Characterization of electrochemically significant materials at Brno University of Technology

Brno University of Technology
Czech Republic

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Characterization of electrochemically significant materials

Credits:

Ondřej Čech
Tomáš Kazda
Ladislav Chladil
• Introduction of the **Brno University of Technology**
  • CVVOZE Research center
  • CEITEC Research center

• **Selected research activities in electrochemistry**
  • Li-ion battery
  • Lithium ion battery for the smart textiles applications
  • Na-ion battery systems
New research centers at BUT:
CEITEC - Central European Institute of Technology
CVVOZE - Centre for Research and Utilization of Renewable Energy
NETME CENTRE – New Technologies for Mechanical Engineering
SIX – Centre of Sensory, Information and Communication Systems
Admass – Advanced Materials, Structures and Technologies

From the national level of the Czech Republic the research centers are partially funded and supported by the National Programme - LO - National Programme for Sustainability I and II
Characterization of electrochemically significant materials at CEITEC

7 programs:
1. Advanced Nanotechnologies and Microtechnologies
2. Advanced Materials
3. Structural Biology
4. Genomics and Proteomics of Plant Systems
5. Molecular Medicine
6. Brain and Mind Research
7. Molecular Veterinary Medicine

CEITEC was created by the European Commission on June 6th 2011. It is a consortium of 6 partners: Masaryk University, Brno University of Technology, Mendel University in Brno, University of Veterinary and Pharmaceutical Sciences in Brno, Veterinary Research Institute and Institute of Physics of Materials of the AS CR. CEITEC is the first type of a scientific center in the Czech Republic to integrate R&D in the fields of life sciences, advanced materials and technologies in such a large range. The research is divided into 61 research groups and the 7 programs.
Advanced equipment in CEITEC suitable for electromaterial research

- MOCVD, LPCVD, PECVD ICP, PECVD CCP,
- NIR/VIS/UV/(VUV) Optical spectrometry, Scanning probe microscope + microRaman + Photoluminiscence system, Scanning Near-Field Optical Microscope,
- Complex custom UHV (MBE, STM, PEEM, LEEM), SIMS, XPS, nanoSAM, PLD+RHEED
- set of MS spectrometers,
- Micro and nanotomography stations,
- HR TEM, HR SEM, SEM/FIB,
- set of X-ray diffractometers,
- Complete Nanolithography infrastructure,
- 500 and 700 MHz NMR spectrometers for high-resolution spectroscopy in liquids and solids,
- HT QMS/thermal analyzer
CVVOZE

Research divisions at CVVOZE

- **Generation, transmission, distribution and use of electrical energy**
  - The basic direction of the related research and development will lie in the optimization of power switchgear parameters in the region of quenching systems

- **Electromechanical energy conversion**
  - development and optimization of the new driving systems in the fields of electric machines, electric instruments, power and control electronics, management systems, and autonomous sources of electrical energy.

- **Chemical and photovoltaic energy**
  - In the field of the electrochemical power sources, parameters of new systems are verified together with a specification of technical parameters of testing and production facilities, such as potentiostat units for measurement of electrochemical processes, sputtering devices for depositing thin films, systems for measurement and cycling of electrochemical sources.
Electrochemistry research at BUT

Current research in electrochemical energy storage systems

Lithium Ion Battery
Basic research of conventional and advanced (5-volt) LiFePO₄, LiCoO₂ and LiMn₂O₄ 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 (... looking for partners in EERA).

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.
Li-ion based battery systems

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.

Table 1. Prepared cathode electrodes based on LiFePO$_4$

<table>
<thead>
<tr>
<th>Code name</th>
<th>Electrode material</th>
<th>Binder</th>
<th>Conductive content</th>
<th>Deposition technique</th>
<th>Cathode Underlayer</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFP-SuP-Prt</td>
<td>LiFePO$_4$</td>
<td>PVDF</td>
<td>Super P</td>
<td>Screen printing</td>
<td>No</td>
</tr>
<tr>
<td>LFP-PEDOT-Prt</td>
<td>LiFePO$_4$</td>
<td>PEDOT:PSS</td>
<td>PEDOT:PSS</td>
<td>Screen printing</td>
<td>No</td>
</tr>
<tr>
<td>LFP-PEDOT-Prt-C</td>
<td>LiFePO$_4$</td>
<td>PEDOT:PSS</td>
<td>PEDOT:PSS</td>
<td>Screen printing</td>
<td>Carbon</td>
</tr>
<tr>
<td>LFP-SuP-BarCoat</td>
<td>LiFePO$_4$</td>
<td>PVDF</td>
<td>Super P</td>
<td>Spiral Bar Coating</td>
<td>No</td>
</tr>
</tbody>
</table>


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Li-ion based battery systems

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

Change of capacity of the LiFePO₄ 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.

Li-ion based battery systems

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

Electrochemical impedance spectra of LFP-SuP-Prt, LFP-PEDOT-Prt, LFP-PEDOT-Prt-C, LFP-SuP-BarCoat; a) Before cycling at different C-rates, b) After cycling at 5 C, c) Before the last cycling at 0.5 C-rates.


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Li-ion based battery systems

High-voltage spinel cathode LiNi$_{0.5}$Mn$_{1.5}$O$_4$

- 5-V cathode materials compared to a conventional cathode have the advantage of a higher working potential, approximately of 1-1.5 V higher, and therefore potentially 20-30% higher power density.

- The disadvantage is the instability of the structure of the most types of high-voltage cathode materials and the instability of the electrolyte in this very wide potential window, exceeding 5 V.

Crystallographic structure of a model $A^{2+}B_2^{3+}O_4^{2-}$ spinel structure
Li-ion based battery systems

High-voltage spinel cathode $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$

Voltage vs. capacity for several positive electrode materials, obtained under normal cycling conditions (20 °C, C/5 rate).

CV curves of Li/LiCr$_{0.05}$Ni$_{0.45}$Mn$_{1.5}$O$_4$ half-cells with electrolytes of 1.0 mol/l LiPF$_6$ in EC-DMC mixture in the voltage ranges from 3.5 V to 5.0 V at a scan rate of 10 µV/s.

Li-ion based battery systems

High-voltage spinel cathode LiNi$_{0.5}$Mn$_{1.5}$O$_4$

Changes of capacity of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ sample for different C rates and temperature.

Comparison of discharge curves for LiNi$_{0.5}$Mn$_{1.5}$O$_4$ for different C rates.

Li-ion based battery systems

Effect of Cr doping on the properties of LiNi\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4}

The capacity decrease with increasing the number of cycles and increasing C-rate for a standard and a cryo-milled sulfur cathode.

Changes of capacity of $S_{\text{ref60}}$ cathode and $S_{\text{cryo}}$ cathode

The capacity decrease with increasing the number of cycles and increasing C-rate for a standard and a cryo-milled sulfur cathode

Comparison of discharge curves for A) $S_{\text{ref60}}$ cathode and B) $S_{\text{cryo}}$ cathode, recorded during the first 50 cycles at 0.2 C. Comparison of charge/discharge curves for: C) $S_{\text{ref60}}$ cathode and D) $S_{\text{cryo}}$ cathode at different C-rates

Material research directions

The price of pure lithium carbonate as the most crucial lithium source for Li-ion batteries grew at the beginning of 2016 well beyond its previous historical maximum.

http://www.crugroup.com


- Mixed sodium titanates for sodium-ion intercalation as a material for negative electrode for sodium-ion batteries

**Price forecast trend for battery-grade lithium hydroxide and lithium carbonate (US$/t CIF)**

<table>
<thead>
<tr>
<th>Year</th>
<th>Hydroxide</th>
<th>Carbonate</th>
</tr>
</thead>
<tbody>
<tr>
<td>2015</td>
<td>8,640</td>
<td>5,575</td>
</tr>
<tr>
<td>2016</td>
<td>9,473</td>
<td>6,292</td>
</tr>
<tr>
<td>2017</td>
<td>9,892</td>
<td>6,854</td>
</tr>
<tr>
<td>2018</td>
<td>10,210</td>
<td>7,410</td>
</tr>
<tr>
<td>2019</td>
<td>10,750</td>
<td>7,750</td>
</tr>
<tr>
<td>2020</td>
<td>11,115</td>
<td>8,115</td>
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<tr>
<td>2021</td>
<td>11,495</td>
<td>8,495</td>
</tr>
<tr>
<td>2022</td>
<td>11,895</td>
<td>8,895</td>
</tr>
<tr>
<td>2023</td>
<td>12,315</td>
<td>9,315</td>
</tr>
<tr>
<td>2024</td>
<td>12,750</td>
<td>9,750</td>
</tr>
<tr>
<td>2025</td>
<td>13,210</td>
<td>10,210</td>
</tr>
</tbody>
</table>

Source: Roskill (February 2016)
Na-ion storage systems

- Mixed sodium titanates for sodium-ion intercalation as a material for negative electrode for sodium-ion batteries

Sodium-ion batteries work on the same principles as the well-known and described lithium-ion batteries; they use same technology. Sodium-ion cells have lower energy density but still offer interesting energy source due to no need for rarer elements. Sodium is abundant, it occupies 2.6 % of the Earth’s crust.
Mixed sodium titanate material $\text{Na}_2\text{Ti}_3\text{O}_7/\text{Na}_2\text{Ti}_6\text{O}_{13}$ was hydrothermally synthesized and electrochemically characterized.

SEM images of hydrothermally synthesized $\text{Na}_2\text{Ti}_3\text{O}_7/\text{Na}_2\text{Ti}_6\text{O}_{13}$ mixed titanate showing a) pristine material after hydrothermal treatment b) calcination at 700 °C c) calcination at 800 °C d) calcination at 900 °C.

XRD spectra of raw and calcined hydrothermally treated titanate.
Na-ion storage systems

Cyclic voltammogram of Na$_2$Ti$_3$O$_7$/Na$_2$Ti$_6$O$_{13}$ mixed sample prepared at 800 °C gathered at 2 mV/s

Cyclic voltammogram of Na$_2$Ti$_3$O$_7$/Na$_2$Ti$_6$O$_{13}$ mixed sample prepared at 800 °C gathered at 0.1 mV/s

First charge/discharge cycle at a low current rate (0.02 C)

Four charge/discharge cycles of mixed titanate with current rate 0.2 C
Special preparation techniques

Preparation of Fibrous Materials Using Electrospinning and Centrifugal Force Spinning

- Fibrous materials have interesting applications in the fields like filtration, bioapplication as tissue scaffolds and in energy storage for separators and carbon/active material composites [electrodes].
Calcined ZrO₂ Nanofibres prepared by electrospinning.

Electrospinning nanofibres PVA/Y-ZrO₂ precursor of Y stabilized ZrO ceramic.

Cross section of pellets made of ceramic nanofibers

Forcespun PA6 fibers

Forcespun chitosan fibers

Forcespun carbon/nanoparticle composite
Overview of Involved Research Groups

The following research groups are associated with the EERA JP Energy Storage:

**SP1: Electrochemical Energy Storage**
- RD 2: Chemical and photovoltaic energy
- Departments of Physics
- Jiří Kazelle
- Vlasta Sedláková
- 8 Academics
- 9 PhD students
- 2 Technicians

**SP3: Thermal Energy Storage**
- Department of Thermodynamics and Environmental Engineering
- Pavel Charvát
- 4 Academics
- 1 Technician

**SP4: Mechanical Energy Storage**
- Department of Fluid Engineering
- Victor Caplan
- Departments of Physics
- Pavel Rudolf
- 10 Academics
- 10 PhD students
- 5 Technicians

**SP6: Techno-Economics**
- Department of Electrical Power Engineering
- Lukáš Radil
- 2 Academics

Centre for Research and Utilization of Renewable Energy

Faculty of Electrical Engineering

Faculty of Mechanical Engineering

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BUT Infrastructure Related to JP ES

In relation to **SP1**
- Material synthesis and characterization facilities (electro and centrifugal force spinning, in-situ powder XRD)
- Cell and battery testing facilities (>21 channels with EIS)
- Modeling tools

In relation to **SP3**
- A drive-in environmental chamber with a solar simulator (environmental chamber temperature range - 40 °C to 80 °C, controlled humidity)

In relation to **SP4**
- High performance cluster and experimental laboratory for hydraulic machines testing up to 300 kW

In relation to **SP6**
- Prudent Energy VRB System consists of a 20 kWh capacity accumulation system
- A set of models of management systems in PSCAD and Modelica
Acknowledgement

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