damage in the structure caused increase in resistivity. Thermally treated samples showed significantly lower resistivity probably due to desorption of oxygen groups and restoration of π conjugation of graphene layer. Supercapacitor performance of the graphene oxide was investigated with galvanostatic charge-discharge experiments. Pristine GO showed poor capacitance which can be connected to already observed high resistivity. Samples that were modified with nitrogen ion beams didn't show much improvement probably due to low penetration depth of ions while thermal treatment was proven beneficial for charge storage application.

References:

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

The Effect of Chemical Titration and Thermal Treatment on Oxygen Functional Groups of GO and GO/WPA Nanocomposites

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Nanocomposites of graphene oxide (GO) and 5, 10, 15, 20, 35, 50 wt.% of 12-tungstophosphoric acid (WPA) were prepared and chemically titrated and thermally treated in order to investigate the oxygen functional groups on GO and GO/WPA nanocomposites. Chemical titration was performed with NaOH, Na₂CO₃, NaHCO₃, while thermal treatment was done at 450 °C in argon atmosphere. Changes in surface chemistry in the samples were monitored using: Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), temperature-programmed desorption (TPD), zeta-potential and adsorption of methylene blue.

Results of FTIR spectroscopy indicate that titration induces structural changes of WPA in the composite, probably due to pH change, while this change was not noticed in the case of thermally treated samples. In both cases, bands at 1720 cm⁻¹ and 1060 cm⁻¹ attributed to C=O and C-O functional groups were removed.

XPS showed that titration and thermal treatment of GO and GO/WPA 15 wt.% have very similar effects. In addition, the ratio of COOH and C=O groups remained unchanged compared to the initial samples, while C-O groups were removed to approximately the same amount.

Thermal treatment of GO and GO/WPA composites removes functional groups to a larger extent than chemical titration due to the lower selectivity of the reduction/deoxidation process.

The stability of suspensions was measured using zeta-potential, which showed increasing stability by increasing wt. % of WPA. Also, more negative values of zeta-potential were observed as pH increased, which can be attributed to proton consumption during titration.

The color adsorption capacity of GO decreased with the removal of functional groups and increased with the presence of WPA in GO/WPA composites. Interestingly, thermal treatment and titration have a completely different impact on adsorption capacity of GO/WPA nanocomposites – thermal treatment blocks adsorption, but titration improves it.

The Synthesis and Characterization of Yb³⁺ and Ho³⁺ Doped SrGd₂O₄

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In this investigation, samples of SrGd₂O₄ doped with different concentration of Yb³⁺ (2, 4, 6 at%) ions and constant concentration of Ho³⁺ (1 at%) were prepared. As for synthesis we chose combustion method assisted with glycine as a fuel and citric acid as a chelator. All samples were burned in the furnace at 500 °C for 1.5h and afterwards additionally thermally treated for 2.5 h at 1000 °C. X-ray diffraction (XRD) showed peaks that correspond to the pure orthorhombic lattice of SrGd₂O₄, space group *Pnma* (JCPDS Card No.:01-072-6387). FE-SEM micrographs revealed agglomerated phenomenon with spherical shape and diameter around 200 nm. Energy dispersive X-ray spectroscopy (EDS) verified uniform distribution of all constituting elements in particles. Powders optical characterization include measurement of up-conversion (UC) emission spectra after excitation at 980 nm, as well as up-converted intensity dependence on excitation power. Dominant green emission ⁵F₄, ⁵S₂ → ⁵I₈ was found in all samples, with the most intense emission with 2 at% of Yb³⁺ and dependence of intensity of UC emission on excitation power confirmed that green emission is facilitated by energy transfer mechanism with two photons.

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Synthesis, Structural and Morphological Properties of Multiferroics

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Magnetoelectric multiferroics, showing simultaneous ferroelectric and ferromagnetic ordering, have aroused wide attention in recent years, because they offer a wide range of potential applications in data storage media, spintronics and multi-state memories. [1] The influence of Ho doping on the crystal structure of bismuth ferrite (BFO) nanopowders was investigated. Namely, BiFeO₃ and Bi_{1-x}Ho_xFeO₃ ultrafine nanopowders were synthesized by the simple, low-cost and energy-saving hydrothermal method. The diffraction pattern was recorded at room temperature and atmospheric pressure in the absence of any re-heating of the sample. A fitting refinement procedure using the Rietveld method was performed which showed the incorporation of Ho³⁺ ions in the BiFeO₃ crystal lattice, where they substitute Bi³⁺ ions. All the samples belong to *R3c* space group. In addition, theoretical investigation using bond valence calculations have been performed in order to mimic pure and Ho doped BiFeO₃ compounds produced in the experiment. The optical properties of the material were examined by the spectroscopic ellipsometry method and the energy gap was found to be 2.71 eV. Transmission electron microscopy (TEM) and the scanning electron microscopy (SEM) was used to determine the particle size and morphology. Bi-based oxides will be electrochemically characterized in an aqueous electrolytes of sodium salts by means of Cyclic Voltammetry, to estimate their potential as sodium storage electrodes.

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References:

[1] T. Rojac, A. Bencan, B. Malic, G. Tutuncu, J.L. Jones, J.E. Daniels, D. Damjanovic, BiFeO₃ ceramics: processing, electrical, and electromechanical properties, *J. Am. Ceram. Soc.* 97 (2014).

Complex Metal Oxide Oxidation State Changes Monitoring by TGA and Dilatometric Means

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Oxidation processes during metal oxide heat treatment are important events that can be monitored by the means of well-known TGA/DTA and dimensional change diagrams. Powders $\text{Mn}_{0.63}\text{Zn}_{0.37}\text{Fe}_2\text{O}_4$ oxide was milled in different time duration and thermal analysis techniques afterwards during heating were observed. Cation that serves this purpose well for is Mn ion that passes through Mn^{2+} to Mn^{3+} state at 360 °C by oxidation and after that from Mn^{4+} to Mn^{3+} reduction process at 580 °C. Minimal data treatment of first derivative on shrinkage for obtaining shrinkage rate diagrams and as well first derivative on thermal gravimetric diagram for obtaining differential thermal gravimetric analysis diagram enable the oxidation and reduction processes monitoring.

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References:

[1] Nebojša Labus, Zorka Vasiljević, Obrad Aleksić, Miloljub Luković, Smilja Marković, Vladimir Pavlović, Slavko Mentus, Maria Vesna, Nikolić, Characterisation of $\text{Mn}_{0.63}\text{Zn}_{0.37}\text{Fe}_2\text{O}_4$ Powders After Intensive Milling and Subsequent Thermal Treatment, *Science of Sintering*, 49 (2017) 455-467, doi: <https://doi.org/10.2298/SOS1704455L>

Experimental Investigation of Octahedral Tilting and Related Effects of $\text{Ca}_{1-x}\text{Gd}_x\text{MnO}_3$ ($x = 0.05, 0.1, 0.15, 0.2$) Compound

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Nanometric size $\text{Ca}_{1-x}\text{Gd}_x\text{MnO}_3$ ($x = 0.05, 0.1, 0.15, 0.2$) powder particles with perovskite-type structure were obtained by applying a modified glycine-nitrate procedure. [1, 2] All samples were investigated by X-ray diffraction (XRD), Infrared (IR) spectroscopy and EPR (electron paramagnetic resonance) measurements. In the perovskites with space group *Pnma*, octahedral tilting is most common and it is of great interest for geologists and materials science. It was experimentally observed how the amount of gadolinium dopants affects on the Mn-O bonds angles and distances, MnO_6 octahedral tilting, the deformation due to the presence of Jahn-Teller distortion around the Mn^{3+} cation and relation between the structural and magnetic behavior. [3] The infrared reflection spectra of $\text{Ca}_{1-x}\text{Gd}_x\text{MnO}_3$ samples confirmed XRD results that $\text{Ca}_{1-x}\text{Gd}_x\text{MnO}_3$ nanopowders are of *Pnma-1* structure and that the octahedral tilting is increased with Gd doping. The EPR spectra are in agreement with the expectation that EPR linewidth depend of Mn-O-Mn angle and that small octahedral tilting brought only a small change of the EPR linewidth.

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References:

- [1] M. Rosić, Lj. Kljajević, D. Jordanov, M. Stoiljković, V. Kusigerski, V. Spasojević, B. Matović, Effects of sintering on the structural, microstructural and magnetic properties of nanoparticle manganite $\text{Ca}_{1-x}\text{Gd}_x\text{MnO}_3$ ($x=0.05; 0.1; 0.15; 0.2$), *Ceramics International*, 41, 2 (2015) 14964–14972.
- [2] M. Rosić, M. Logar, J. Zagorac, A. Devečerski, A. Egelja, V. Kusigerski, V. Spasojević, B. Matović, Investigation of the structure and the magnetic behaviour of nanostructured $\text{Ca}_{1-x}\text{Gd}_x\text{MnO}_3$ ($x=0.05; 0.1; 0.15; 0.2$) obtained by modified glycine nitrate procedure, *Ceramics International*, 39, 2 (2013) 1853–1861.
- [3] M. Rosić, D. Zagorac, D. Milivojević, N. Paunović, J. Zagorac, Z. Dohčević-Mitrović, B. Matović, Theoretical and experimental study of octahedral tilting of $\text{Ca}_{1-x}\text{Gd}_x\text{MnO}_3$ ($x=0.05; 0.1; 0.15; 0.2$) nanometric powders, *Journal of Alloys and Compounds* 678 (2016) 219-227.

A Series of Magnesium Vanadium Oxide Materials Potentially Applicable for Aqueous RMBs

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Rechargeable magnesium ion batteries (RMBs) have many benefits, including high abundance of Mg resources, high theoretical specific capacity, good atmospheric stability and safety of handling, eco friendliness, low cost, and therefore are seen as a candidate for partial replacement of the lithium-ion batteries. Layered materials show great prospects for application as host materials for magnesium ion storage in the batteries.

A series of magnesium vanadium oxide materials with different structural characteristics was prepared using simple precipitation method and appropriate thermal treatment. The obtained materials were studied electrochemically regarding their potential application as cathode materials for aqueous RMBs. Electrochemical properties of different magnesium vanadium oxide materials, measured in Mg-containing aqueous electrolyte, were compared and discussed. The possibility of improving the electrochemical performances of the obtained materials was considered.

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A Comparison of the Capacities of ZnMn_2O_4 and $\text{ZnCr}_{0.15}\text{Mn}_{1.85}\text{O}_4$ in Aqueous Media

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To protect the environment from potentially hazardous components from commercial Li-ion batteries (i.e., contain toxic and flammable electrolytes as well as Li is uneconomical and a rare earth metal), a viable alternative need to be found for the components of these batteries. Thus, our focus is on replacement of an organic electrolyte using an aqueous one. Additionally, the work also examines the replacement of Li with Zn as production of Zn-based cathode material is more economical compared to Li and less toxic. Due to occurrence of the Jahn Teller effect in ZnMn_2O_4 , Mn^{3+} ions are partially replaced with Cr^{3+} ions to diminish this phenomenon and to obtain a higher capacity. Namely, due to the Jahn-Teller distortion, not all cations of Zn^{2+} ions may intercalate in the crystal lattice sites. When the Jahn-Teller effect lowers, more Zn^{2+} ions may intercalate into sites; thus, a higher capacity may be obtained. The materials ZnMn_2O_4 and $\text{ZnCr}_{0.15}\text{Mn}_{1.85}\text{O}_4$ were synthesized by glycine nitrate combustion method. The materials were characterized by XRPD, SEM, EDS and cyclic voltammetry. The aqueous solutions of ZnCl_2 were used as electrolytes as potentially more ecological alternatives compared to the organic ones already commercially used. The cathode capacities obtained for the ZnMn_2O_4 under 5 mV s^{-1} and 20 mV s^{-1} ranged from 17.7 mA h g^{-1} to 6.9 mA h g^{-1} . The cathode capacities obtained for $\text{ZnCr}_{0.15}\text{Mn}_{1.85}\text{O}_4$ under 5 mV s^{-1} and 20 mV s^{-1} ranged from 86.3 mA h g^{-1} and 24.6 mA h g^{-1} , respectively. Over the intercalation and deintercalation process of the Zn^{2+} ions into the $\text{ZnCr}_{0.15}\text{Mn}_{1.85}\text{O}_4$, a release of oxygen occurred. The stable capacity obtained for both rates (5 mV s^{-1} and 20 mV s^{-1}) indicates that the $\text{ZnCr}_{0.15}\text{Mn}_{1.85}\text{O}_4$ material is applicable for both rates used. Further examination of the ZnMn_2O_4 material must be conducted in terms of increasing the capacity through its doping with other ions or its use in an aqueous solution of other salts.

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Mixed Ni-Mg Spinel Ferrites Used as Materials for Charge Storage Electrodes

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Problems that countries all over the world have in common are dependence of economy and energy production on fossil fuels. There is a growing need for energy production and storage routes that are safe for the environment, renewable, efficient and cheap. One of the directions in which science is moving forward is discovering materials suitable for use in batteries and supercapacitors to improve their operating potential, electrical capacity or biocompatibility. The objective is also to synthesize materials for batteries or supercapacitors that are cheap, consist of earth abundant elements and have high electrochemical activity.

In this work, mixed nickel-magnesium ferrites $\text{Ni}_x\text{Mg}_{1-x}\text{Fe}_2\text{O}_4$, with x being 0, 0.1, 0.3, 0.5, 0.7, 0.9 and 1, were synthesized via sol-gel combustion synthesis with citric acid used as fuel and nitrate ions used as oxidizing agents. Combusted powders were calcined at 700 °C. The structure and morphology of the powders were characterized with X-ray diffraction method (XRD), field emission scanning electron microscopy (FESEM), Raman and FTIR spectroscopy. The band gap was calculated by using UV/Vis diffuse reflectance spectroscopy (DRS). Samples were cast on nickel foam and tested as energy storage materials in a three-electrode setup in 3 M KOH aqueous solution as electrolyte. The methods used were cyclic voltammetry (CV) and constant current chronopotentiometry to obtain galvanostatic charge-discharge (GCD) curves. Results show that all of the synthesized materials show battery-type charge storage in alkaline electrolyte due to the formation of metal cation oxyhydroxides. With increasing nickel content, electrochemical activity drops. The highest value of capacity, 34.3 mA h g⁻¹ at the current density of 500 mA g⁻¹ is ascribed to magnesium ferrite, MgFe₂O₄.

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Al³⁺ Cation Interaction with Pristine and Defective Graphene Using Microsolvated Cluster Model: DFT Study

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Electrochemical capacitors are used to store electrochemical energy while involving no redox process in the bulk of the active material. Instead, the charge is accumulated by the electrostatic attraction of ions from the electrolyte. Different types of the advanced active material and electrolytes are developed in recent years while microscopic interactions between the ions and the electrode surface still remain elusive. Carbon based materials are currently most popular choice for the electrode material as well as the non-conventional aqueous electrolyte. In order to understand fundamentals of the interaction between the ions and the electrode, beside various electrochemical characterization methods, it is also crucial to employ different computational modeling methods of which density functional theory (DFT) is the most common choice.

Herein, we examine the adsorption of hydrated Al³⁺ cation on the pristine and defective (Stone-Wales, N-doped divacancy and carbonyl O-doped divacancy defect) graphene surface using DFT at PBE+D3/def2-SVP level of theory. [1] Microsolvated cluster Al³⁺(H₂O)₆ and COSMO model are employed simultaneously to account for the water solvation effects. Our approach includes calculation of the adsorption energies which are decomposed into interaction and deformation energies, while interaction energy is further decomposed using energy decomposition analysis (EDA) approach. Two possible cases of Al³⁺ adsorption of graphene are considered – direct and indirect (water mediated). In the cases of pristine and SW graphene both adsorption types are not energetically feasible (0.36 and 0.32 eV) due to the large deformation penalty (0.67 and 0.69 eV for direct and 0.01 and 0.27 eV for indirect interaction) which is mostly pronounced for the Al³⁺(H₂O)₆ cluster. EDA analysis indicate that the stabilizing interactions are both dispersion and polarization interaction. On the other hand, electrostatic interactions have destabilizing effect in the system due to the water cluster that shields Al³⁺ from graphene's π electrons. Direct adsorption on the N-doped divacancy is also unfavorable (0.08 eV), although much less compared to the direct adsorption on pristine and SW graphene, again due to the deformation penalty. Indirect cluster adsorption on the N-doped graphene is somewhat favorable (-0.57 eV) which is due the proton transfer from the one of the H₂O molecules that coordinate Al³⁺ to the nitrogen atom. This highly reflects on the polarization and repulsion contribution to the interaction energy. The most negative adsorption (-1.47 and -1.36 eV) and interaction (-2.87 and -1.64 eV) energies are found in the case of both direct and indirect carbonyl O-doped divacancy which is ascribed to the favorable spatial orientation of the carbonyl group that allows Al³⁺(H₂O)₆ cluster to be adsorbed with the minimal deformation. Negatively charged oxygen atom provides platform for charge transfer to the Al³⁺ and simultaneously strong electrostatic interaction with highly charged Al³⁺ cation, especially in the direct type of adsorption. This effect is quantified with increased polarization and dispersion interaction obtained within EDA framework.

These results indicate energetically viable interaction of Al³⁺(H₂O)₆ cluster with carbonyl O-doped graphene which should be considered when designing carbon-based electrodes in combination with non-conventional aqueous electrolyte.

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References:

[1] A. Gezović, J. Mišurović, B. Milovanović, M. Etinski, J. Krstić, V. Grudić, R. Dominko, S. Mentus, M. J. Vujković, High Al-ion storage of vine shoots-derived activated carbon: New concept for affordable and sustainable supercapacitors, *Journal of Power Sources*, 538 (2022) 231561.

Data-driven Design of New Mg-based Hydride Materials – A Synergy of Experiments and DFT

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Hydrogen absorption/desorption is one of the key processes underlying many clean energy applications, such as thermal energy storage, hydrogen storage, hydrogen compression, and nickel-metal hydride batteries. For all those applications fast and reliable characterization of new materials, and in particular, information regarding energetics of hydride formation reaction is of main interest. In the last decades, DFT (density functional theory) approach showed good predictive potential for the ground state properties and calculation of hydride formation energies. Recently, MEGNet implementation [1] of graph neural networks showed promising results for fast and reliable prediction of formation energies for molecules and crystals. Here, we consider the development of a machine learning model based on the available DFT predicted structures and experimentally measured hydride formation enthalpies. The proposed model [2] is capable to predict hydride formation behavior for a wide variety of intermetallic compounds and distinguish the behavior of the polymorphs. In particular, based only on the crystal structure of the starting intermetallic compound, we were able to predict hydride formation enthalpy with accuracy comparable to DFT calculated values. Further, we demonstrate the application of this model for proposing new materials in Mg-Ni-M compound space with the desired enthalpy for hydrogen storage.

References:

- [1] C.Chen, W.Ye, Y.Zuo, C.Zheng, S.P.Ong, Chem. Mater., Graph Networks as a Universal Machine Learning Framework for Molecules and Crystals, 31 (2019) 3564.
- [2] K.Batalović, J.Radaković, B.Paskaš Mamula, B.Kuzmanović, M.Medić Ilić, Predicting Heat of Hydride Formation by the Graph Neural Network – Exploring Structure-Property Relation for Metal Hydrides, preprint <http://dx.doi.org/10.2139/ssrn.4055259>

Electron trapping and energy density in polymers at low electric field

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The price and environmental aspects of electricity storage significantly affect the application of green technologies. The electrochemical batteries are currently the best choice for storing electricity for most industrial needs and products. Environmental and safety risks associated with this type of battery, their price and a limited lifespan are the reasons why great efforts are being made in the search for a more suitable type of battery. Polymer capacitors show very low energy density compared to the electrochemical conventional batteries and therefore cannot be widely used for electricity disposal. At the same time, all other features of polymer capacitors that characterize battery systems are ideal. The good characteristics of polymer capacitors are high power density, very long life and environmental friendliness. Innovative approaches that could expand the use of polymer capacitors are desirable. The influence of charge trapping in electrostatic dielectric capacitors on their energy density has not been considered so far. This experimental study shows the effects of electron trapping on energy density in a gamma irradiated LDPE/ZIF8 composite under low electric field conditions.

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The scientific man does not aim at an immediate result. He does not expect that his advanced ideas will be readily taken up. His work is like that of the planter — for the future. His duty is to lay the foundation for those who are to come, and point the way. He lives and labors and hopes.

”

Nikola Tesla



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