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# Workshop Electrode Materials for Sodium-Ion Batteries

TU Wien  
26. February 2019



Dr. Jiri Libich



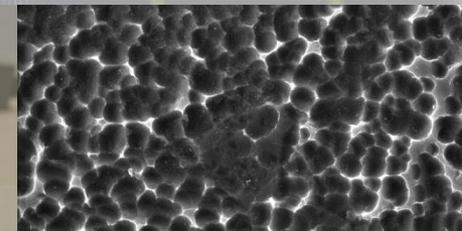
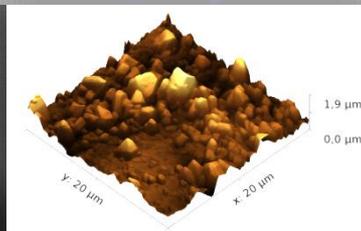
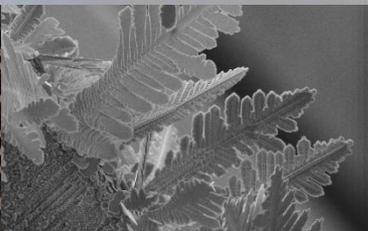
FACULTY OF ELECTRICAL **department of electrical**  
ENGINEERING **and electronic technology**  
AND COMMUNICATION



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



# Brno University of Technology

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



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



# Faculty of Electrical Engineering and Communication (FEEC)

- Over 3500 students
- Divided to 14 departments



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



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



# 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

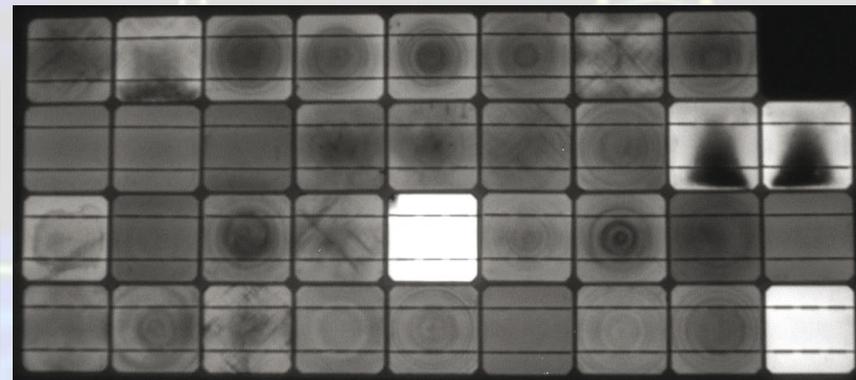
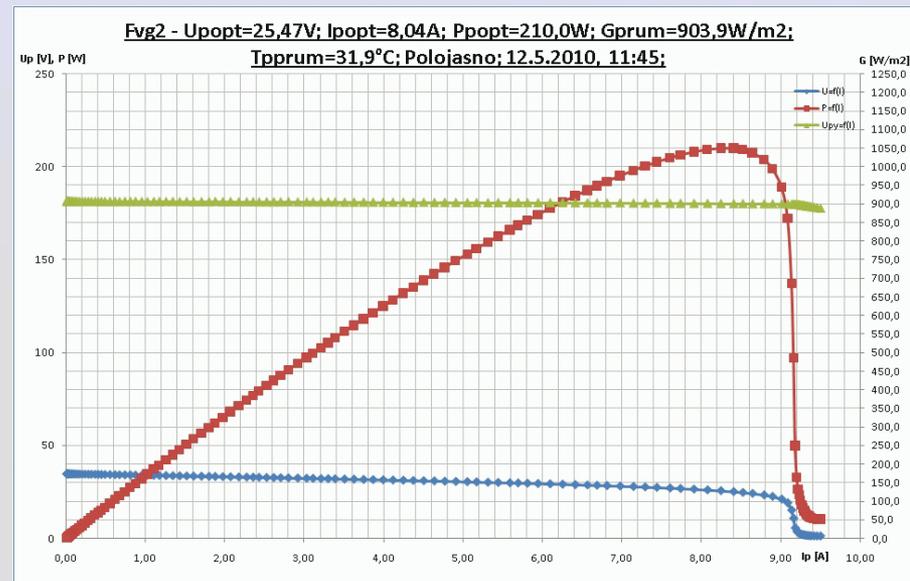
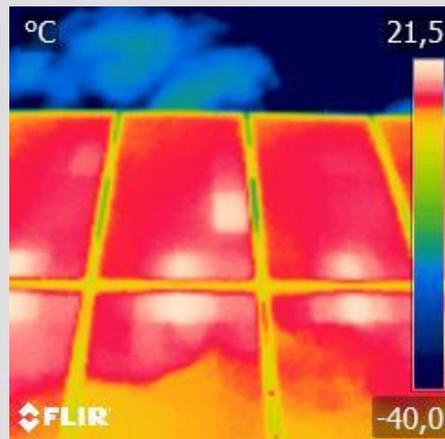
- Diagnostics of material properties – XRD
  - Climate tests
  - Corrosion Tests
  - Surface Diagnostics – ESEM, AFM
- Materials

- Diagnostics of the soldering process, technology
  - Surface treatment
- Technology

- 3D Modeling and Simulations
  - Design of electronics and firmware
- Simulations and computer design

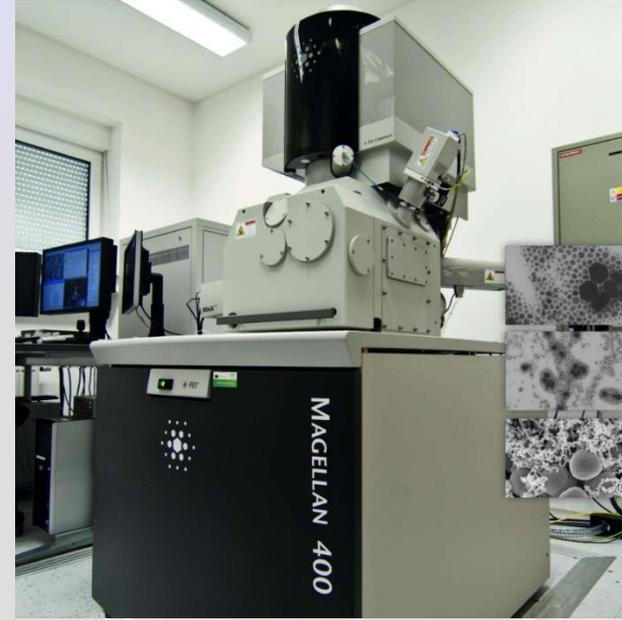
# Energy sources – Renewable

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

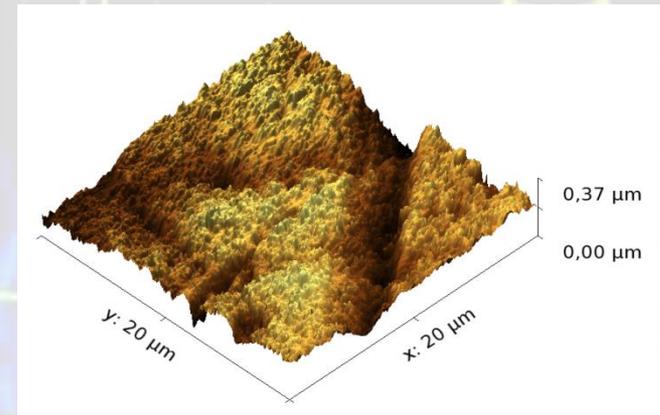
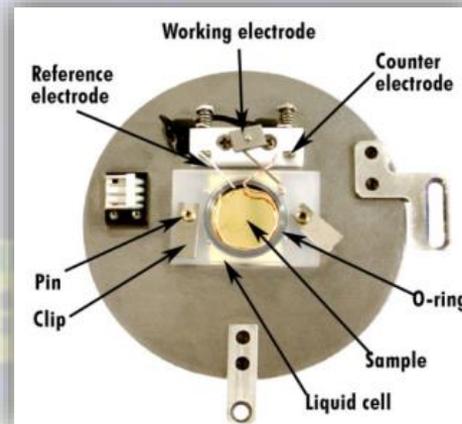
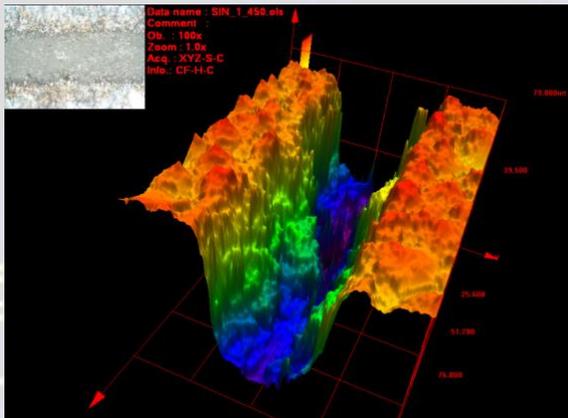
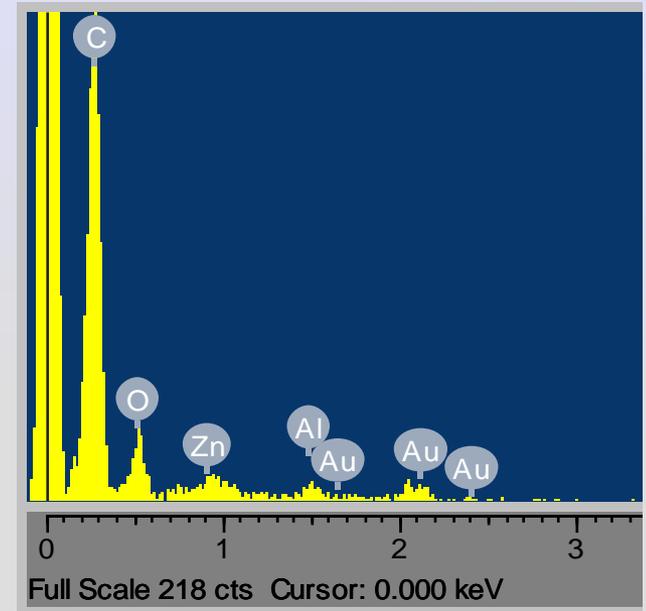
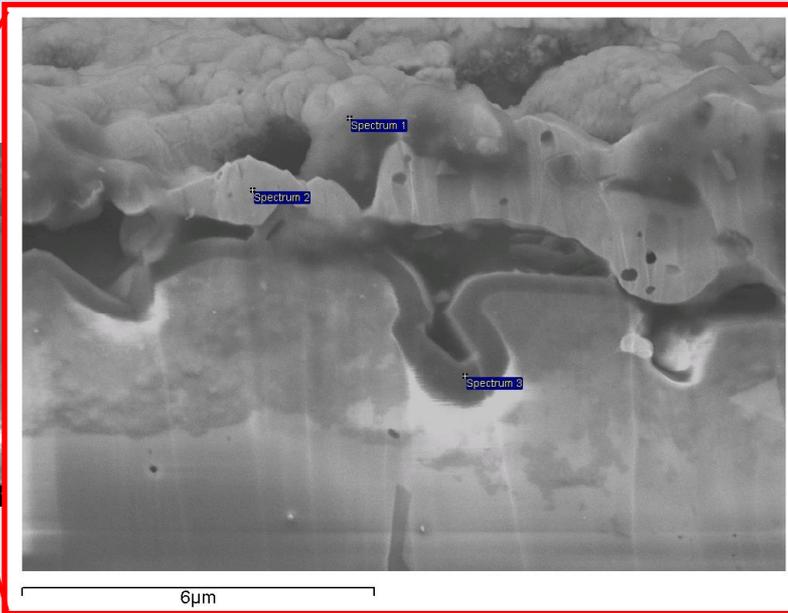
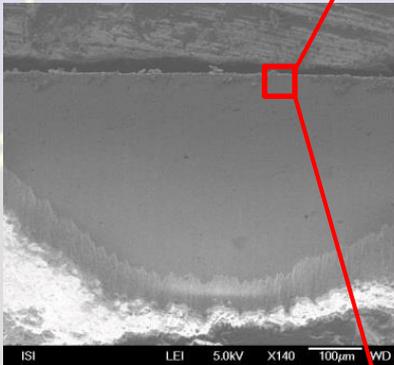


# Materials

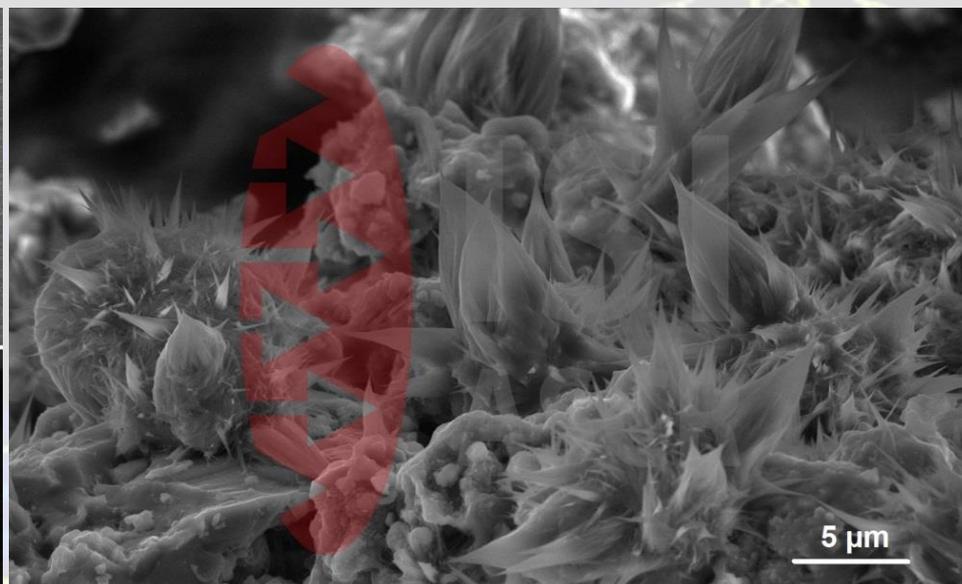
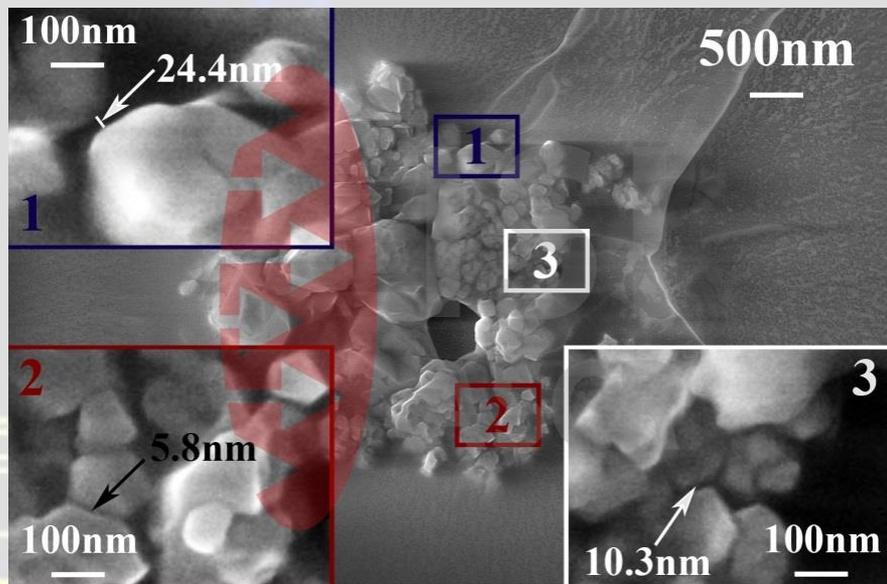
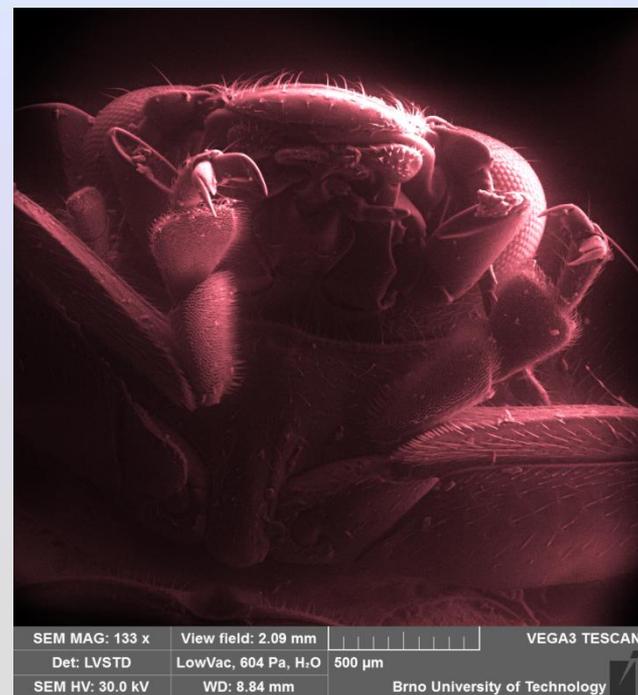
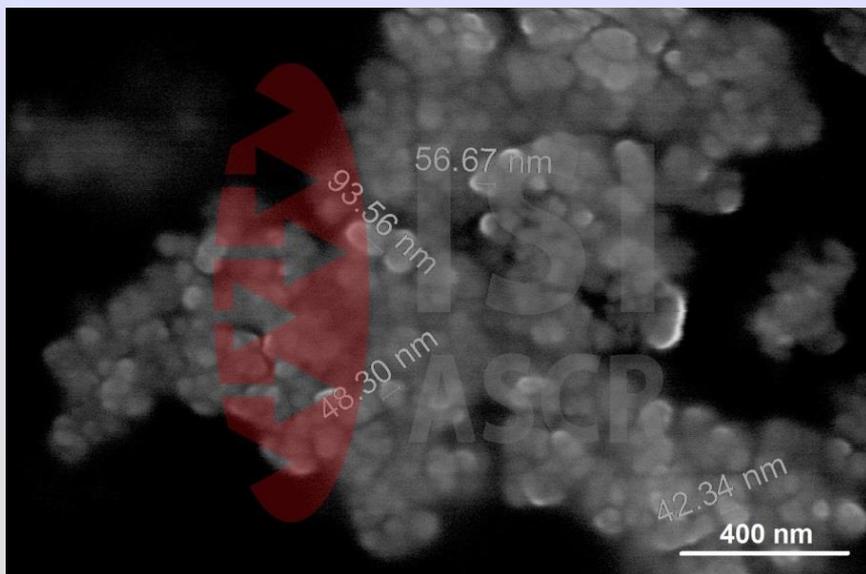
- Instruments: ESEM, AFM, XRD



# Materials

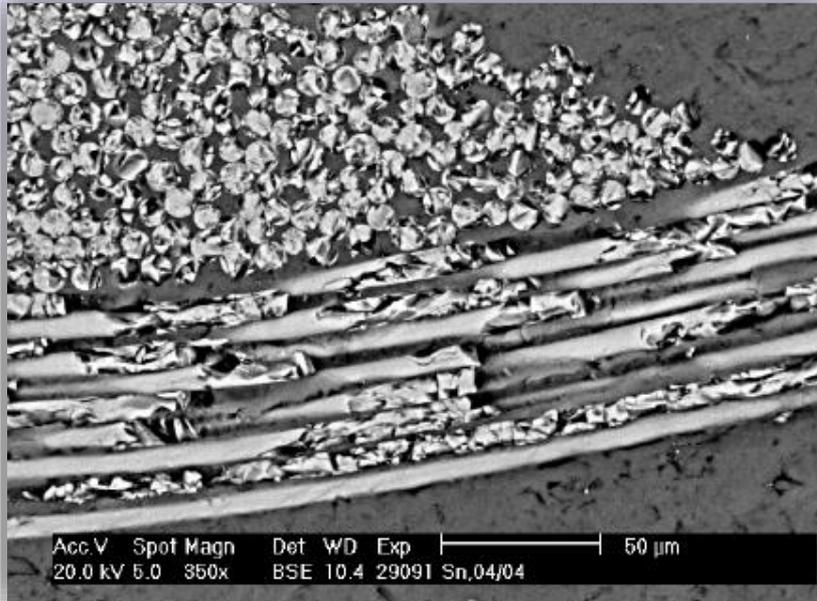


# Materials



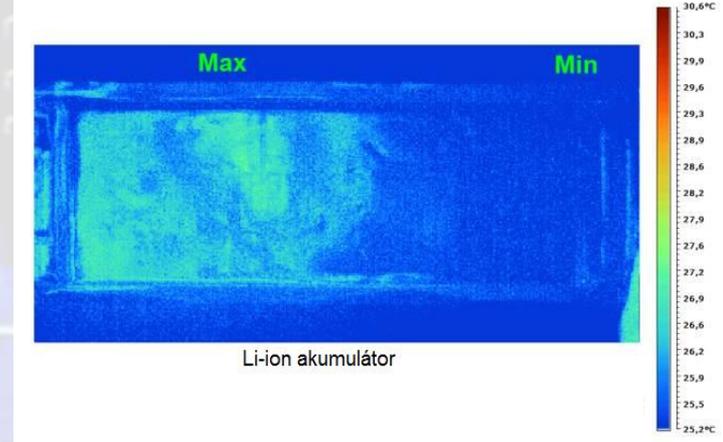
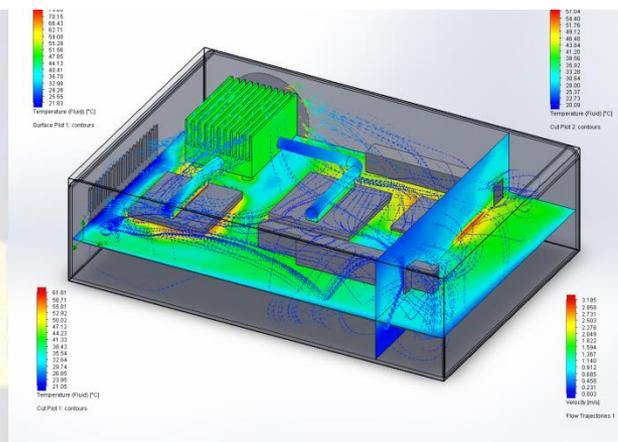
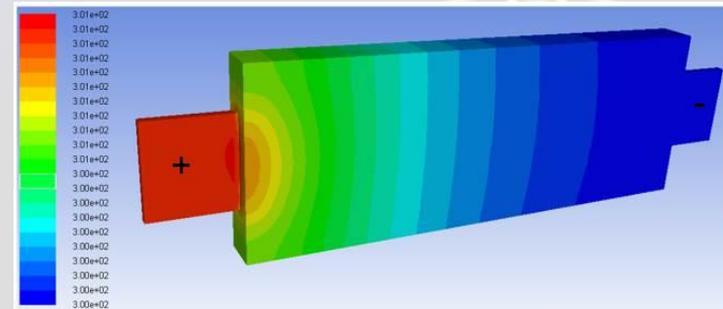
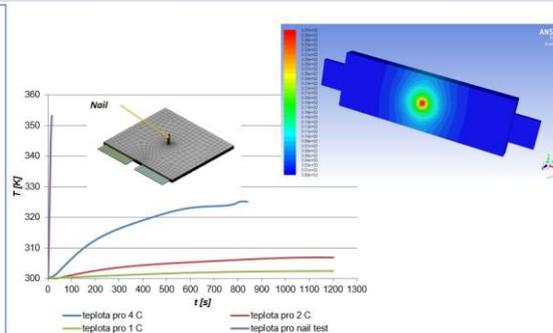
# Technology

- Assembly and interconnection technologies, defect analysis



# 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.



# Energy sources – Electrochemistry

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

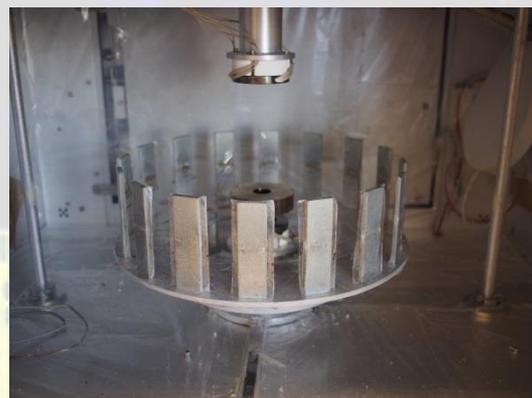
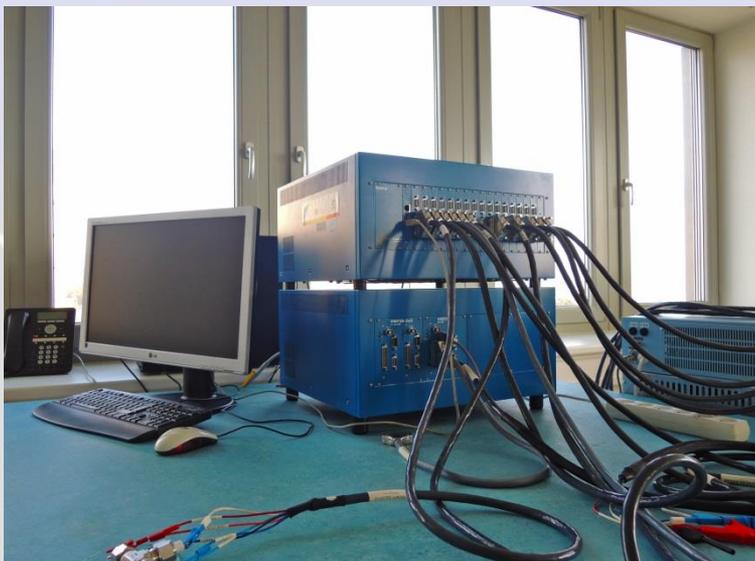


- Selected research activities in terms of electrochemistry
  - Li-ion battery
  - Lithium ion battery for the smart textiles applications
- Post-Li battery systems (Na-Ion, Li-Sulphur)
  - Lead-acid batteries
  - High-temperature ceramic materials
  - Flow-through redox systems



# Energy sources – Electrochemistry

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



# Energy sources – Electrochemistry

## Current research in electrochemical energy storage systems

- Lithium-Ion Batteries and Post-Lithium systems
  - Basic research of conventional and advanced (5 Volts)  $\text{LiFePO}_4$ ,  $\text{LiCoO}_2$  and  $\text{LiMn}_2\text{O}_4$  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.



# Energy sources – Electrochemistry

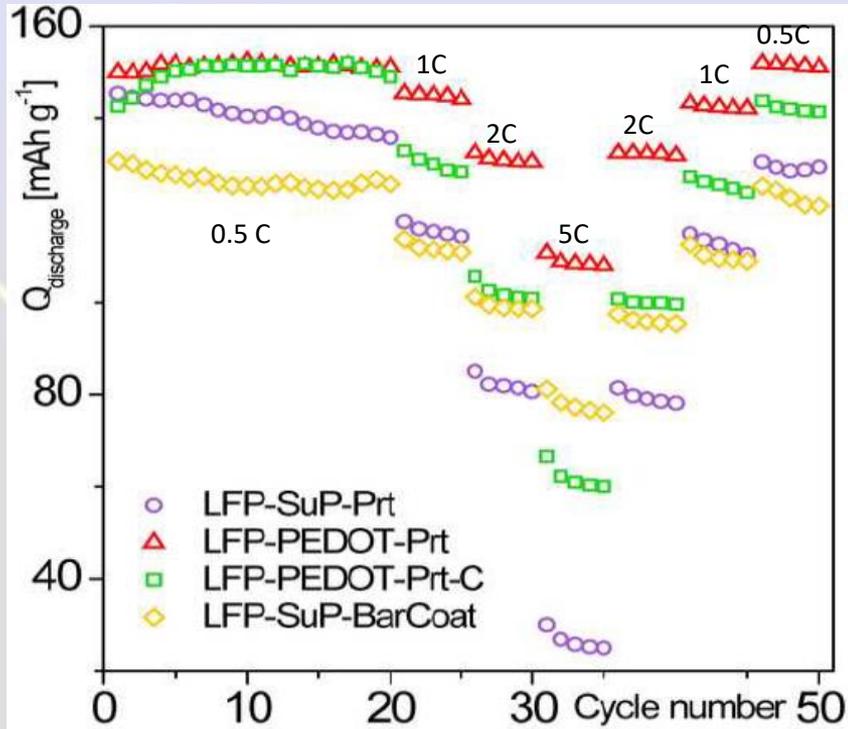
## Cathode material for lithium ion accumulators prepared by screen printing for the smart textiles applications

- $\text{LiFePO}_4$  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

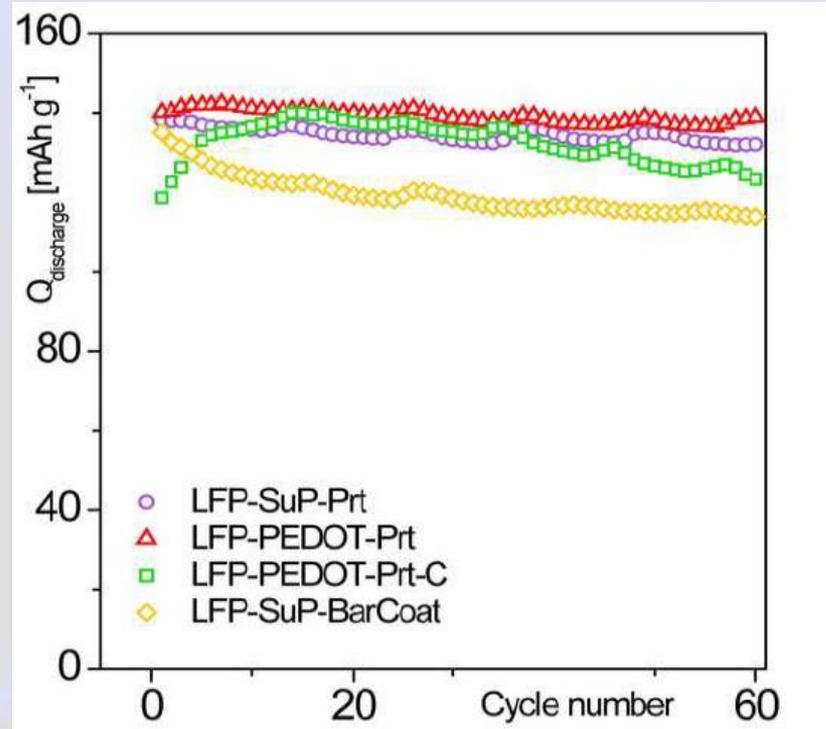
Code name	Electrode material	Binder	Conductive content	Deposition technique	Cathode Underlayer
LFP-SuP-Prt	$\text{LiFePO}_4$	PVDF	Super P	Screen printing	No
LFP-PEDOT-Prt	$\text{LiFePO}_4$	PEDOT:PSS	PEDOT:PSS	Screen printing	No
LFP-PEDOT-Prt-C	$\text{LiFePO}_4$	PEDOT:PSS	PEDOT:PSS	Screen printing	Carbon
LFP-SuP-BarCoat	$\text{LiFePO}_4$	PVDF	Super P	Spiral Bar Coating	No



# Energy sources – Electrochemistry



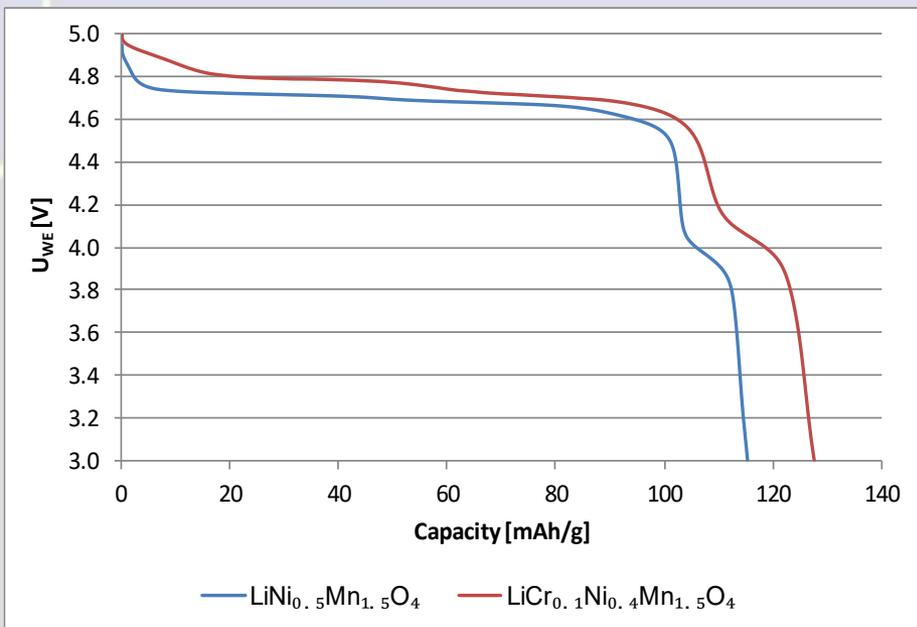
Change of capacity of the  $\text{LiFePO}_4$  electrode layers for different C-rates: 0.5, 1, 2, 5, 2, 1, and 0.5.



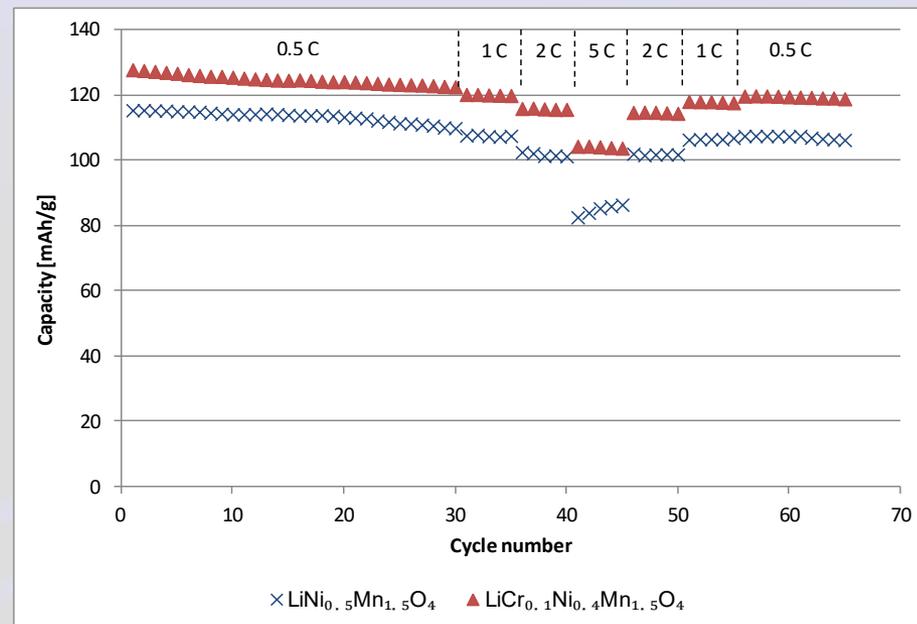
The cycling performance LFP-SuP-Prt, LFP-PEDOT-Prt, LFP-PEDOT-Prt-C, LFP-SuP-BarCoat, at 1 C for 60 cycles.

# Energy sources – Electrochemistry

- 5 Volts cathode materials:  
Effect of Cr doping to the properties of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$



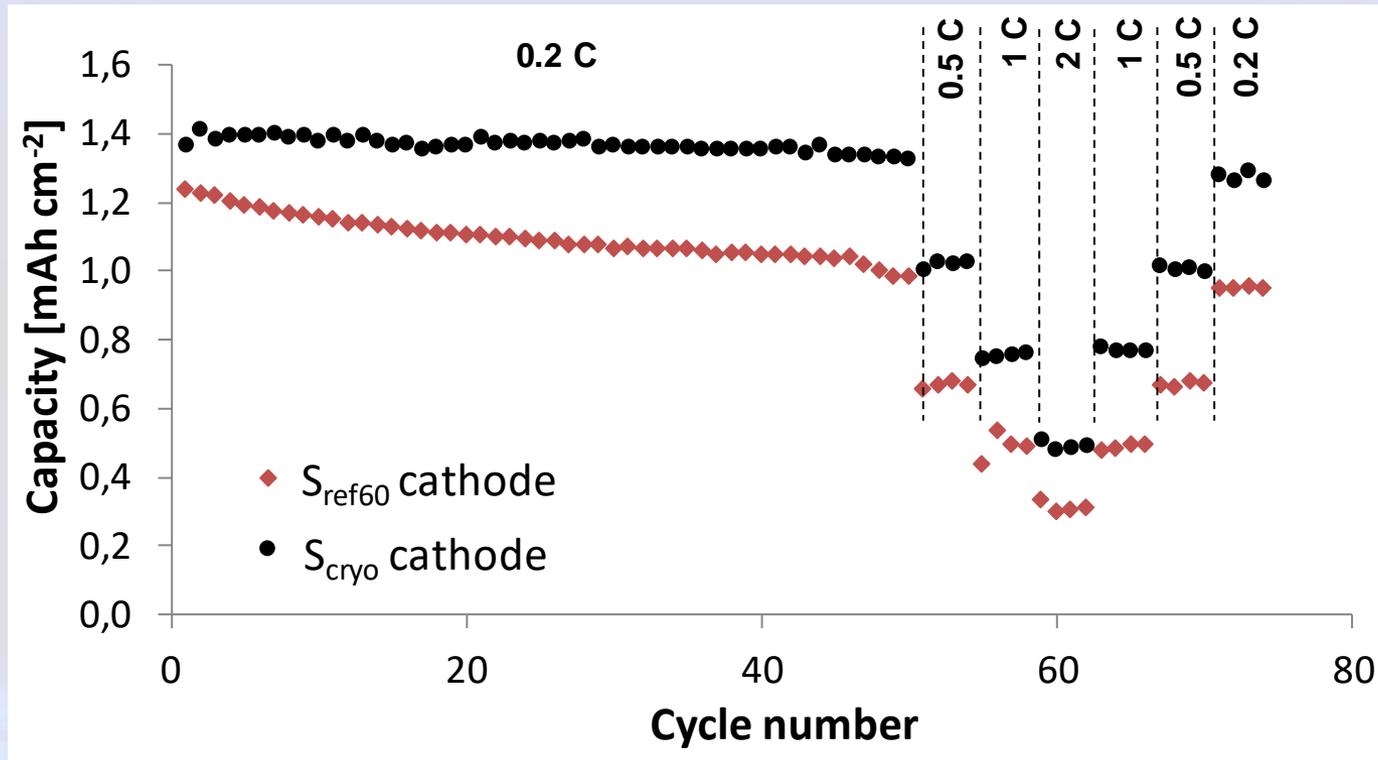
Comparison of first discharge curves of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  and  $\text{LiCr}_{0.1}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$  at 0.5 C



Comparison of capacity change depending on the load for materials  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  and  $\text{LiCr}_{0.1}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$

# Energy sources – Electrochemistry

- Li-Sulfur Battery Systems



Changes of capacity of S<sub>ref60</sub> cathode and S<sub>cryo</sub> cathode

# Na-Ion Storage Systems

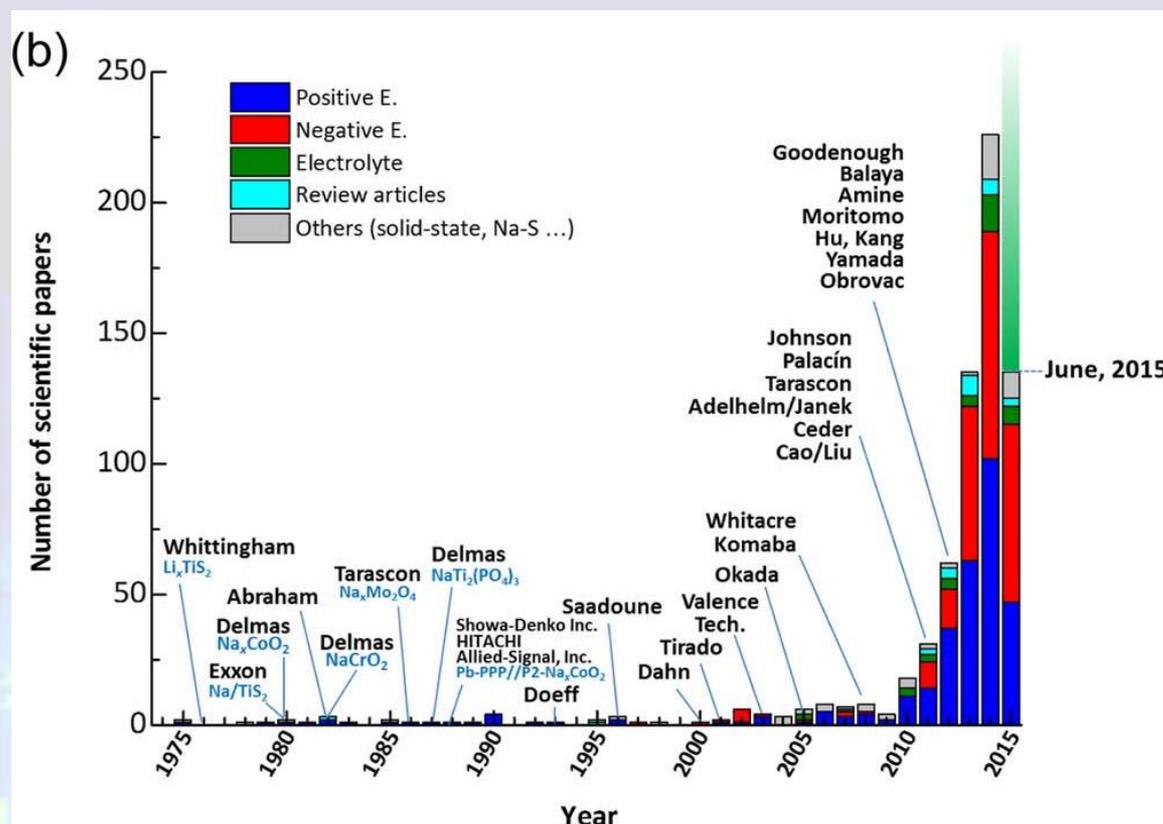
## Energy sources – Electrochemistry

- Sodium is abundant, 6<sup>th</sup> most abundant elements in the earth crust (lithium occupies 33<sup>th</sup> position), it reach year produciton over 225 M tonnes (lithium 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<sub>4</sub> (sodium perchlorate) or NaPF<sub>6</sub> (sodium hexafluorophosphate)
- Cathode materials for sodium-ion batteries, similar to convention stable cathode materials for lithium-ion batteries. Cathode material NaCoO<sub>2</sub> (sodium cobalt oxide) or NaNi<sub>1/2</sub>Mn<sub>1/2</sub>O<sub>2</sub> (Sodium nickel manganese oxide)



# Na-Ion Storage Systems

- Anode materials are issue, Lithium-Ion batteries use mainly 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

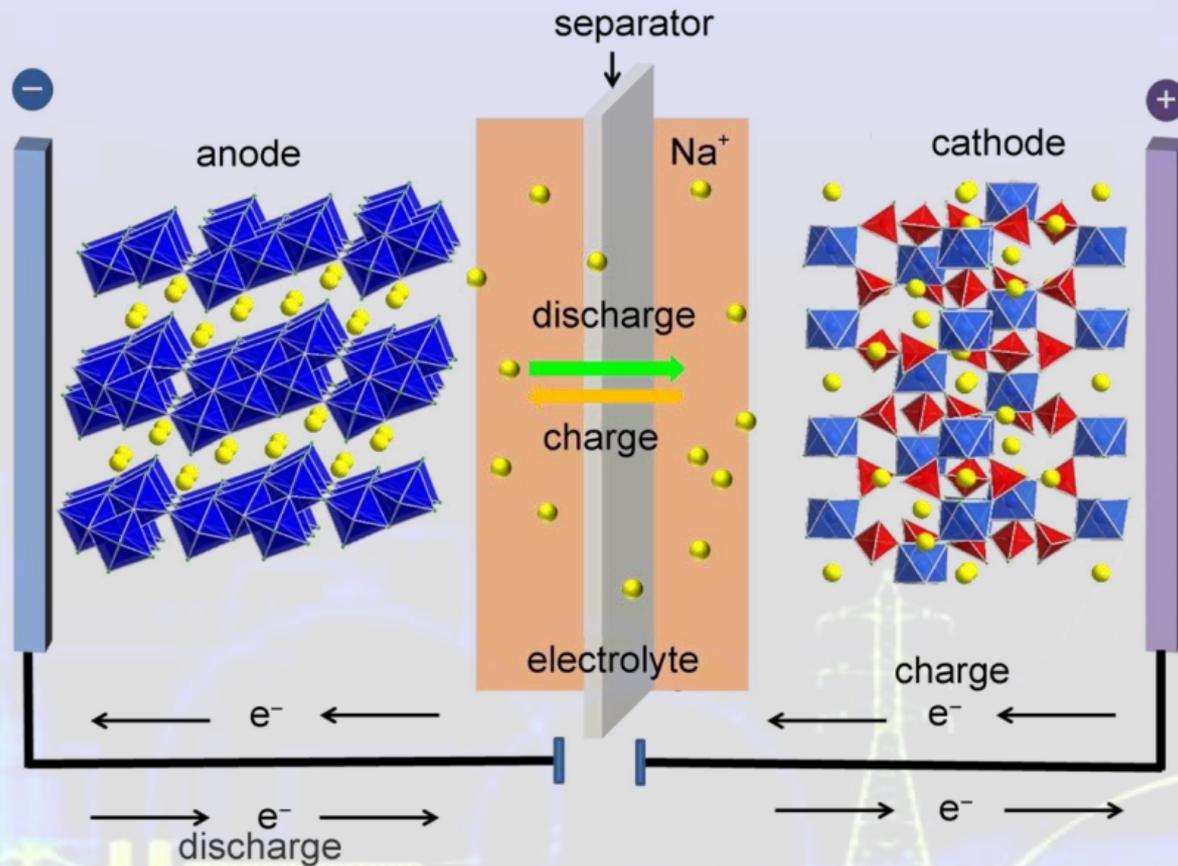


G. Rousse et al., Chemistry of Materials 25 (2013) 4946–4956.



# Energy sources – Electrochemistry

## Na-Ion Storage Systems

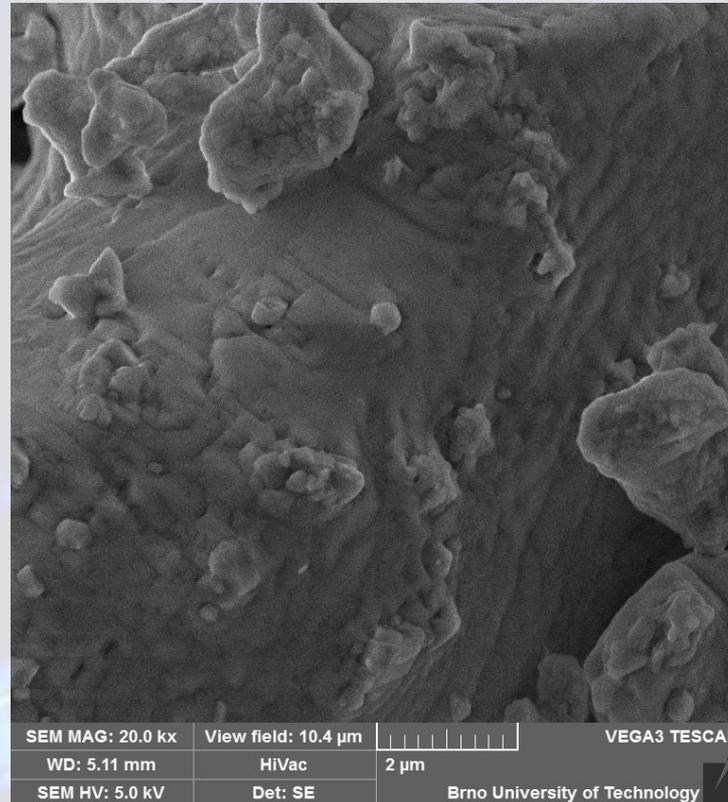


Schematic illustration of sodium-ion battery working principle  
(identical to lithium-ion battery, 'rocking chair')

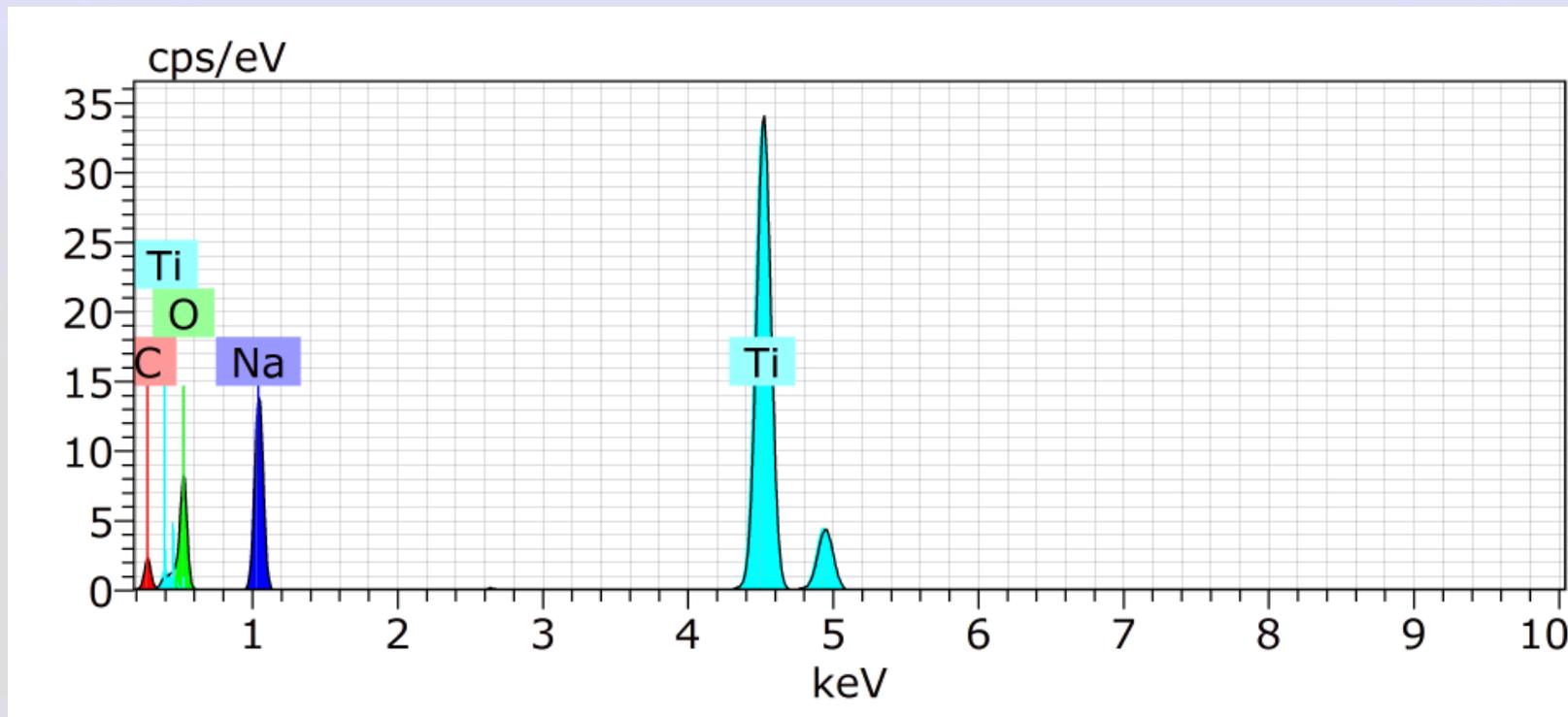


# Na-Ion Storage Systems

- Goal is to prepare sodium-titanate material that will be able to accommodate sodium atoms, analogy to commercial available and used (in limited range) lithium titanate oxide (LTO)
- Various ways, solid-liquid or solid synthesis of  $\text{Na}_x\text{Ti}_y\text{O}_z$  material

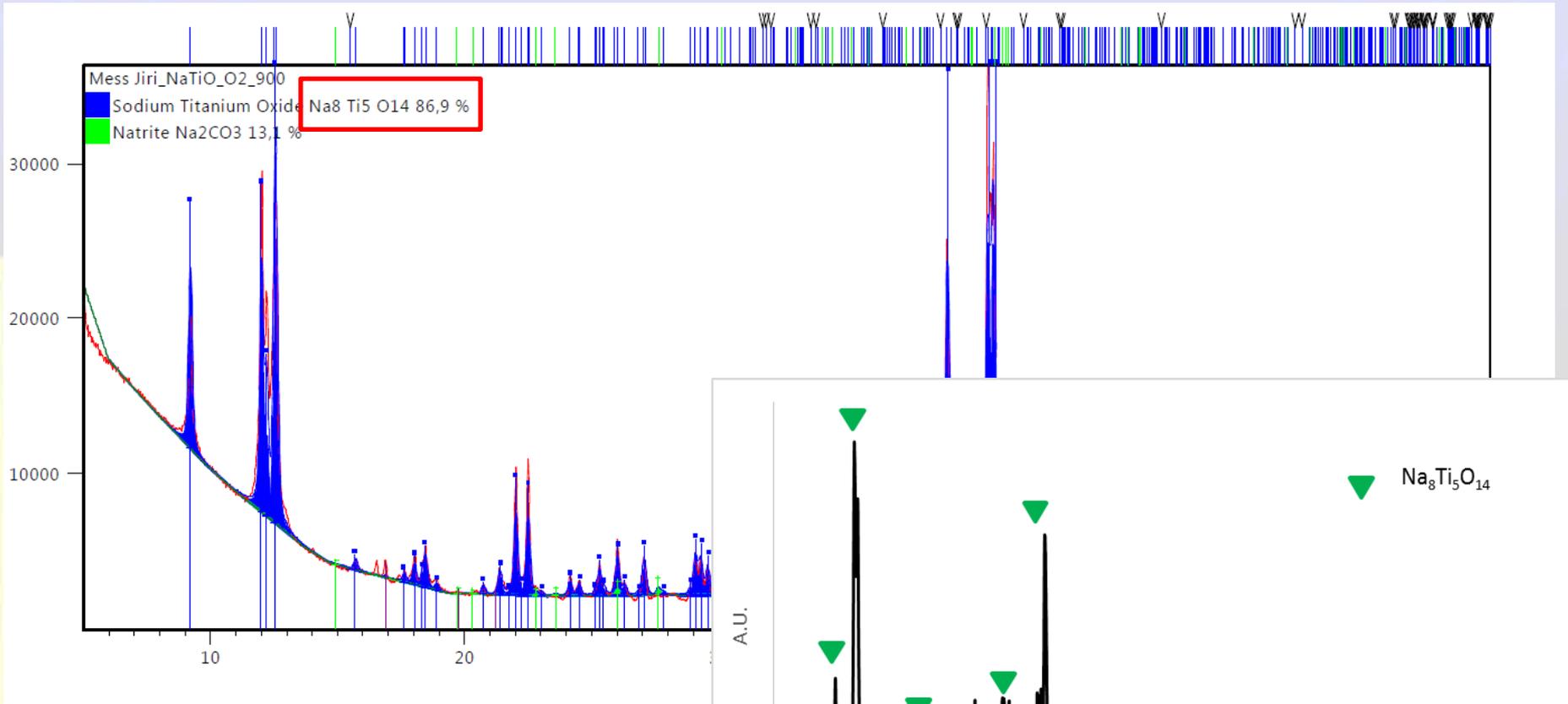


# Na-Ion Storage Systems

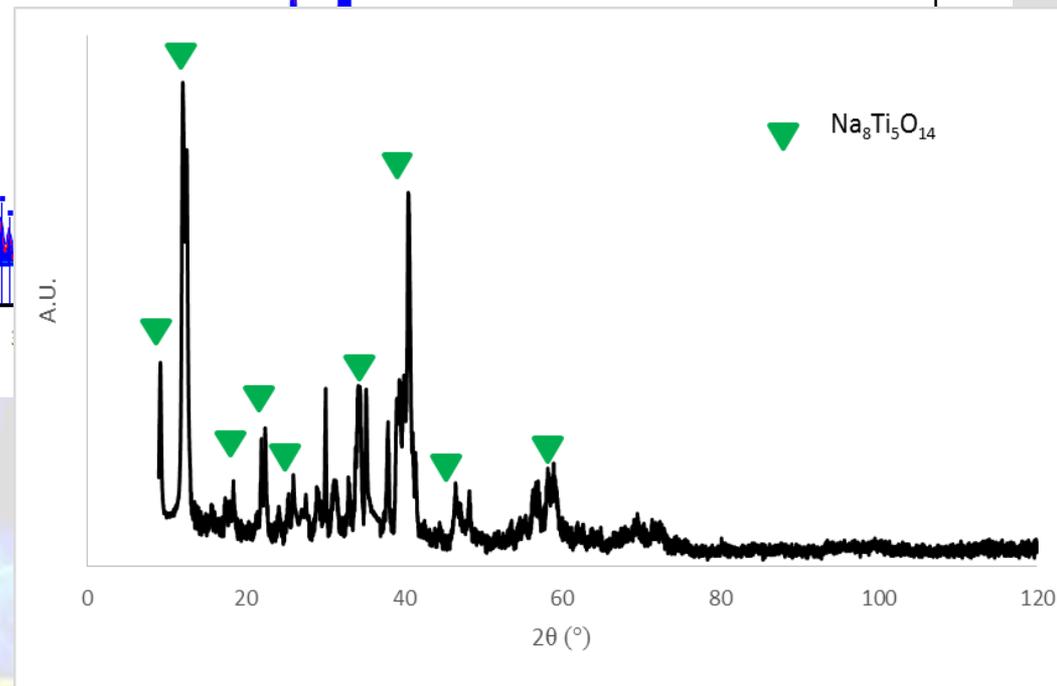


EDX analytical technique used for the elemental analysis or chemical characterization of a sample

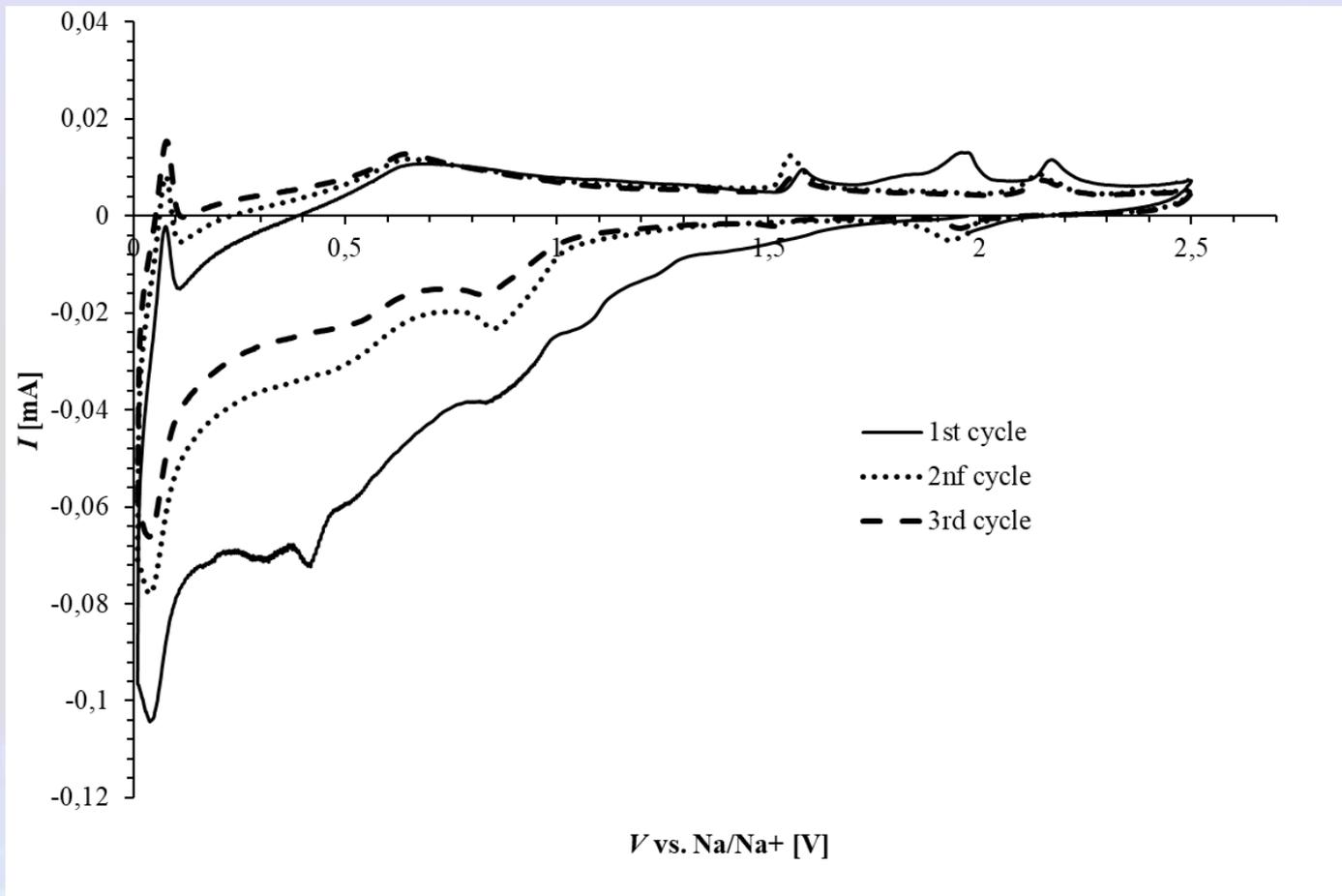
# Na-Ion Storage Systems



XRD analysis of NaTiO sample



# Na-Ion Storage Systems

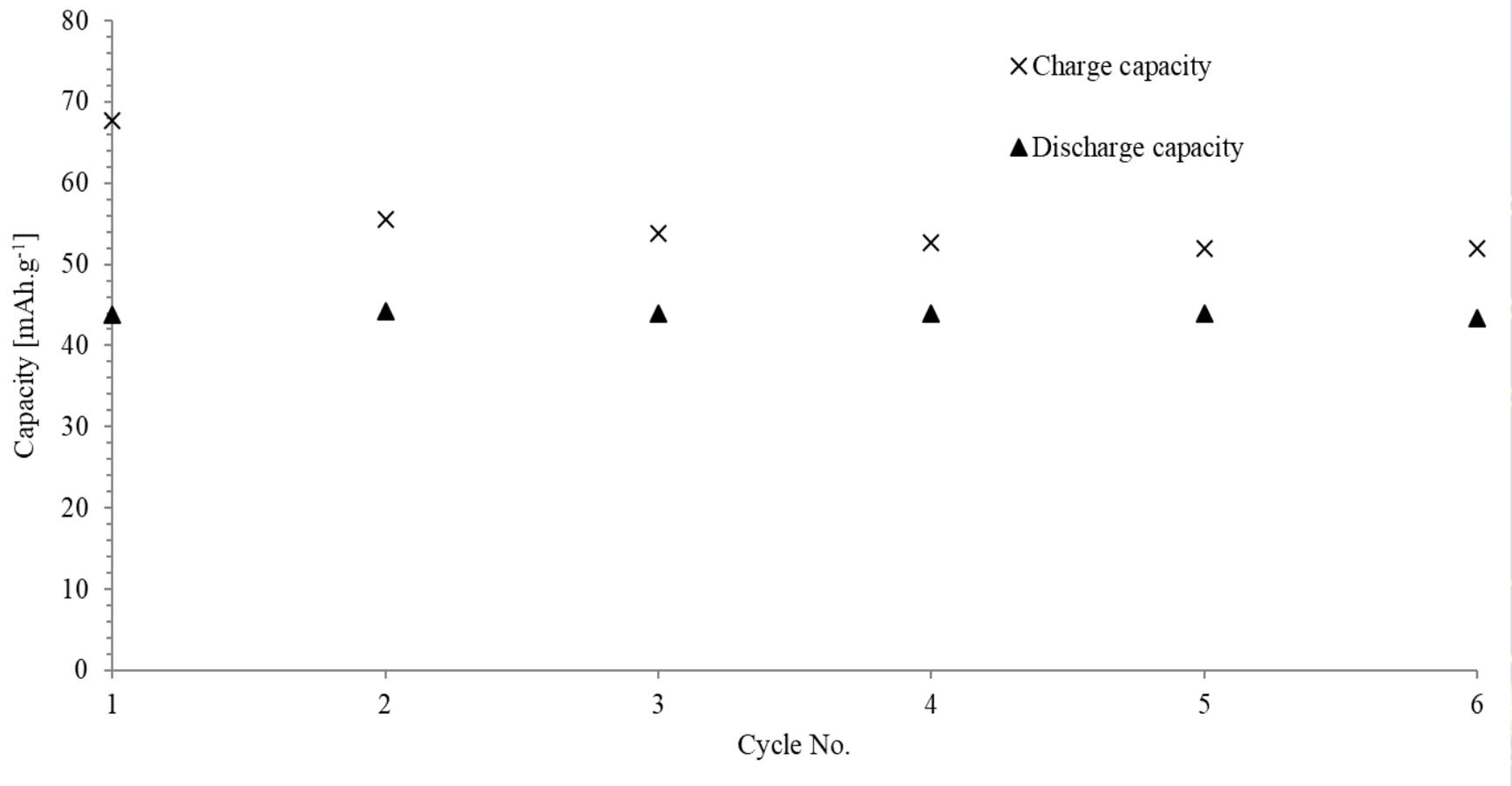


Cyclic voltammety (CV) of NaTiO material



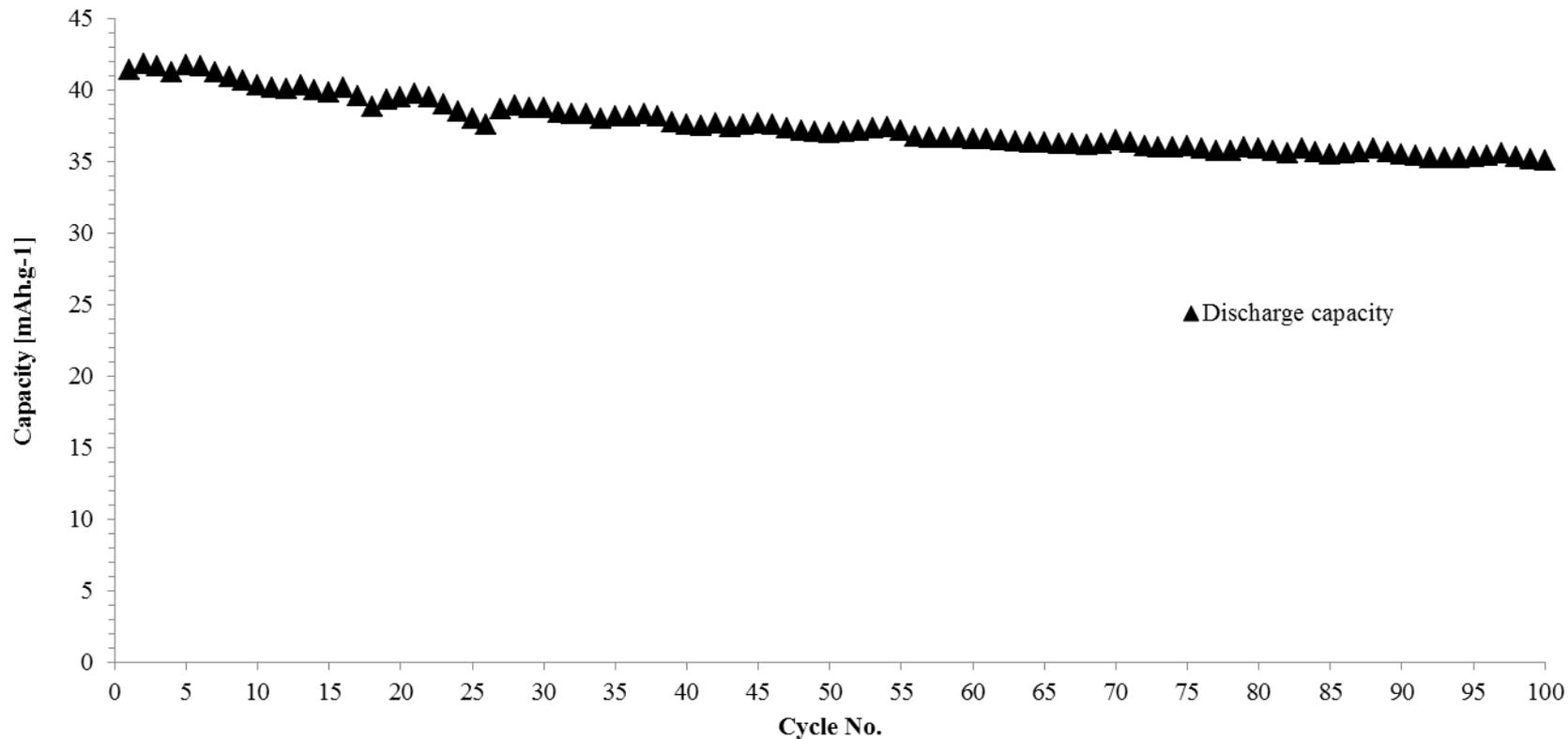
# Na-Ion Storage Systems

- Theoretical calculated capacity of  $\text{Na}_8\text{Ti}_5\text{O}_{14}$  is  $\sim 51 \text{ mAh/g}$



First initializing charge-discharge cycles

# Na-Ion Storage Systems



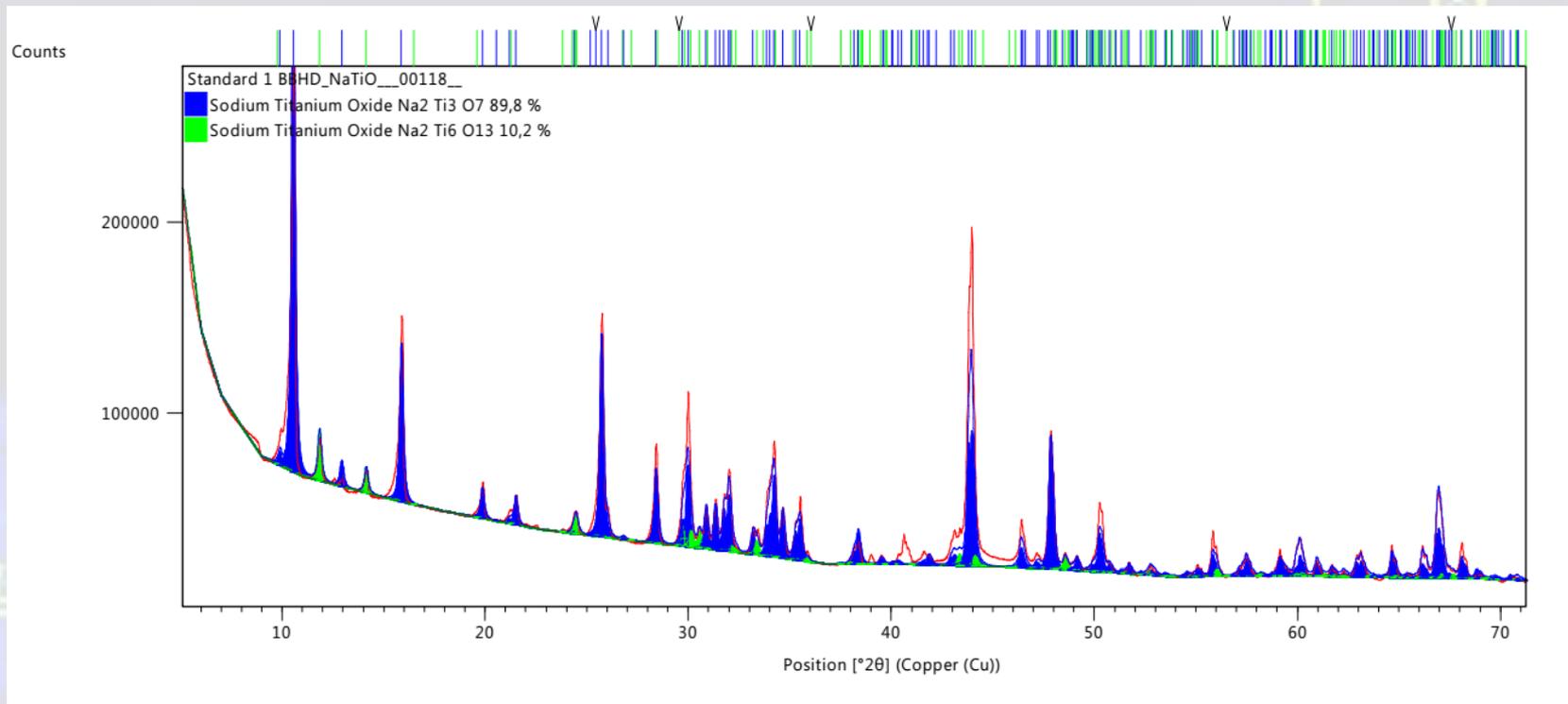
Galvanostatic cycling at rate 0.2 C



# Na-Ion Storage Systems

## Current work

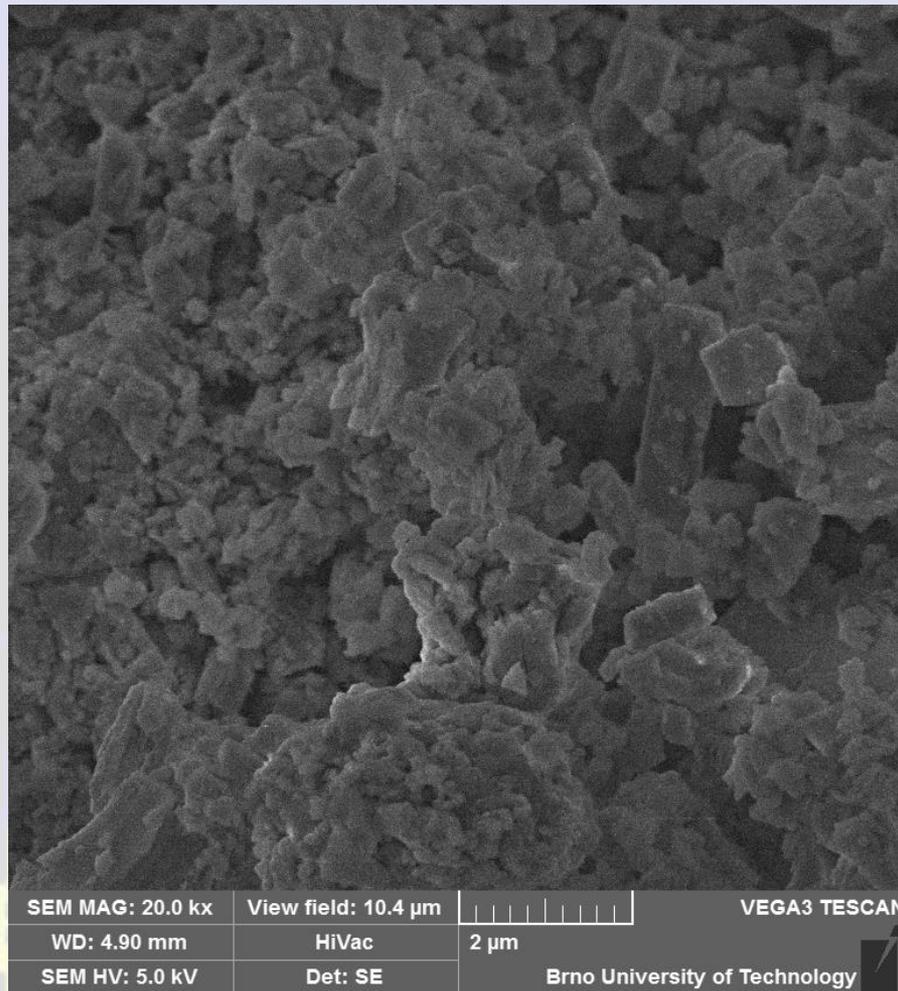
- The series of sodium-titanate materials with formula  $\text{Na}_x\text{Ti}_y\text{O}_z$  were prepared with help of sol-gel process.
- Afterwards the electrochemical testing take a part, from the series of synthesized materials, few exhibited interesting results, as the most promising one with the stoichiometry  $\text{Na}_2\text{Ti}_3\text{O}_7$



# Na-Ion Storage Systems

## Current work

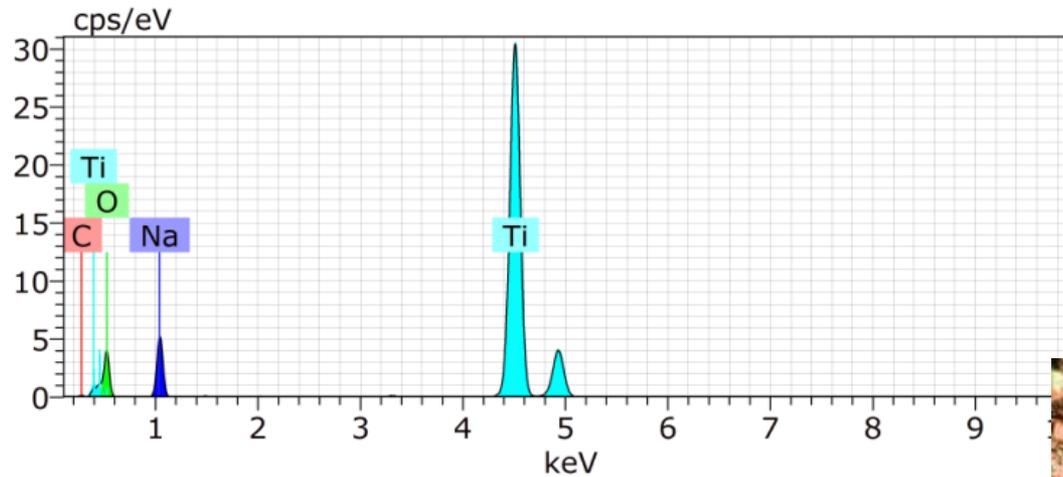
- SEM,



# Na-Ion Storage Systems

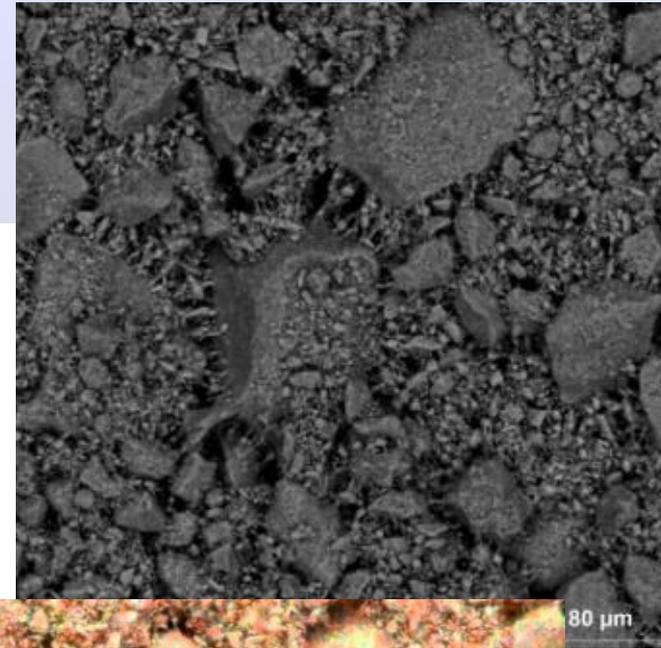
## Current work

- EDX



Spectrum: vz 5

Element	AN	Series	norm. C [wt.%]	Atom. C [at.%]	Error (3 Sigma) [wt.%]
Carbon	6	K-series	1,58	3,14	1,13
Oxygen	8	K-series	42,58	63,40	16,41
Sodium	11	K-series	10,51	10,90	2,33
Titanium	22	K-series	45,33	22,56	3,95
Total:			100,00	100,00	



# Na-Ion Storage Systems

## Current work

- Porozimetry
  - Specific surface area:  $2.3 \text{ m}^2/\text{g}$
  - Total volume  $5.1\text{E-}3 \text{ cm}^3/\text{g}$
  - Average pore Diameter  $1.5 \text{ nm}$
- Electrochemical testing in progress



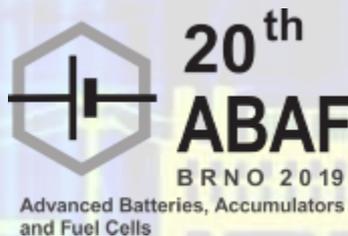
# Conclusion

- Was prepared and tested  $\text{Na}_8\text{Ti}_5\text{O}_{14}$  anode material, we would like to prepare pure sodium titanate material with lower stoichiometry with molecule formula  $\text{Na}_2\text{TiO}_3$ . This formula reaches theoretical 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...



# Brno University of Technology

- Cooperation in EU projects
  - Possess the facility background for excellent research
  - Offer cooperation within bilateral project regarding staff and student mobility, Erasmus ...
  - Help you to provide the invitation letters, conclude memorandum between TUV Wien 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](mailto:libich@feec.vutbr.cz)
  - University <https://www.vutbr.cz/en/>
  - Conference meeting <https://www.aba-brno.cz/>



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



# Thank you for your attention!

