EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

International mobility of researchers at the Brno University of Technology, CZ.02.2.69/0.0/0.0/16_027/0008371

Workshop

Electrode Materials for Sodium-Ion Batteries

2. June 2018

Dr. Jiri Libich

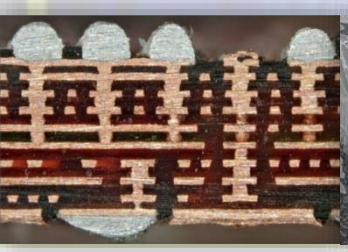
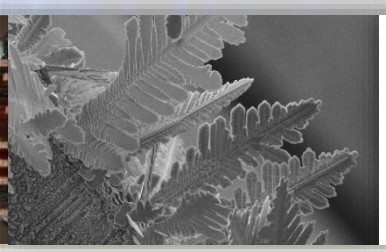
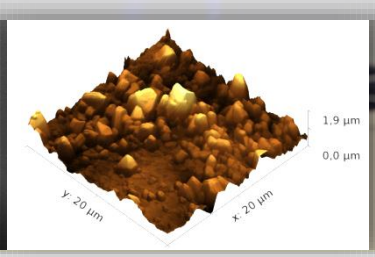
UNIVERSIDAD DE LAS PALMAS DE GRAN CANARIA

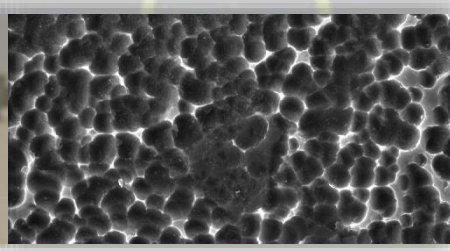
FACULTY OF ELECTRICAL ENGINEERING AND COMMUNICATION
department of electrical and electronic technology

Centre for Research and Utilization of Renewable Energy

Presentation outline

- Brno, Czech Republic
- Brno University of Technology
- Department Profile (Department of Electrical and Electronic Technology)
- Our work relate with electrochemical power sources
- Research field – Sodium-ion batteries
- Conclusion

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

Supported by project: International mobility of researchers at the Brno University of Technology, CZ.02.2.69/0.0/0.0/16_027/0008371

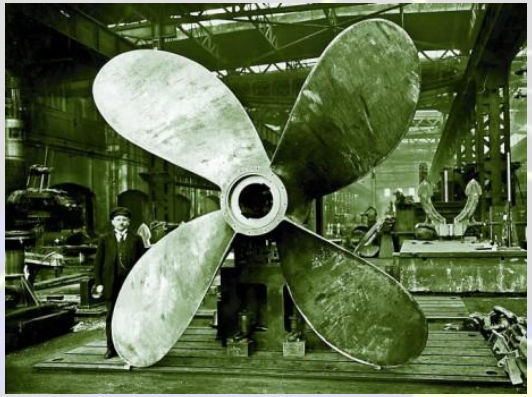
- Czech Republic, approx. 10 560 000 population

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research, Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

Supported by project: International mobility of researchers at the Brno University of Technology, CZ.02.2.69/0.0/0.0/16_027/0008371

- Czech Republic is famous for:
- J. Heyrovský, invention of Polarograph (1924), Nobel Prize
- O. Wichterle, Contact lens (1961)
- J. Ressel, Propeller (1827)
- J. K. Rad, Cube sugar (1843)
- S. Brebera, Semtex plastic explosive (1966)
- J. Čapek, writer, invented word ‘Robot’ (1920)

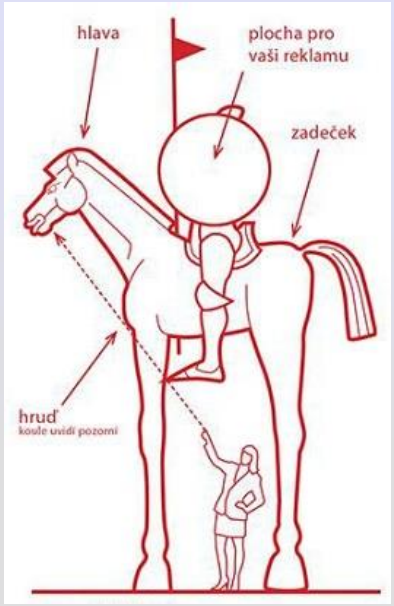


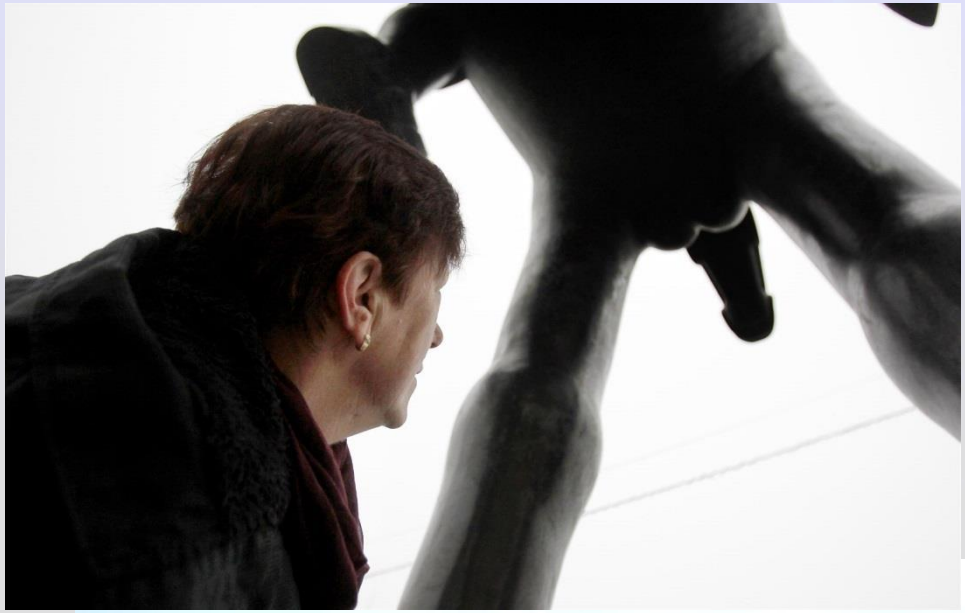
EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

Supported by project: International mobility of researchers at the Brno University of Technology, CZ.02.2.69/0.0/0.0/16_027/0008371

- Brno, population 380 000





EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

Supported by project: International mobility of researchers at the Brno University of Technology, CZ.02.2.69/0.0/0.0/16_027/0008371

Brno University of Technology

- Established 1899
- Over 24 000 students
- Divided to 8 faculties and 2 institutes

BRNO UNIVERSITY OF TECHNOLOGY

CEITEC	Central European Institute of Technology BUT
FA	Faculty of Architecture
FBM	Faculty of Business and Management
FCE	Faculty of Civil Engineering
FEEC	Faculty of Electrical Engineering and Communication
FFA	Faculty of Fine Arts
FCH	Faculty of Chemistry
FIT	Faculty of Information Technology
FME	Faculty of Mechanical Engineering
IFE	Institute of Forensic Engineering

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

Supported by project: International mobility of researchers at the Brno University of Technology, CZ.02.2.69/0.0/0.0/16_027/0008371

Faculty of Electrical Engineering and Communication (FEEC)

- Over 3500 students
- Divided to 14 departments

BRNO UNIVERSITY OF TECHNOLOGY
FACULTY OF ELECTRICAL ENGINEERING AND COMMUNICATION

- Our department : Department of Electrical and Electronic Technology (UETE)

FACULTY OF ELECTRICAL ENGINEERING AND COMMUNICATION
department of electrical and electronic technology

1. Electrochemical power sources (batteries)
2. Renewable energy (photovoltaics, wind power)
3. 3D modeling and simulation
4. Dielectric materials and isolants
5. Technology od PCB, design, interconnection structures

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research, Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

Supported by project: International mobility of researchers at the Brno University of Technology, CZ.02.2.69/0.0/0.0/16_027/0008371

Profile of Department of Electrical and Electronic Technology (UETE)

• Lithium, lead acid, redox flow batteries, fuel-cells • Post-Lithium systems (Li-Sulphur, Na-Ion) • Photovoltaic (FV)	Energy sources
• Diagnostics of material properties – XRD • Climate tests • Corrosion Tests • Surface Diagnostics – ESEM, AFM	Materials
• Diagnostics of the soldering process, technology • Surface treatment	Technology
• 3D Modeling and Simulations • Design of electronics and firmware	Simulations and computer design

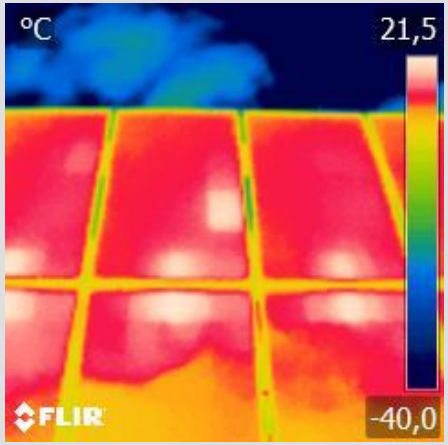
EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research, Development and Education

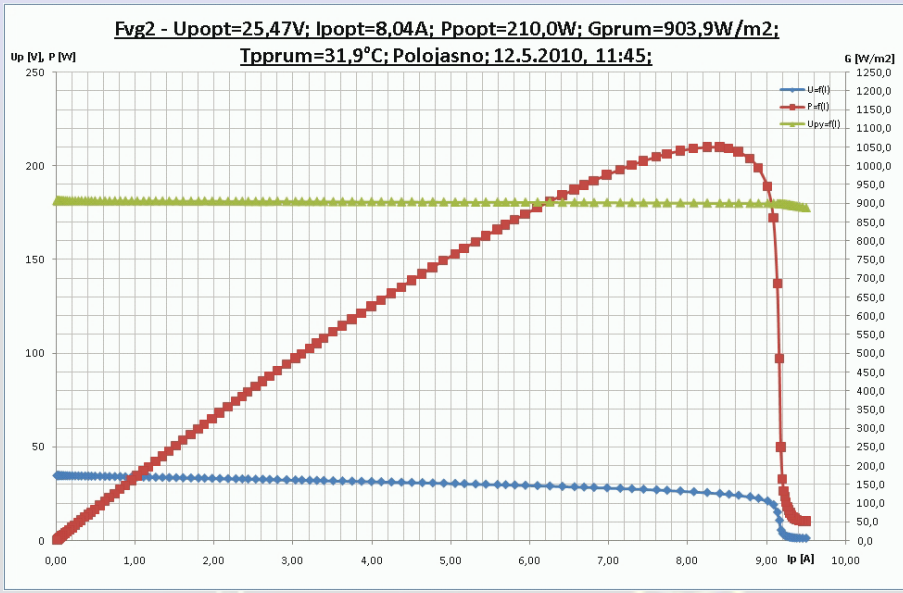
MINISTRY OF EDUCATION, YOUTH AND SPORTS

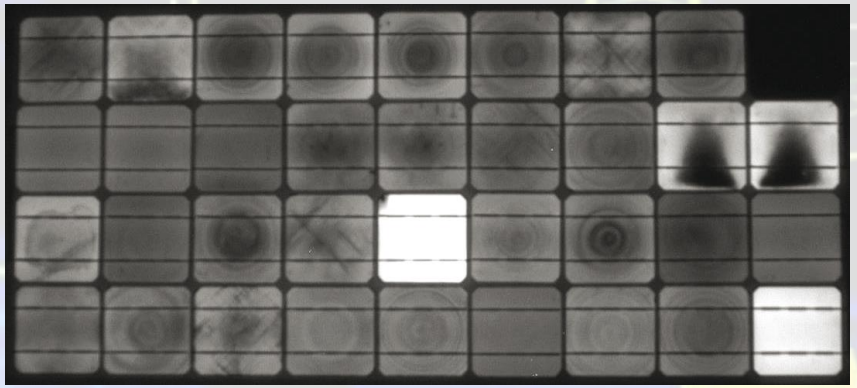
Supported by project: International mobility of researchers at the Brno University of Technology, CZ.02.2.69/0.0/0.0/16_027/0008371

Enegy sources – Renewable

- Diagnostic of photovoltaic panels with help of PASAN instrument
  - Efficiency testing
  - Localization of defects by method electroluminescence







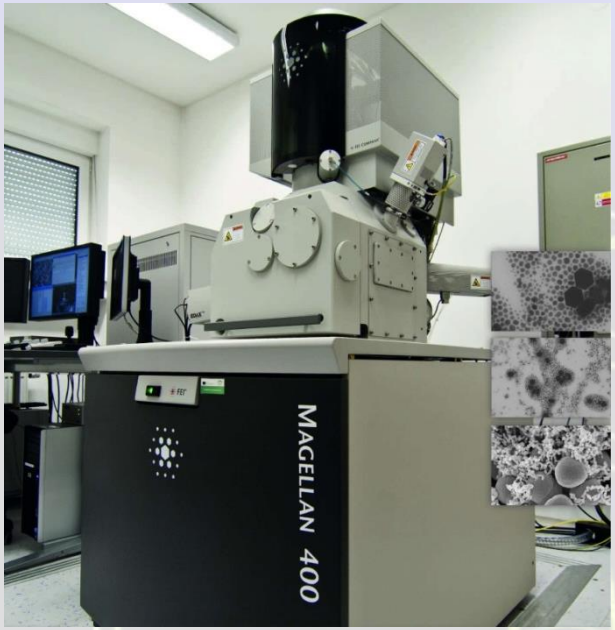
EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

Supported by project: International mobility of researchers at the Brno University of Technology, CZ.02.2.69/0.0/0.0/16_027/0008371

Materials

- Instruments: ESEM, AFM, XRD

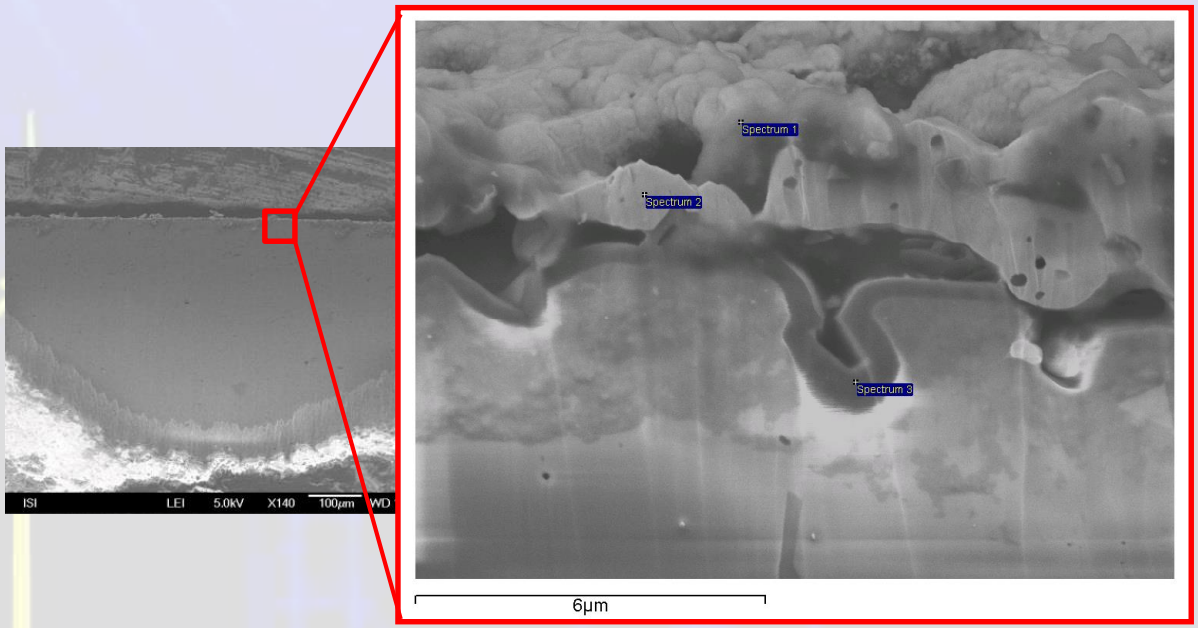


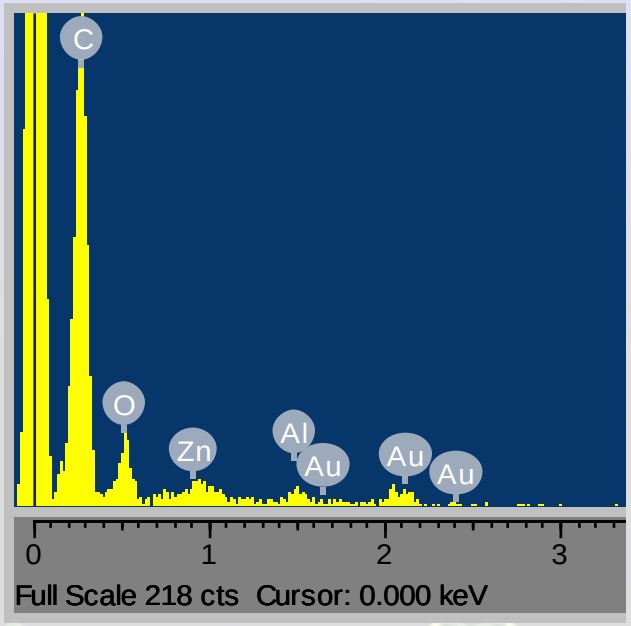
EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

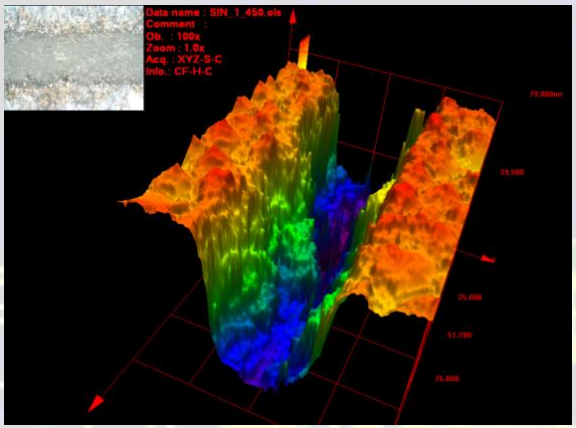
MINISTRY OF EDUCATION, YOUTH AND SPORTS

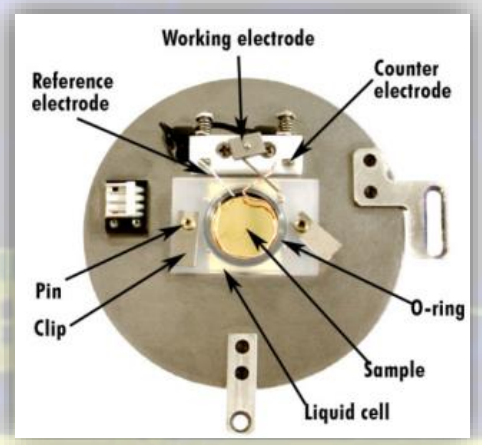
Supported by project: International mobility of researchers at the Brno University of Technology, CZ.02.2.69/0.0/0.0/16_027/0008371

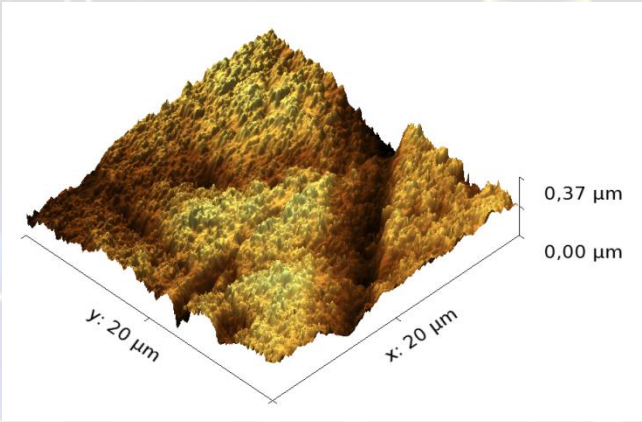
Materials









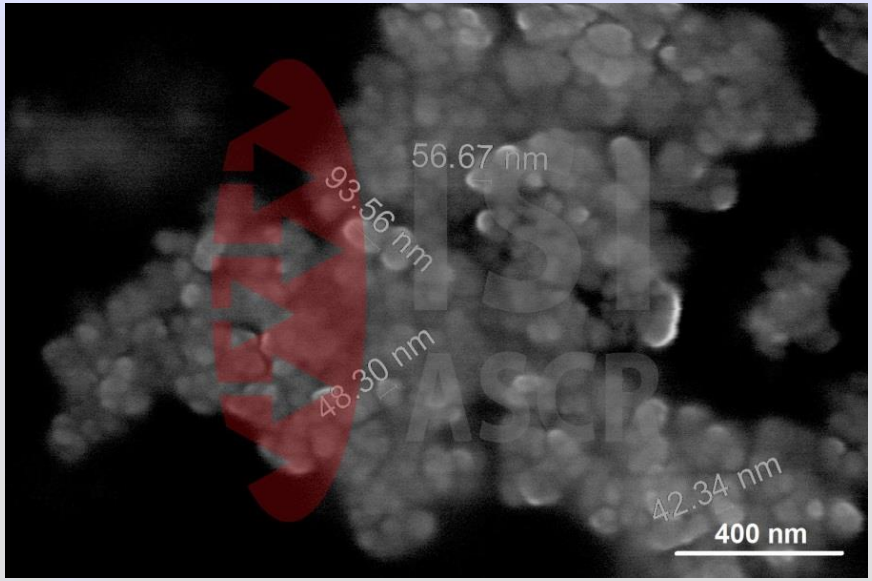


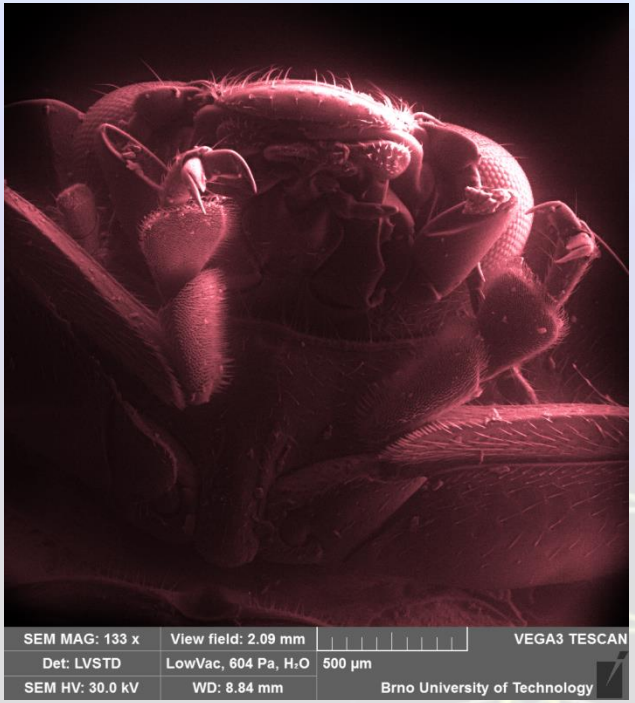
EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

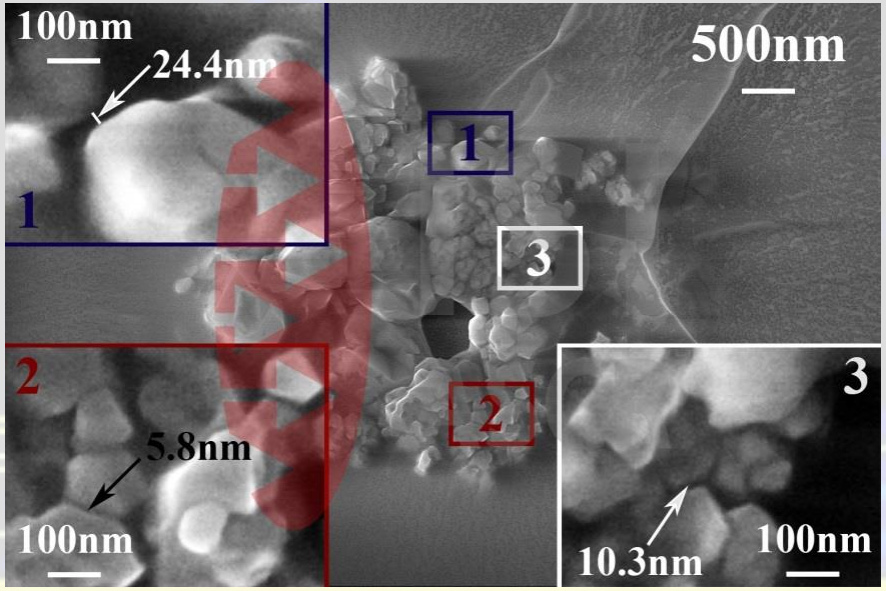
MINISTRY OF EDUCATION, YOUTH AND SPORTS

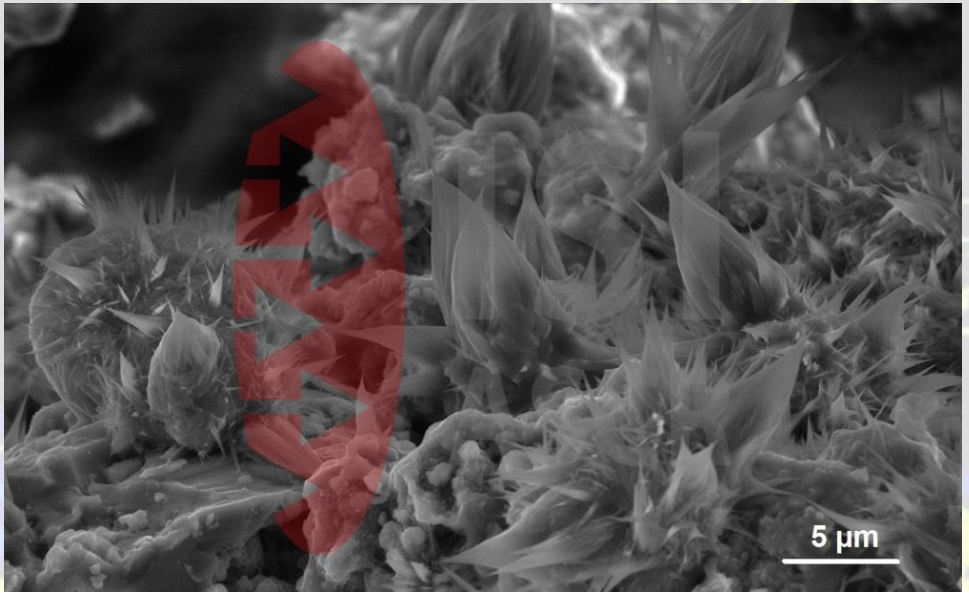
Supported by project: International mobility of researchers at the Brno University of Technology, CZ.02.2.69/0.0/0.0/16_027/0008371

Materials









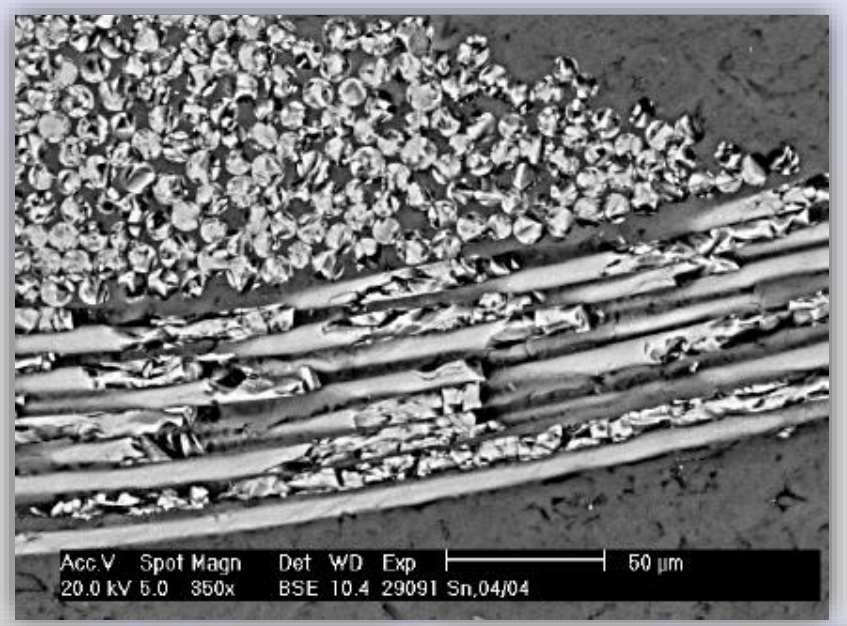
EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

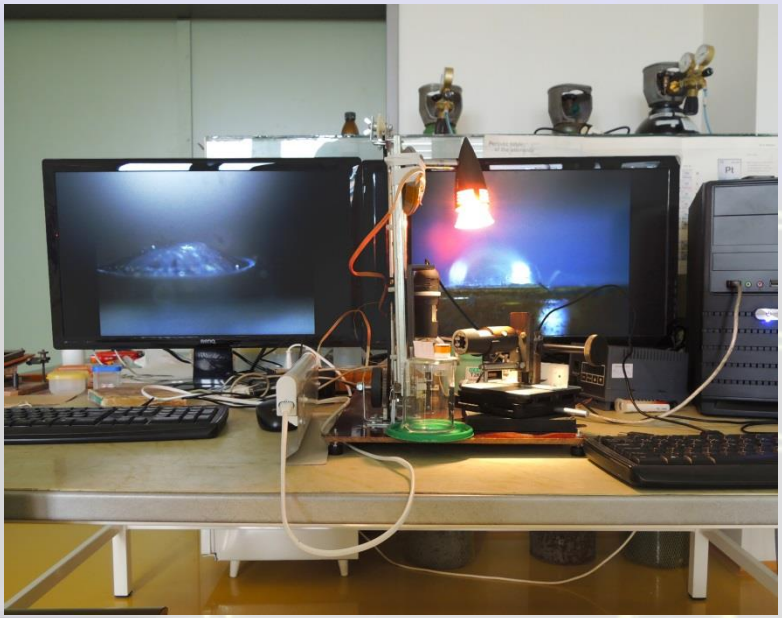
MINISTRY OF EDUCATION, YOUTH AND SPORTS

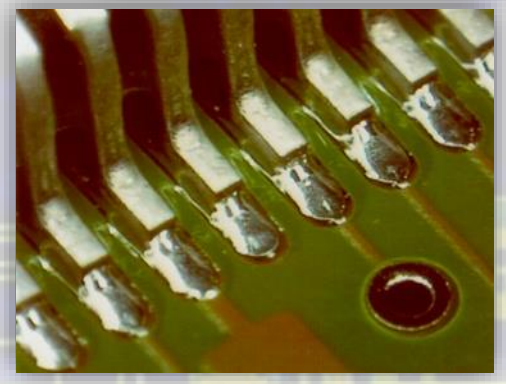
Supported by project: International mobility of researchers at the Brno University of Technology, CZ.02.2.69/0.0/0.0/16_027/0008371

Technology

- Assembly and interconnection technologies, defect analysis







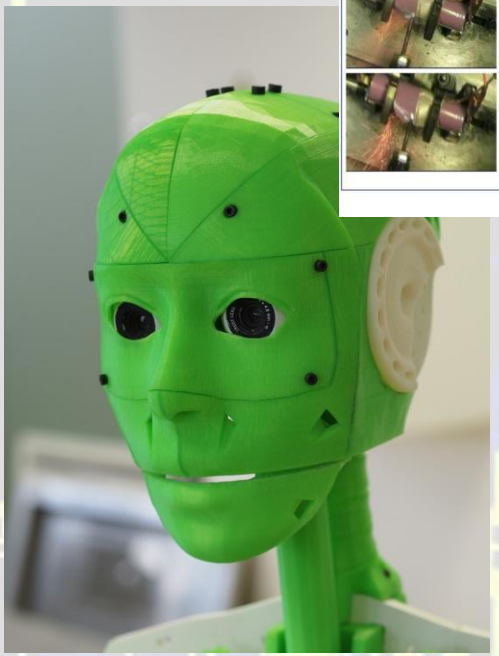
EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

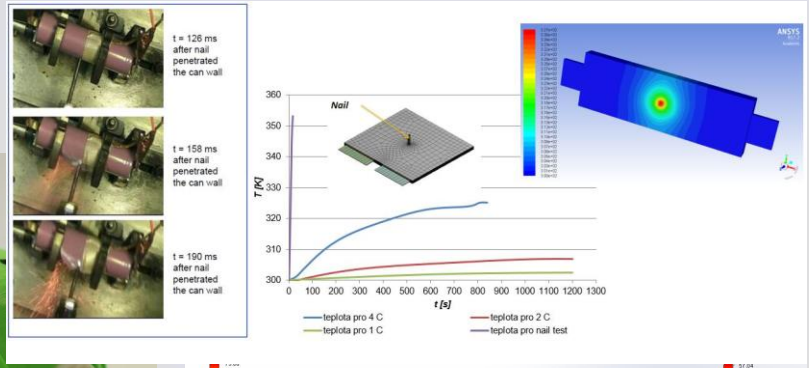
MINISTRY OF EDUCATION, YOUTH AND SPORTS

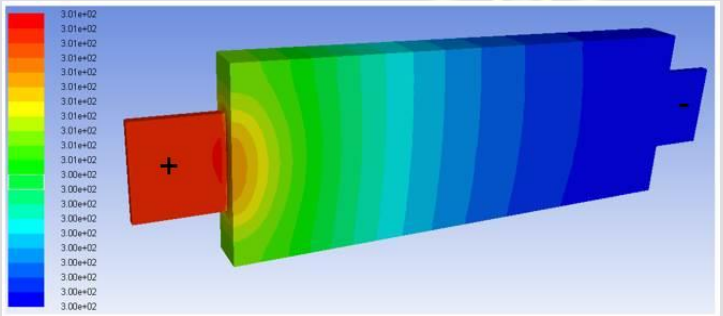
Supported by project: International mobility of researchers at the Brno University of Technology, CZ.02.2.69/0.0/0.0/16_027/0008371

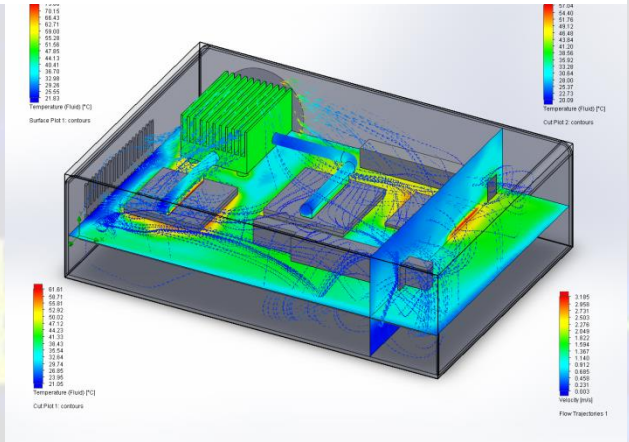
Simulation and 3D computer design

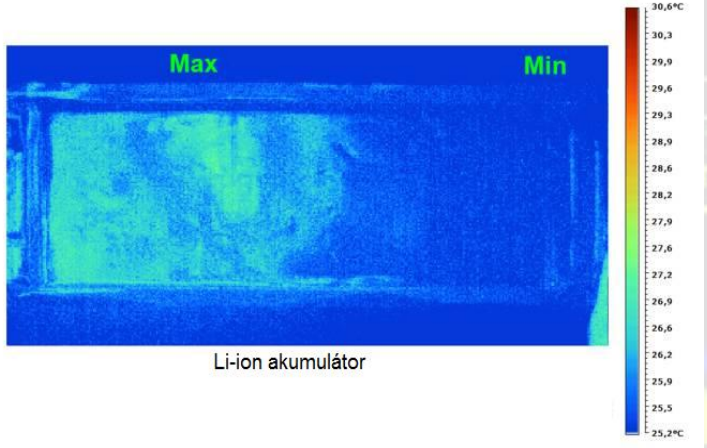
- SolidWorks, Ansys
- In systems using finite volumes and elements
- Designing a numerical model to create a uniform flow under all standardized conditions.
- Creation of a numerical model of ultrasound beam propagation.
- Analysis of the influence of climatic conditions on the gas meter prototype (heat transfer).
- Simulation of electric strength, electric fields and antistatic prevention on a prototype.











EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research, Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

Supported by project: International mobility of researchers at the Brno University of Technology, CZ.02.2.69/0.0/0.0/16_027/0008371

Enegy sources – Electrochemistry

- University has a long tradition of research in energy storage application

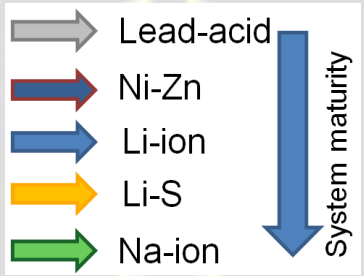
1970s Ni-Cd

1979 Ni-Zn

2005 Li-ion

2017

1966 lead-acid



- Selected research activities in terms of electrochemistry
  - Li-ion battery
  - Lithium ion battery for the smart textiles applications
- Post-Li battery systems (Na-Ion, Li-Sulphur)
- Lead-acid batteries
- High-temperature ceramic materials
- Flow-through redox systems

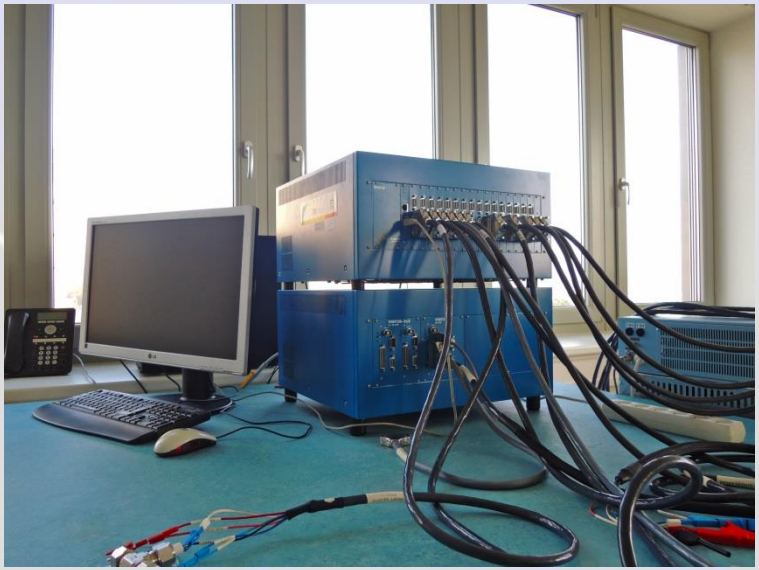
EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research, Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

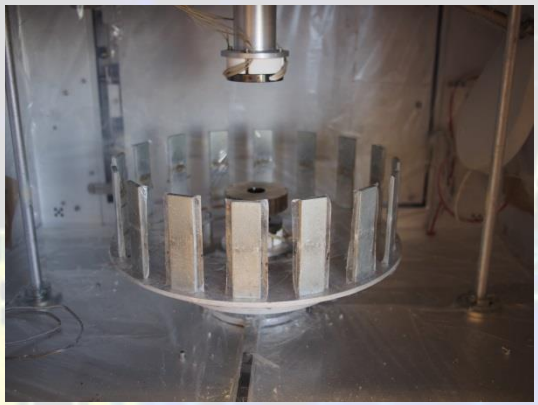
Supported by project: International mobility of researchers at the Brno University of Technology, CZ.02.2.69/0.0/0.0/16_027/0008371

Enegy sources – Electrochemistry

- Equipments: Potentiostat , Gloveboxes, Sputtering device, Forcespinning…








EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

Supported by project: International mobility of researchers at the Brno University of Technology, CZ.02.2.69/0.0/0.0/16_027/0008371

Enegy sources – Electrochemistry
Current research in electrochemical energy storage systems

- Lithium-Ion Batteries and Post-Lithium systems
  - Basic research of conventional and advanced (5 Volts) $LiFePO_4$, $LiCoO_2$ and $LiMn_2O_4$ batteries in relation to their function, stability and safety.
  - Study of electrolytes for Li-ion batteries – stability at high voltage, flammability,...
  - Development of Li – sulfur system
  - Preparation of complete Li-ion cells + degradation tests
  - Development of Na – Ion system
- Advanced and Alternative Systems
  - Application-oriented research focused on Pb-A battery – resolving the PCL3 effect
  - Investigation of performance aspects of vanadium redox flow with focus on electrode degradation and general vanadium redox kinetics.
  - Continue the development of sodium systems
- Supporting Activities
  - Development of the equivalent electrical circuit models for the studied structures and analytical models describing the aging structures.

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

Supported by project: International mobility of researchers at the Brno University of Technology, CZ.02.2.69/0.0/0.0/16_027/0008371

Enegy sources – Electrochemistry

Cathode material for lithium ion accumulators prepared by screen printing for the smart textiles applications

- $LiFePO_4$ based cathode electrode for printed secondary lithium based cells.
- An ink formulation was developed for the screen printing technique.
- Standard PVDF-based binder and conductive additives were replaced by conductive polymers Advanced and Alternative Systems

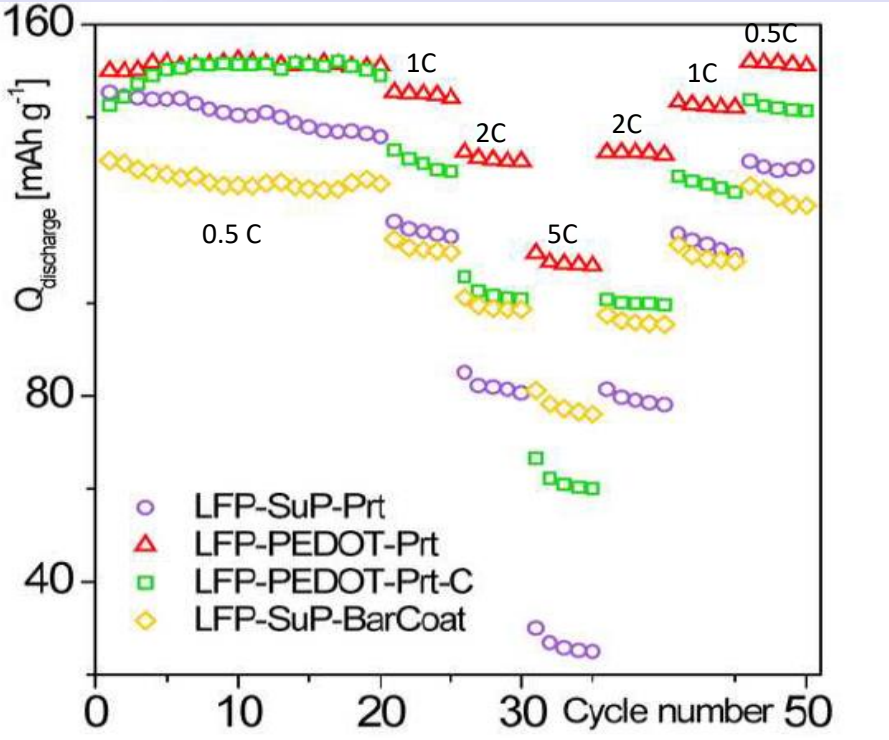
Code name	Electrode material	Binder	Conductive content	Deposition technique	Cathode Underlayer
LFP-SuP-Prt	$LiFePO_4$	PVDF	Super P	Screen printing	No
LFP-PEDOT-Prt	$LiFePO_4$	PEDOT:PSS	PEDOT:PSS	Screen printing	No
LFP-PEDOT-Prt-C	$LiFePO_4$	PEDOT:PSS	PEDOT:PSS	Screen printing	Carbon
LFP-SuP-BarCoat	$LiFePO_4$	PVDF	Super P	Spiral Bar Coating	No

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research, Development and Education

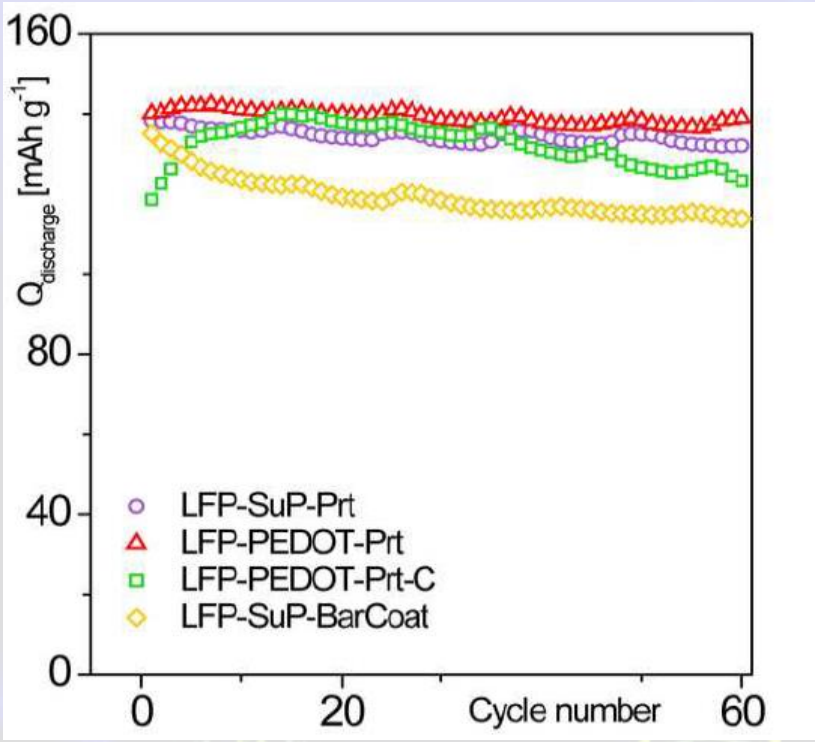
MINISTRY OF EDUCATION, YOUTH AND SPORTS

Supported by project: International mobility of researchers at the Brno University of Technology, CZ.02.2.69/0.0/0.0/16_027/0008371

Enegy sources – Electrochemistry



Change of capacity of the $LiFePO_4$ electrode layers for different C-rates: 0.5, 1, 2, 5, 2, 1, and 0.5.



The cycling performance LFP-SuP-Prt, LFP-PEDOT-Prt, LFP-PEDOT-Prt-C, LFP-SuP-BarCoat, at 1 C for 60 cycles.

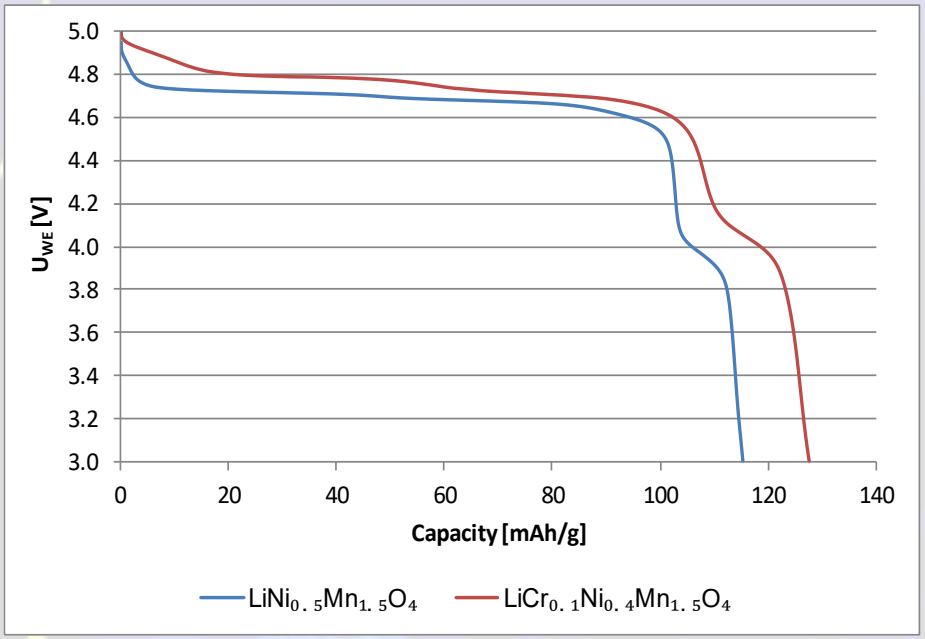
EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research, Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

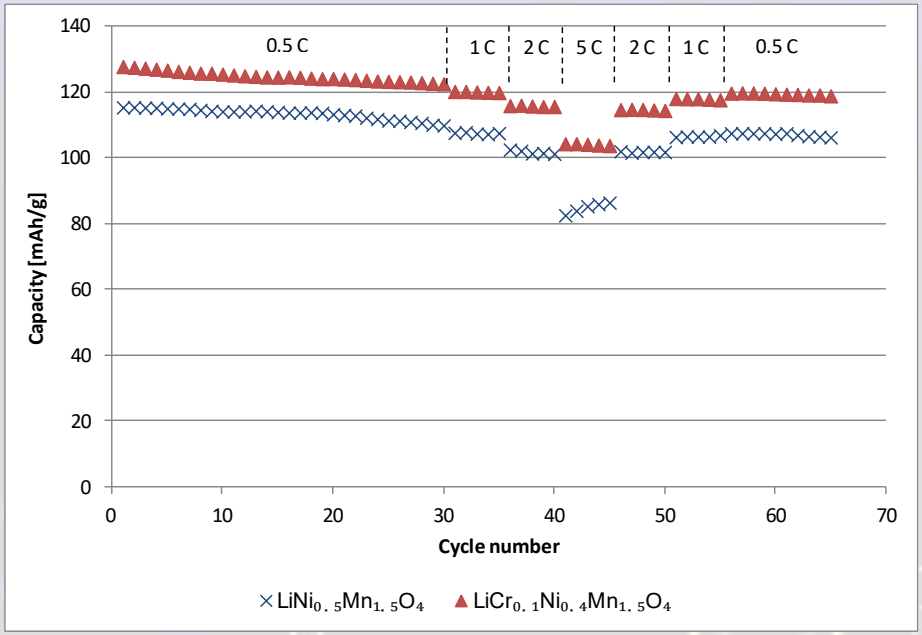
Supported by project: International mobility of researchers at the Brno University of Technology, CZ.02.2.69/0.0/0.0/16_027/0008371

Enegy sources – Electrochemistry

- 5 Volts cathode materials:
  Effect of Cr doping to the properties of LiNi0.5Mn1.5O4



Comparison of first discharge curves of $LiNi_{0.5}Mn_{1.5}O_4$ and $LiCr_{0.1}Ni_{0.5}Mn_{1.5}O_4$ at 0.5 C



Comparison of capacity change depending on the load for materials $LiNi_{0.5}Mn_{1.5}O_4$ and $LiCr_{0.1}Ni_{0.5}Mn_{1.5}O_4$

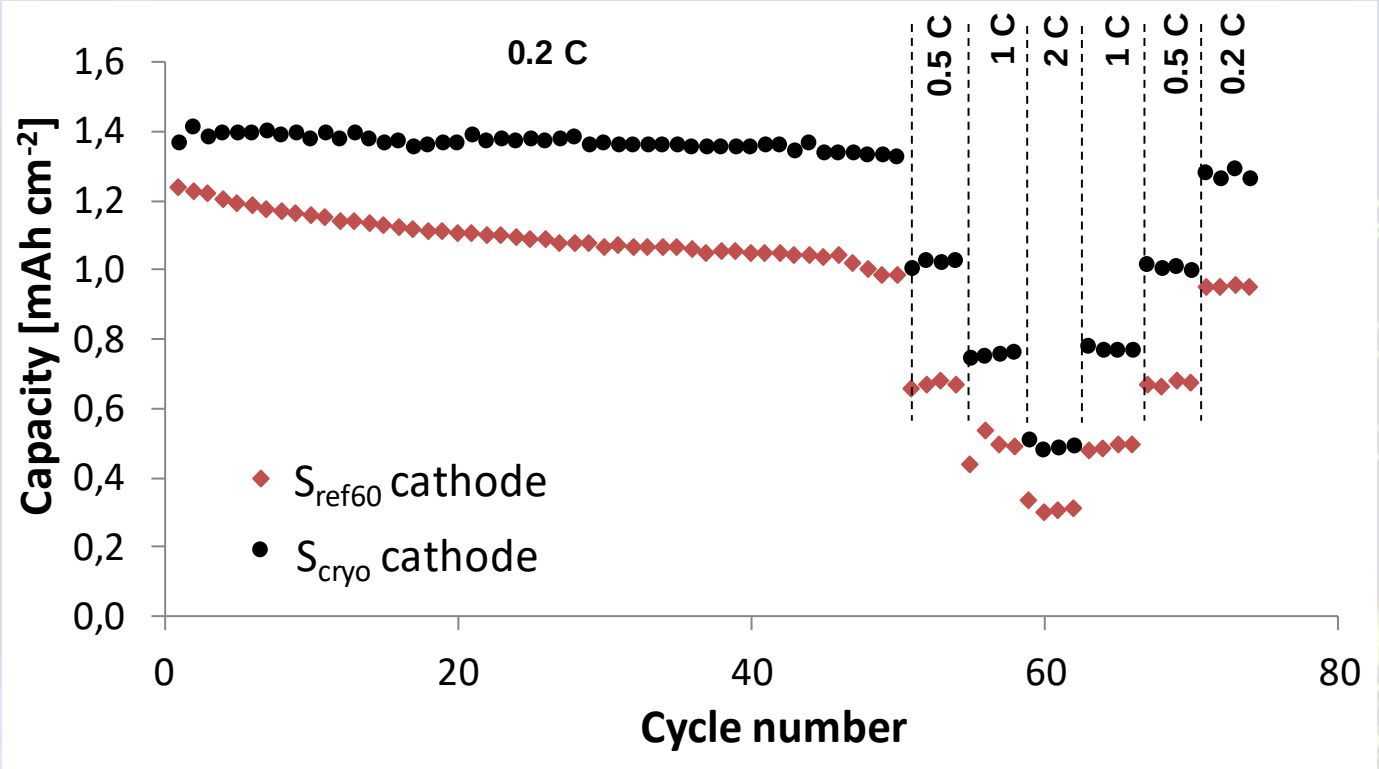
EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

Supported by project: International mobility of researchers at the Brno University of Technology, CZ.02.2.69/0.0/0.0/16_027/0008371

Enegy sources – Electrochemistry

- Li-Sulfur Battery Systems



Changes of capacity of Sref60 cathode and Scryo cathode

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

Supported by project: International mobility of researchers at the Brno University of Technology, CZ.02.2.69/0.0/0.0/16_027/0008371

Enegy sources – Electrochemistry
Na-Ion Storage Systems

- Sodium is abundant, 6th most abundant elements in the earth crust (lithium occupies 33th position), it reach year produciton over 225 M tonnes (litihum just around 0.043 M tonnes)

- Sodium-Ion batteries, most promisable system, next generation of electrochemical power sources, batteries for renewable energy harvesting, cheap, environmental friendly…

- Sodium-ion batteries work on the same principles as the well-known and described lithium-ion batteries, they use same technology most of them use aprotic electrolytes DMC (dimethyl carbonate), EC (ethylene carbonate), PC (propylene carbonate) with salts as $NaCLO_4$ (sodium perchlorate) or $NaPF_6$ (sodium hexafluorophosphate)

- Cathode materials for sodium-ion batteries, similar to convention stable cathode materials for lithium-ion batteries. Cathode material $NaCoO_2$ (sodium cobalt oxide) or $NaNi_{1/2}Mn_{1/2}O_2$ (Sodium nickel manganese oxide)

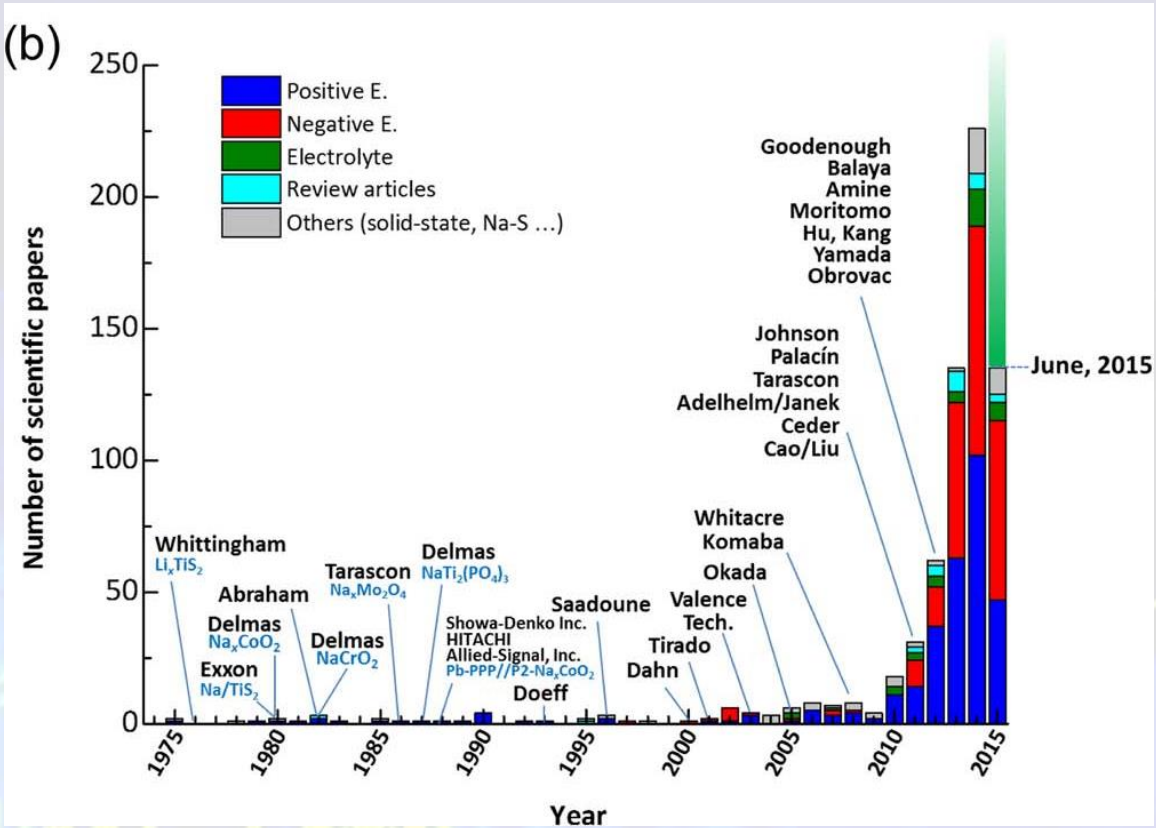
EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

Supported by project: International mobility of researchers at the Brno University of Technology, CZ.02.2.69/0.0/0.0/16_027/0008371

Enegy sources – Electrochemistry
Na-Ion Storage Systems

- Anode materials are issue, Lithium-Ion batteries use manly graphite as active electrode materials for negative electrode (anode), in case of sodium ion it is not possible to use graphite, because sodium ion having large diameter and cannot be inserted among graphite sheets



G. Rousse et .al., Chemistry of Materials 25 (2013) 4946–4956.

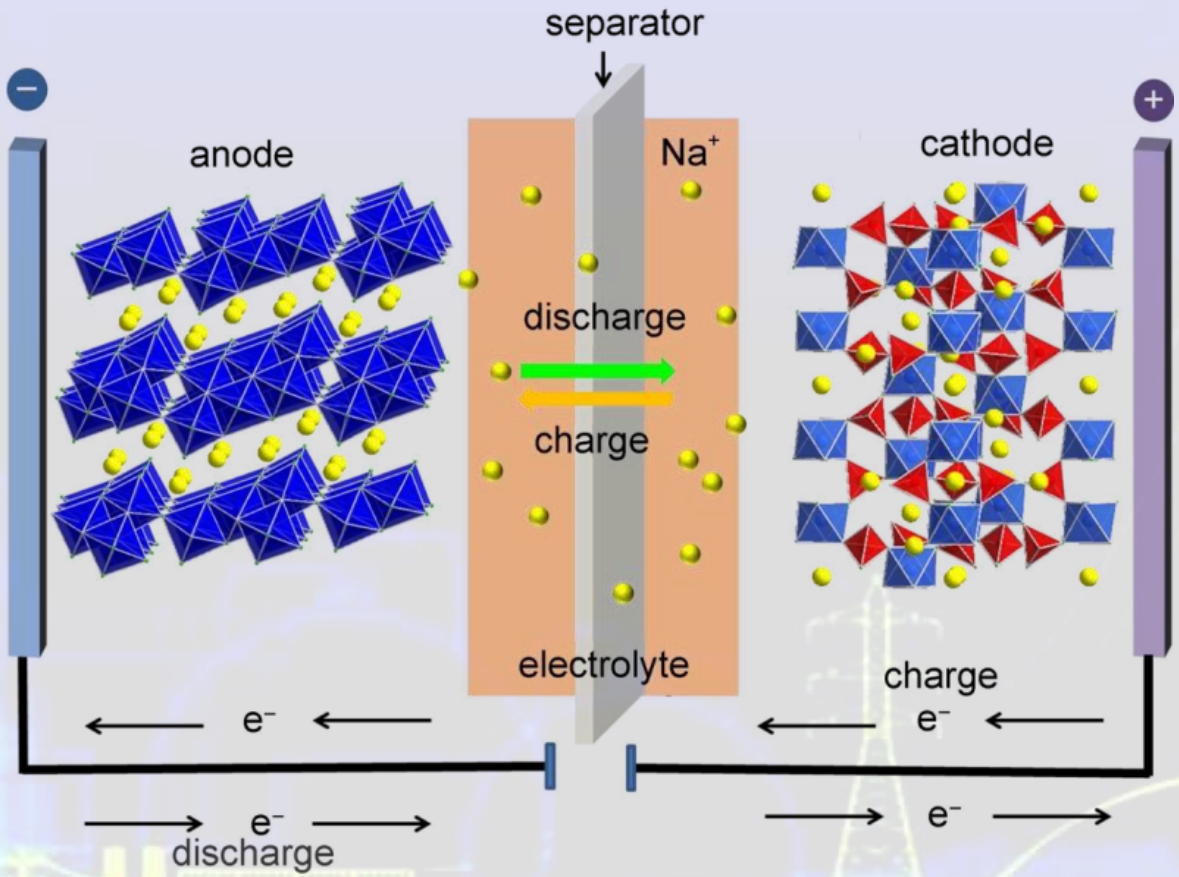
EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

Supported by project: International mobility of researchers at the Brno University of Technology, CZ.02.2.69/0.0/0.0/16_027/0008371

Enegy sources – Electrochemistry

Na-Ion Storage Systems



Schematic illustration of sodium-ion battery working principle
(identical to lithium-ion battery, ‘rocking chair’)

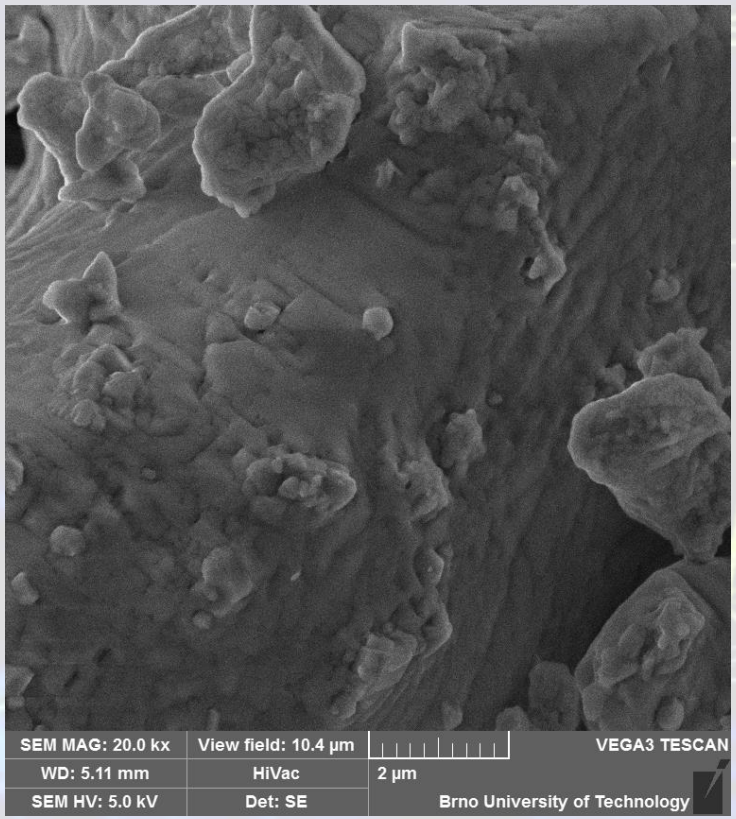
EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

Supported by project: International mobility of researchers at the Brno University of Technology, CZ.02.2.69/0.0/0.0/16_027/0008371

Enegy sources – Electrochemistry
Na-Ion Storage Systems

- Goal is to prepare sodium-titanate material that will be able to accommodate sodium atoms, analogy to comercial available and used (in limited range) lithium titanate oxide (LTO)
- Various ways, solid-liquid or solid synthesis of $Na_xTi_yO_z$ material



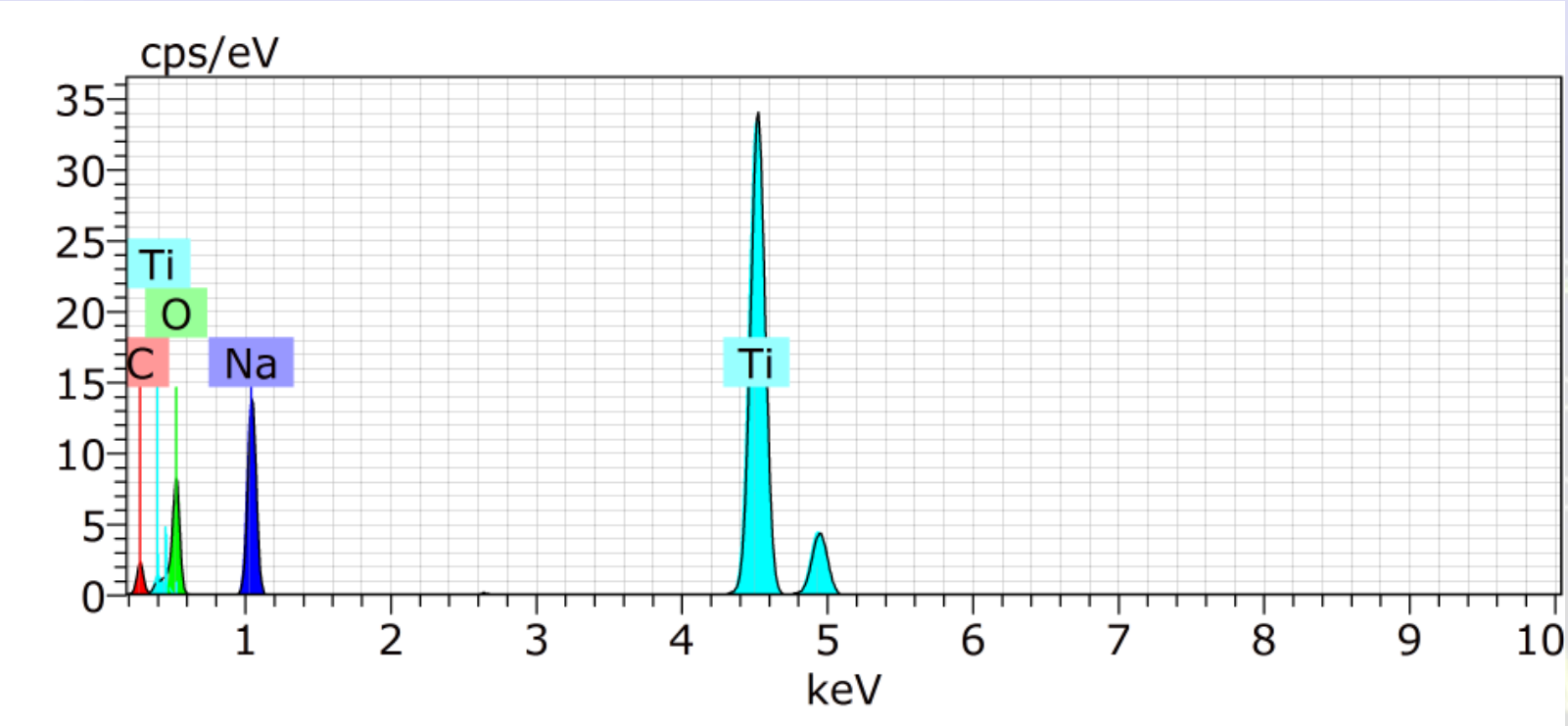
EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

Supported by project: International mobility of researchers at the Brno University of Technology, CZ.02.2.69/0.0/0.0/16_027/0008371

Enegy sources – Electrochemistry

Na-Ion Storage Systems



EDX analytical technique used for the elemental analysis or chemical characterization of a sample

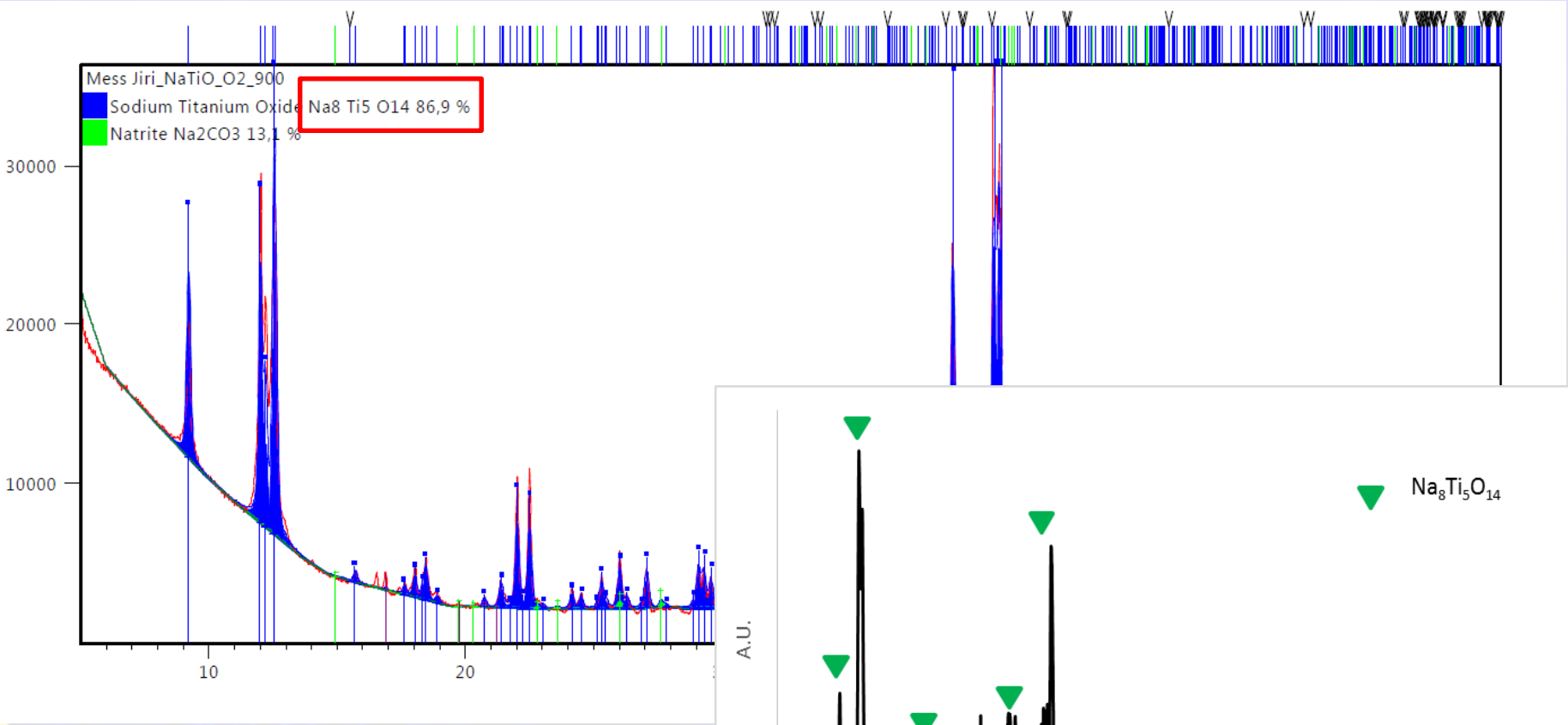
EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

Supported by project: International mobility of researchers at the Brno University of Technology, CZ.02.2.69/0.0/0.0/16_027/0008371

Enegy sources – Electrochemistry

Na-Ion Storage Systems



XRD analysis of NaTiO sample

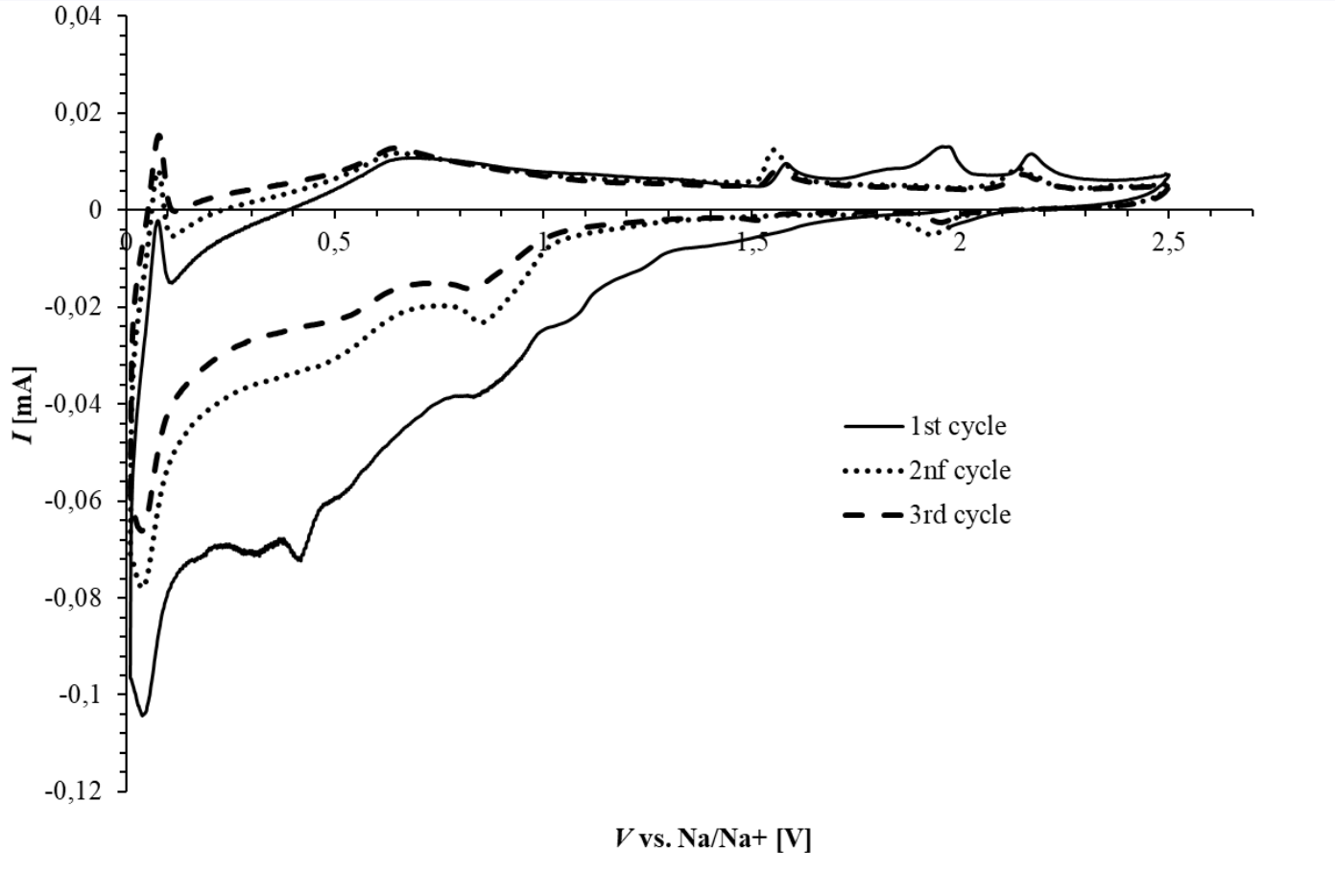
EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

Supported by project: International mobility of researchers at the Brno University of Technology, CZ.02.2.69/0.0/0.0/16_027/0008371

Enegy sources – Electrochemistry

Na-Ion Storage Systems



Cyclic voltammetry (CV) of NaTiO material

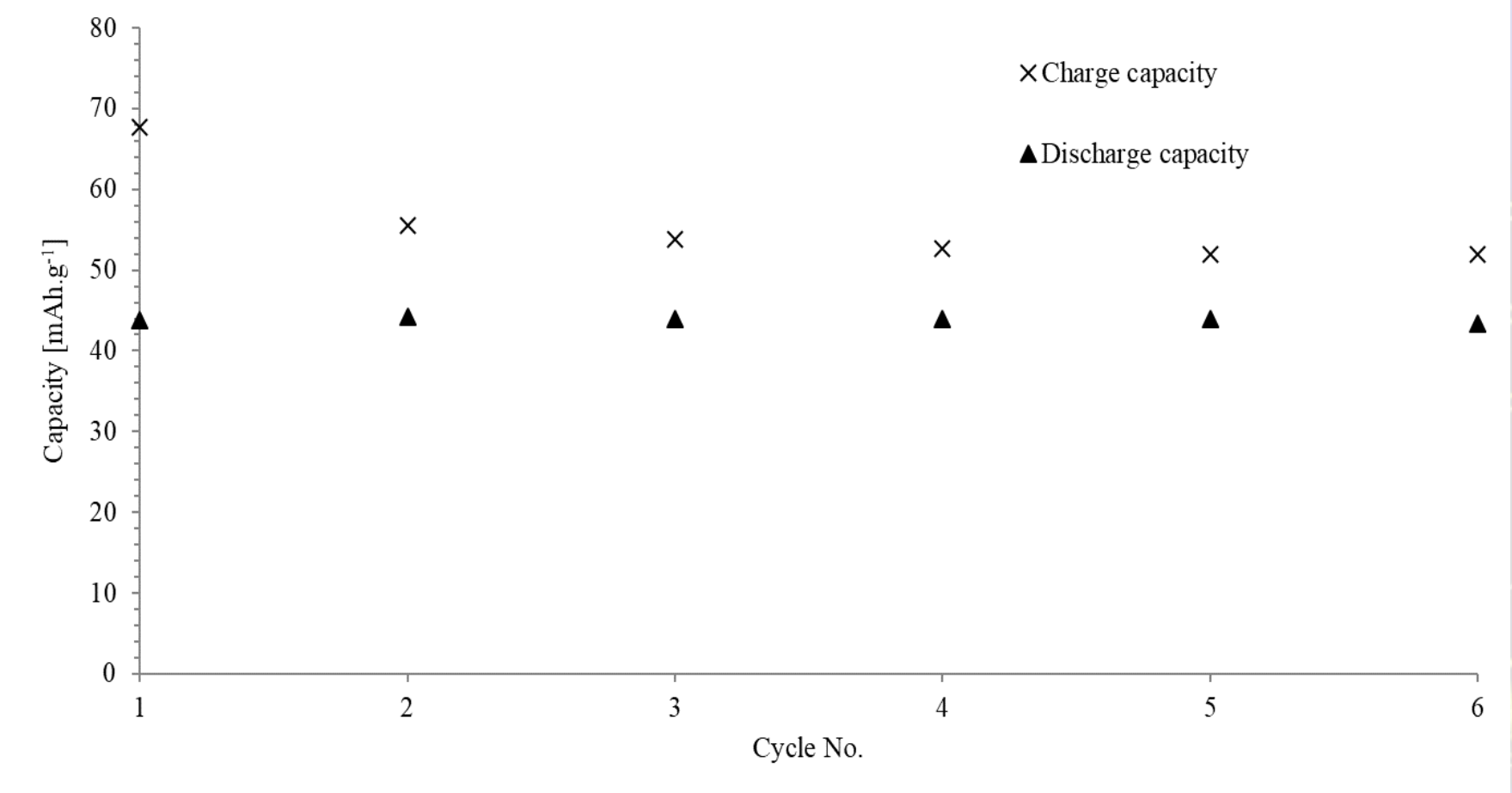
EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

Supported by project: International mobility of researchers at the Brno University of Technology, CZ.02.2.69/0.0/0.0/16_027/0008371

Enegy sources – Electrochemistry
Na-Ion Storage Systems

- Theoretical calculated capacity of $Na_8Ti_5O_{14}$ is ~ 51 mAh/g



First initializating charge-discharge cycles

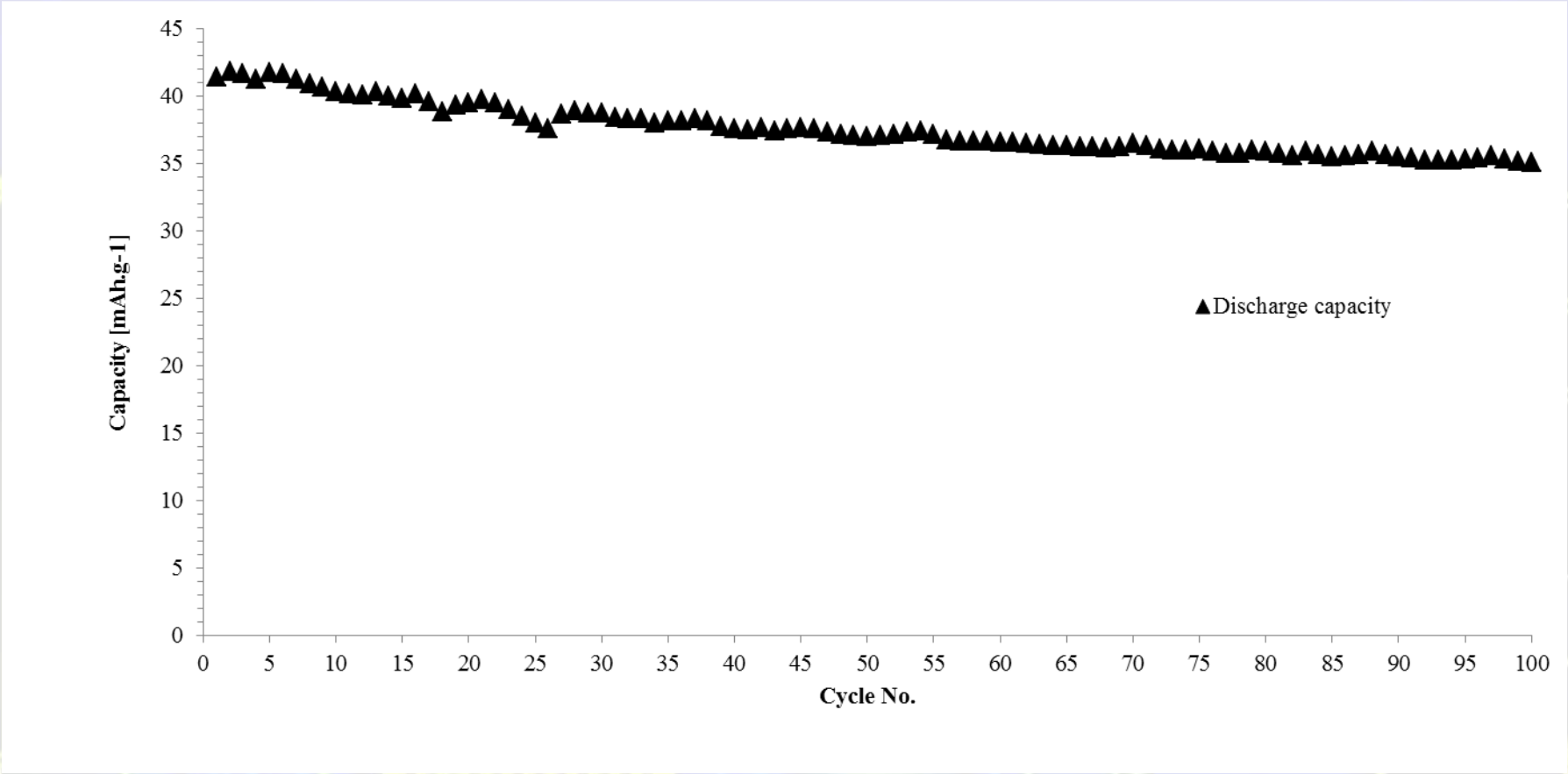
EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

Supported by project: International mobility of researchers at the Brno University of Technology, CZ.02.2.69/0.0/0.0/16_027/0008371

Enegy sources – Electrochemistry

Na-Ion Storage Systems



Galvanostatic cycling at rate 0.2 C

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

Supported by project: International mobility of researchers at the Brno University of Technology, CZ.02.2.69/0.0/0.0/16_027/0008371

Conclusion

- Was prepared and tested $Na_8Ti_5O_{14}$ anode material, we would like to prepare pure sodium titanate material wit lower stechiometry with molecule formula Na_2TiO_3. This formula reach teoreticla capacity around 188 mAh/g, lower than graphite 372 mAh/g, but for stationary application it is still very interesting solution

- In the year 2017 French start-up company CNRS released prototype of sodium ion rechargeable battery, in cylindrical cell of standard format 18650. The battery reached energy density 90 WH/kg and lifespan over 2000 cycles…

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

Supported by project: International mobility of researchers at the Brno University of Technology, CZ.02.2.69/0.0/0.0/16_027/0008371

Brno Univesity of Technology

- Cooperation in EU projects
- Possess the facility background for excellent research
- Offer cooperation within bilateral project regarding stuff and student mobility, Erasmus …
- Help you to provide the invitation litters, conclude memorandum between ULPGC and BUT, we are widely opened to any collaboration
- You are most welcome to visit us on our international meeting ABAF (Advanced Batteries, Accumulators and Fuel Cells), annually held in Brno, or anytime…

- Jiri Libich, libich@feec.vutbr.cz
- University https://www.vutbr.cz/en/
- Conference meeting https://www.aba-brno.cz/

19th ABAF
BRNO 2018
Advanced Batteries, Accumulators and Fuel Cells

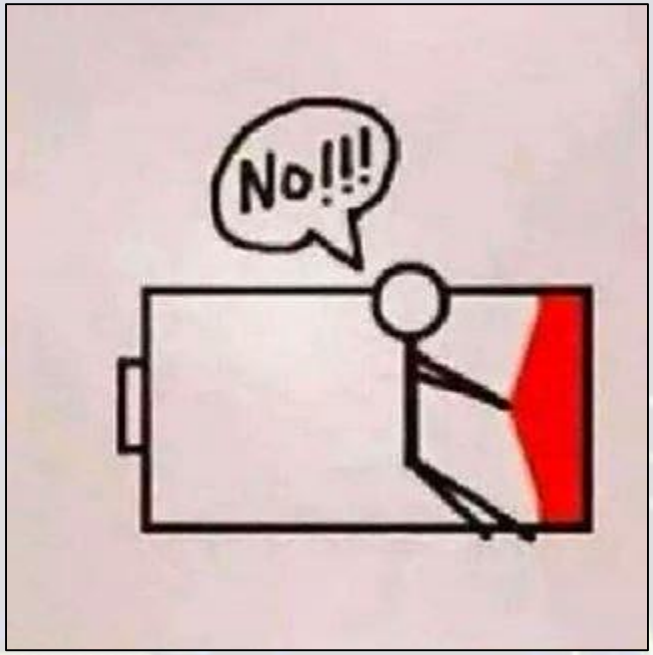
FACULTY OF ELECTRICAL ENGINEERING AND COMMUNICATION
department of electrical and electronic technology

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research, Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

Supported by project: International mobility of researchers at the Brno University of Technology, CZ.02.2.69/0.0/0.0/16_027/0008371

Thank you for your attention!



EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

Supported by project: International mobility of researchers at the Brno University of Technology, CZ.02.2.69/0.0/0.0/16_027/0008371