Li-iónové batérie nové materiály a ich elektrochemická charakterizácia

Přírodovědecká fakulta Univerzity Karlovy
Katedra analytické chemie
22.03.2023

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Motivation

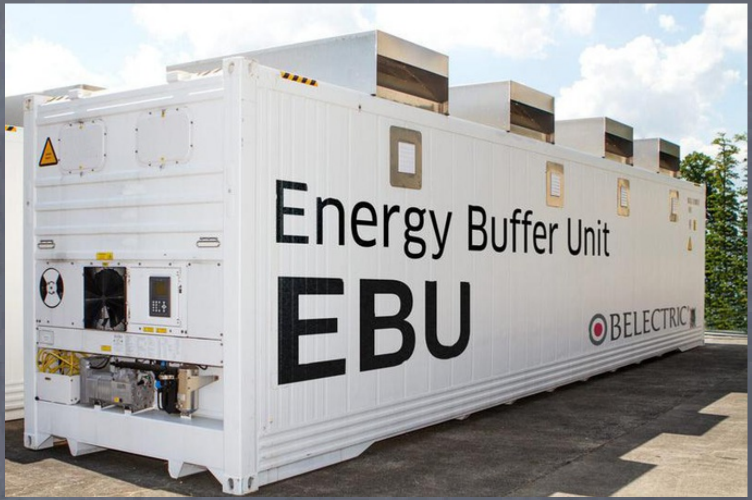
- Electromobility
- Stationary applications, smart grid
- Industry 4.0
- Energy independence
- Small portable devices

Motivation

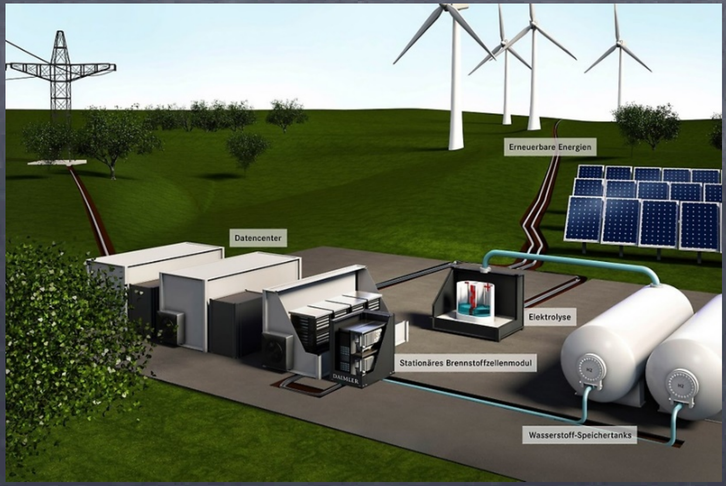


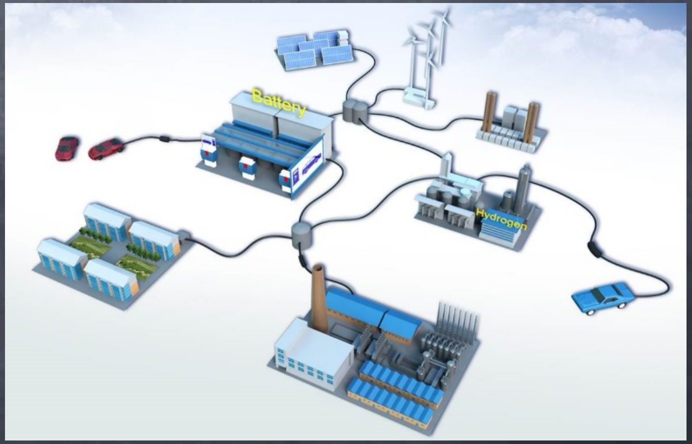
Electromobility


Motivation



Stationary application, smart grid





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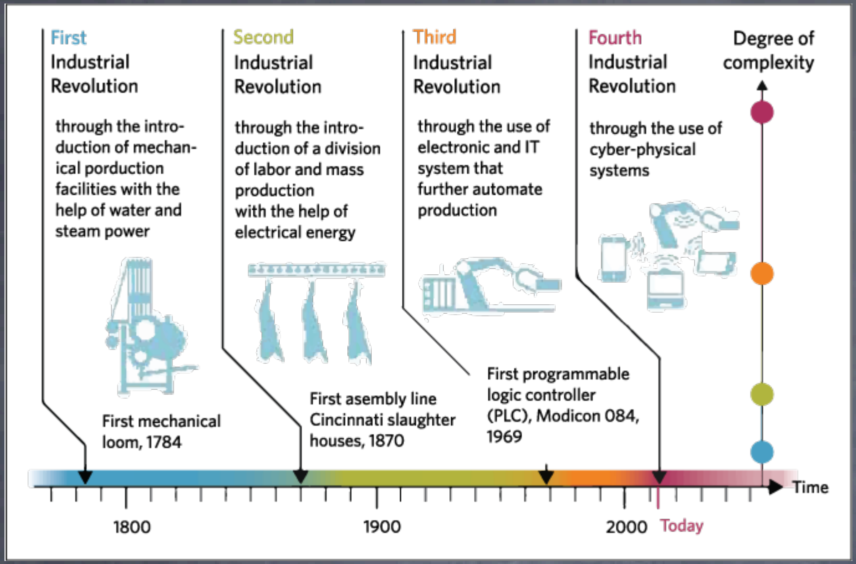
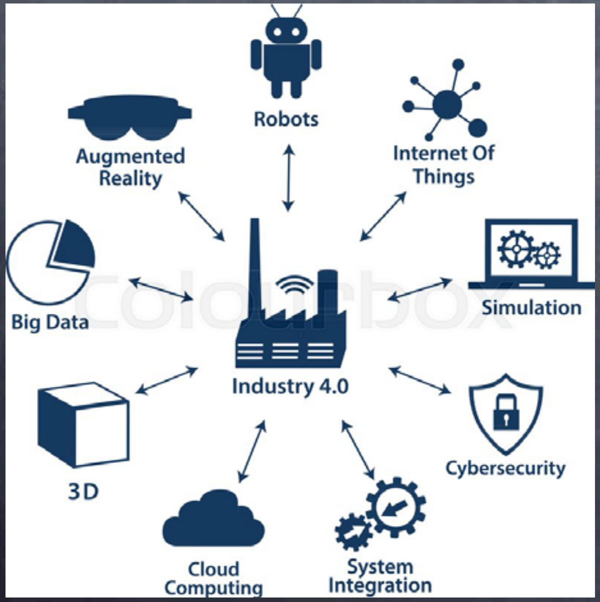
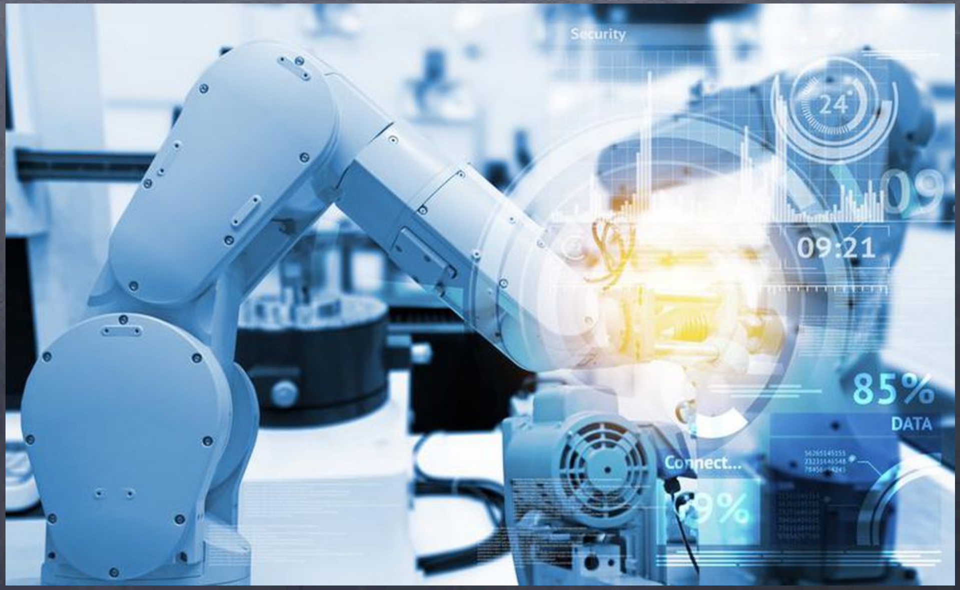
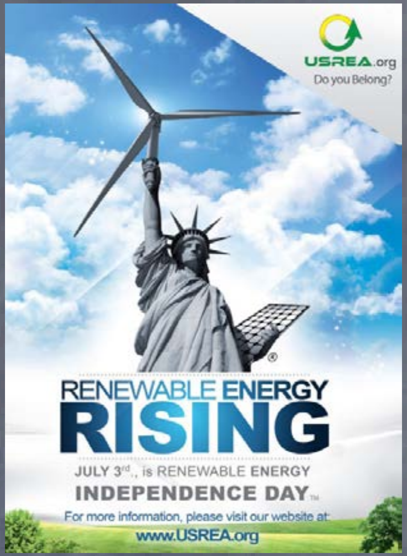


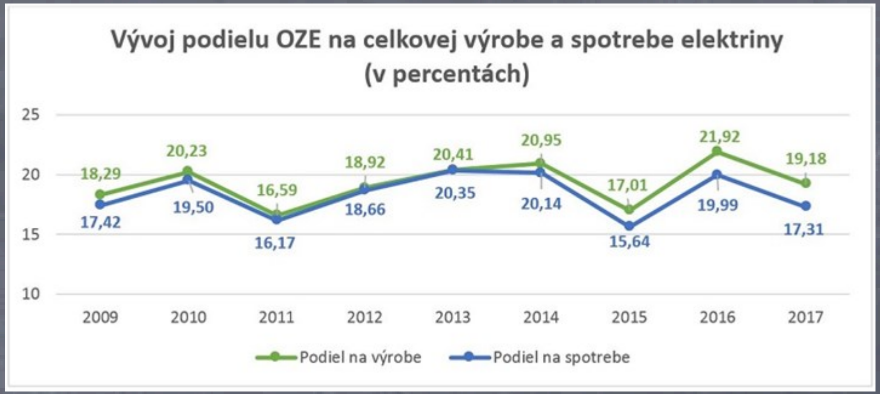
Industry 4.0





Motivation





Energy independence

IPCEI Projects

Raw and advanced materials	Battery cells	Battery systems	Recycling and sustainability
ACIS	Alumina Systems	ACIS	Borealis
Arkema	BMW	Alumina Systems	Enel X
Borealis	Cellforce Group	AVL	Engitec
Ferroglobe	ElringKlinger	BMW	FIAMM
Fluorsid	FCA	Endurance	Fortum
Green Energy Storage	Green Energy Storage	Enel X	Hydrometal
Hydrometal	InoBat Auto	Energo Aqua	Italmatch Chemicals
Italmatch Chemicals	Manz	FCA	Keliber
Keliber	Midac	FIAMM	Liofit
Prayon	Northvolt	FPT Industrial	Little Electric Cars
SGL Carbon	SGL Carbon	Green Energy Storage	Midac
Solvay	Skeleton Technologies	InoBat Energy	SGL Carbon
Tokai Carbon Group	Sunlight Systems	Manz	Tesla
VARTA Micro Innovation	Tesla	Miba eMobility	Valmet Automotive
	VARTA Micro Innovation	Midac	ZTS VaV
		Rimac Automobili	
		Rosendahl Nextrom	
		Skeleton Technologies	
		Sunlight Systems	
		Tesla	
		Valmet Automotive	
		Voltlabor	

Cathode materials used in Li-ion batteries

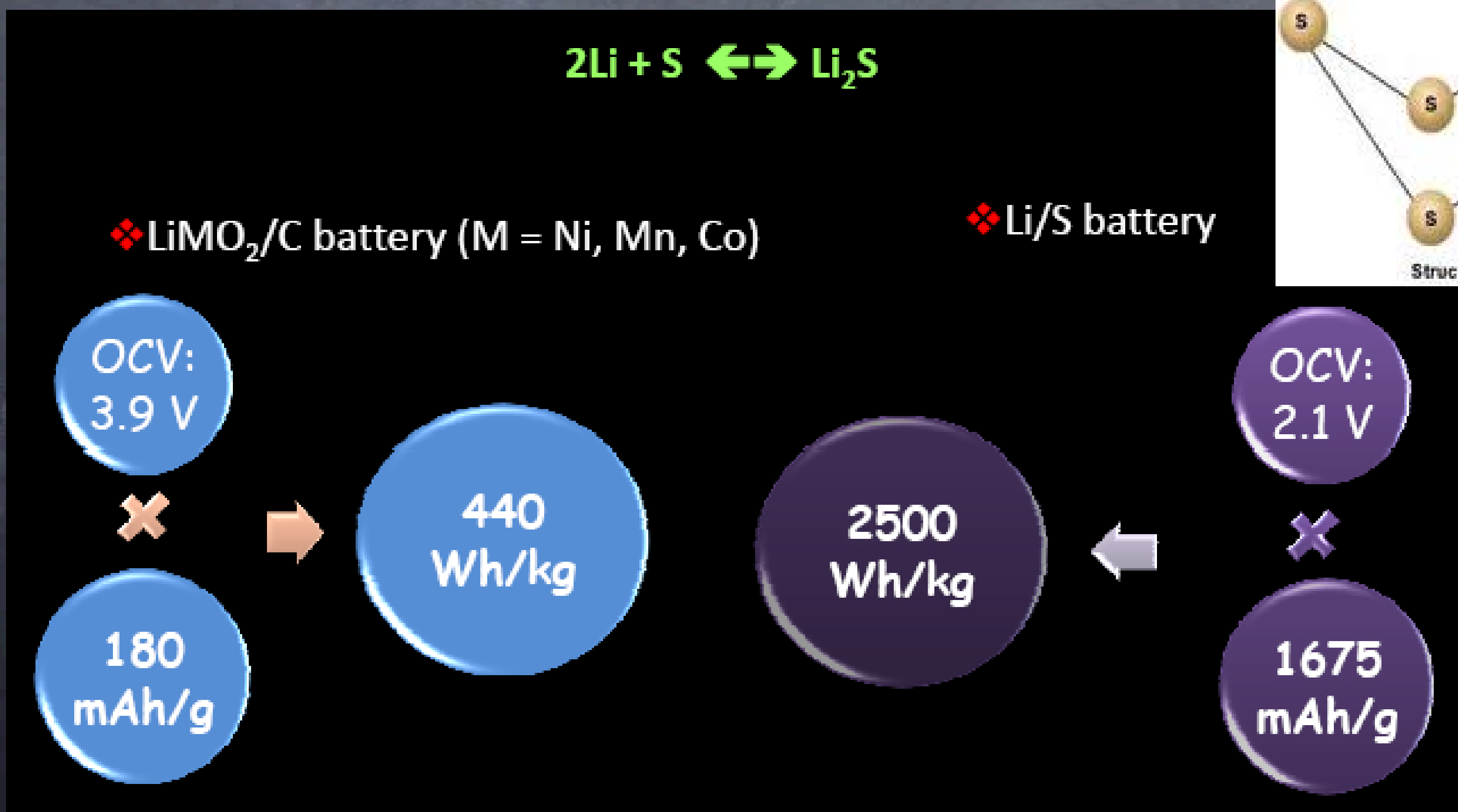
- Lithium Cobalt Oxide ($LiCoO_2$ or LCO)
- Lithium Manganese Oxide ($LiMn_2O_4$ or LMO)
- Lithium Nickel Manganese Cobalt Oxide ($LiNiMnCoO_2$ or NMC)
- Lithium Iron Phosphate ($LiFePO_4$ or LFP)
- Lithium Nickel Cobalt Aluminum Oxide ($LiNiCoAlO_2$ or NCA)
- Lithium Titanate ($Li_4Ti_5O_{12}$ or LTO)

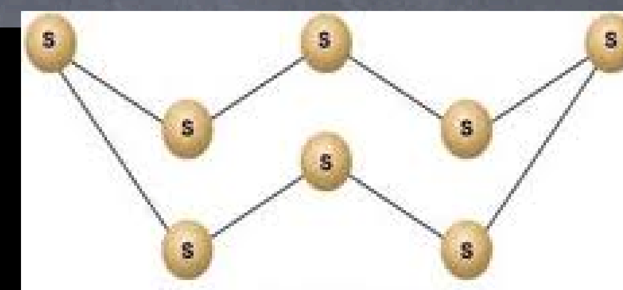
Li-S batteries

$$C_{teor} = \frac{n \cdot F}{M_w \cdot 3{,}6} \ \text{mAh/g}$$

$M_w(LiCoO_2) = 98$ g/mol

$M_w(S) = 32$ g/mol

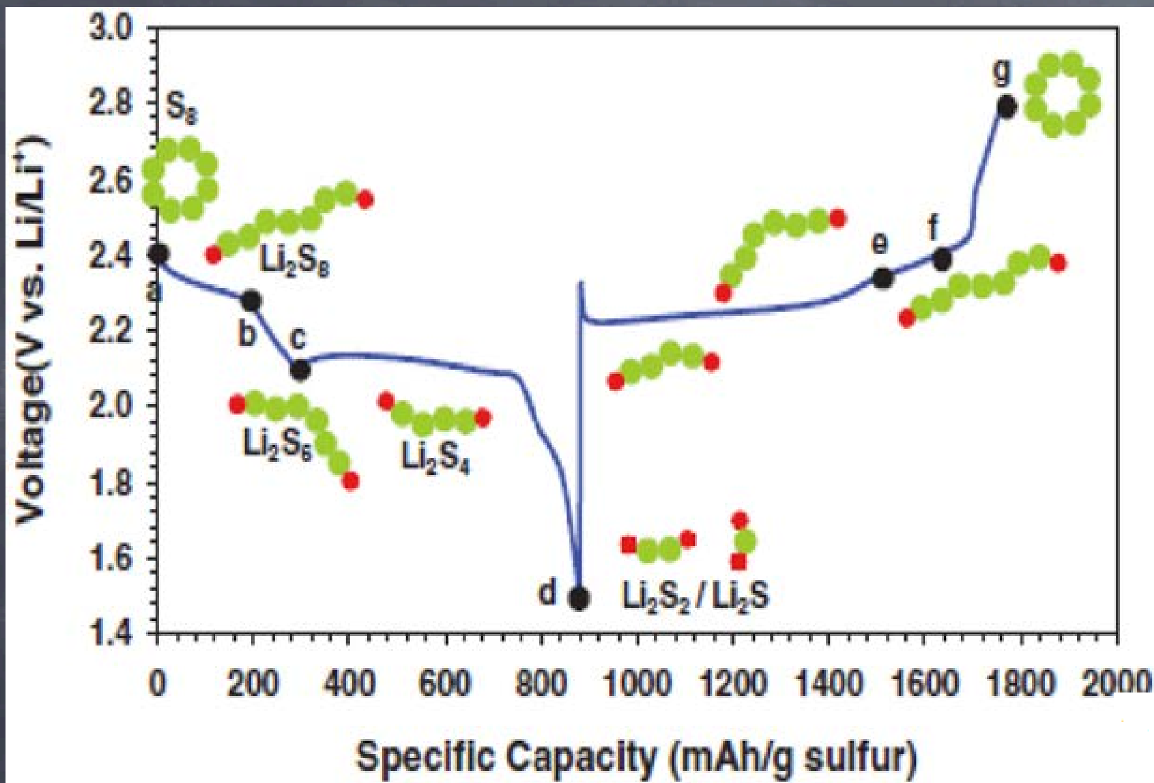




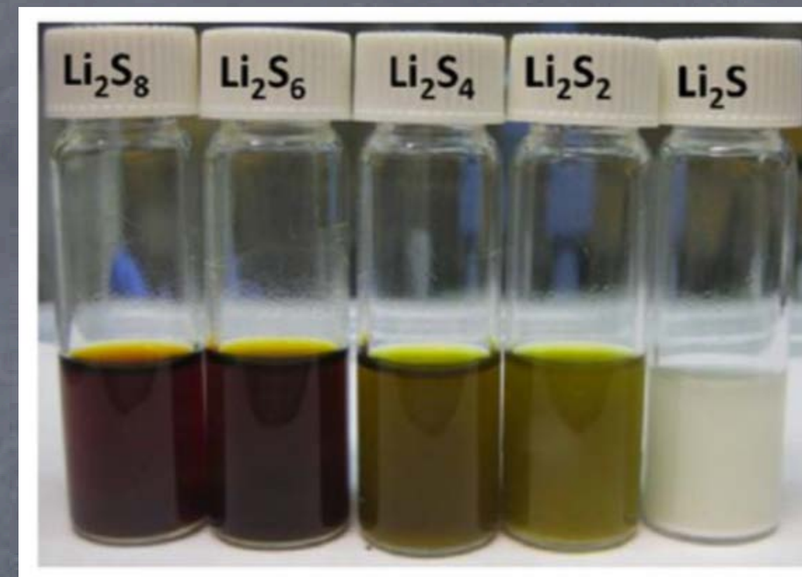
Structure of a sulphur molecule, S_8

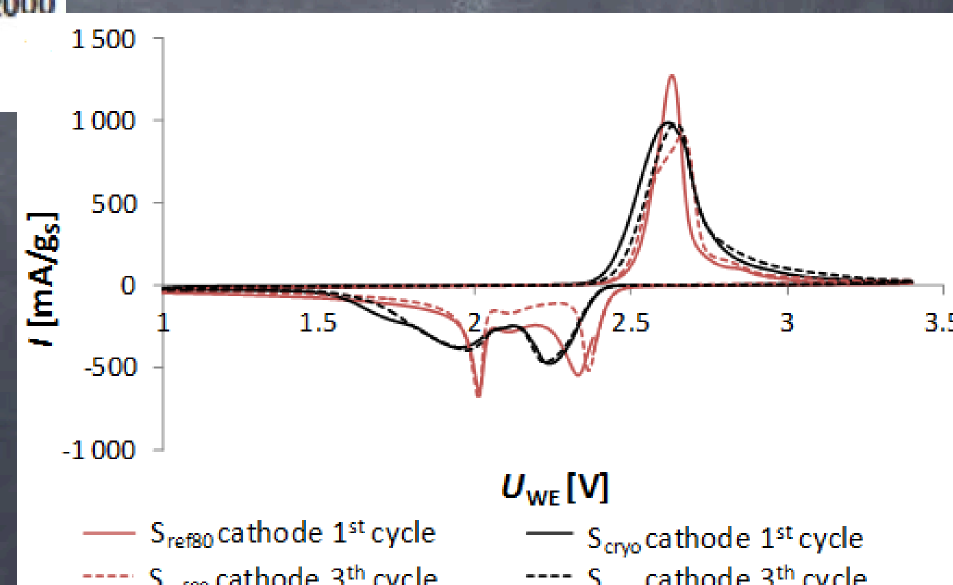
Li-S electrochemical reaction

$$16Li^{+} + 16e^{-} + S_8 \rightarrow 8Li_2S$$



M. Barghamadi et al., *J. Electrochem. Soc.* 160 (2013) A1256–A1263



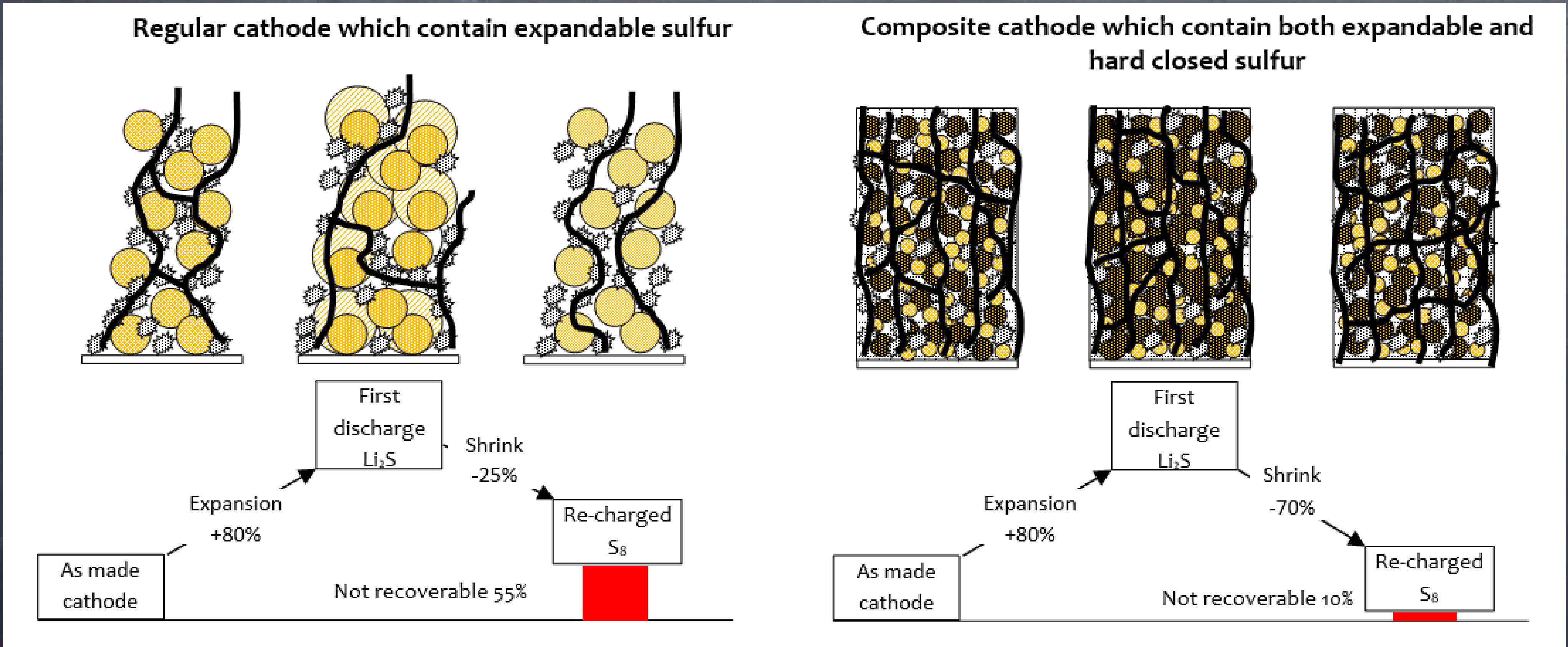


- Two discharge platos = two reduction peaks on CV.
- Oxidation peak is related to the long charge plato what confirms formation of lower polysulfides Li_2S_2 and Li_2S.

T. Kazda, M. Krbal, M. Pouzar, J. Vondrák, A. Straková Fedorková, et al. J. Power Sources 331 (2016) 293.

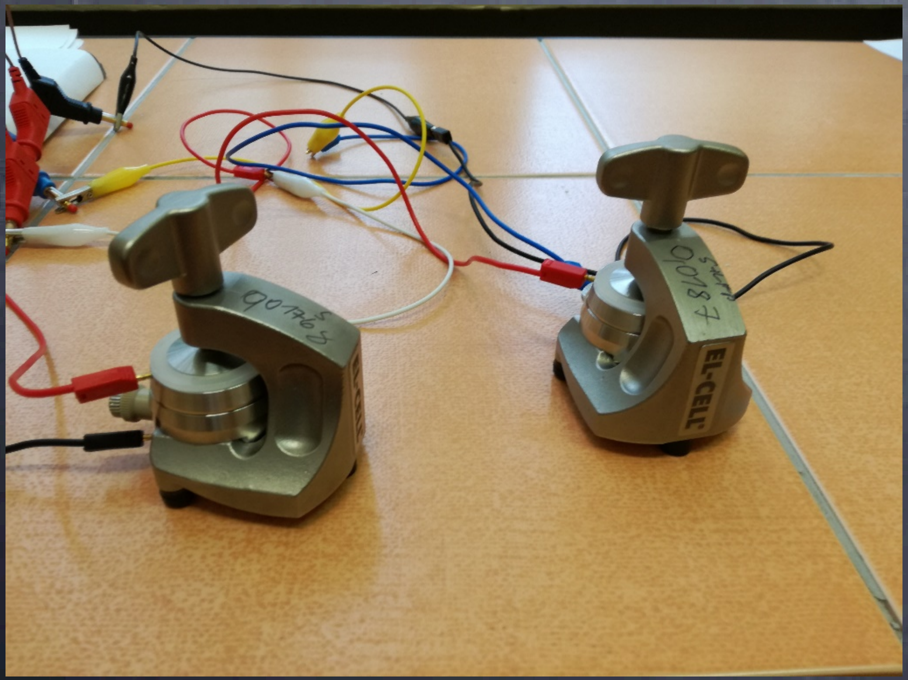
Main goals

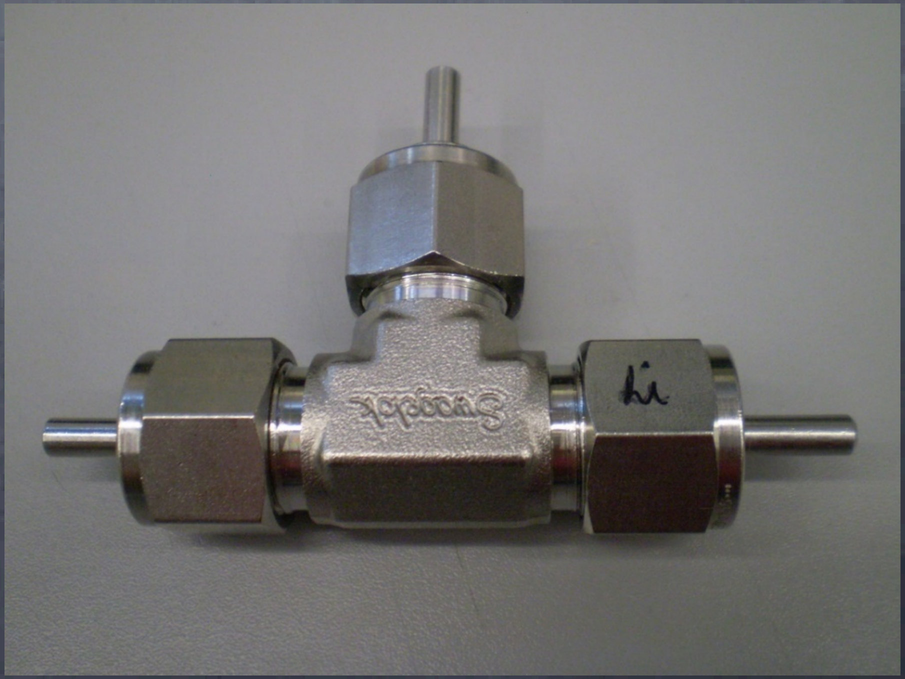
Composite cathode material based on carbon-sulfur matrix with nanoparticles, nanofibres and conductive polymers.



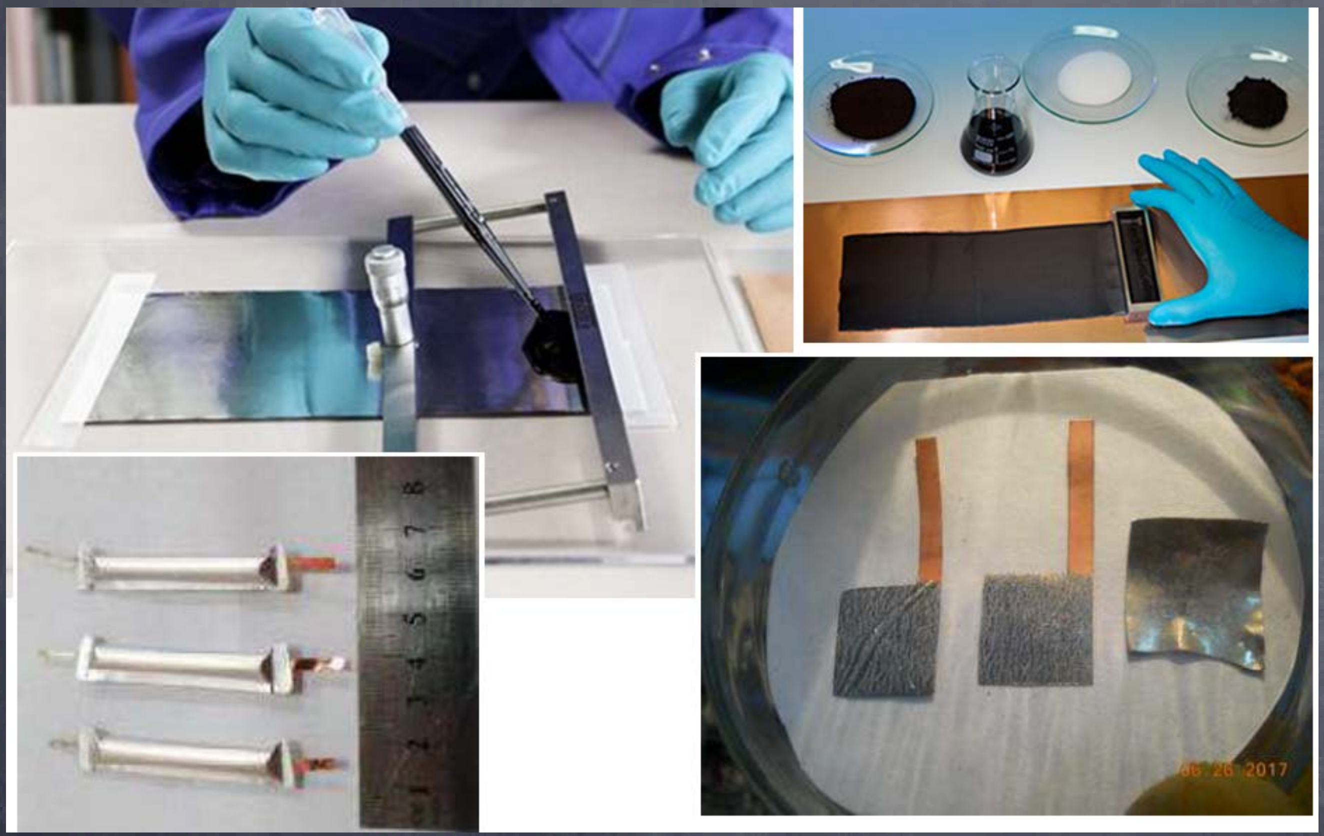
Low-cost, safe, no heavy metals, 3x higher capacity, good stability and, efficiency and life time.

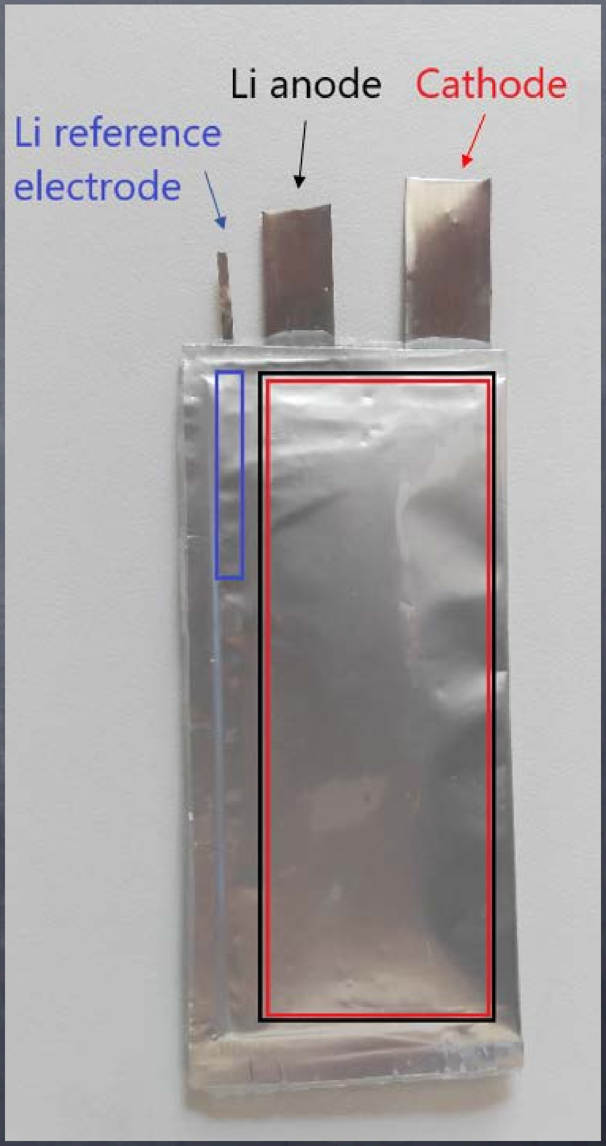
Samples preparation and testing





Prototype preparations and testing





Anode: Li, W ≈ 0.5 mm

Electrolyte: DME:DOL 2:1 + 0.7 M LiTFSI + 0.25 M $LiNO_3$

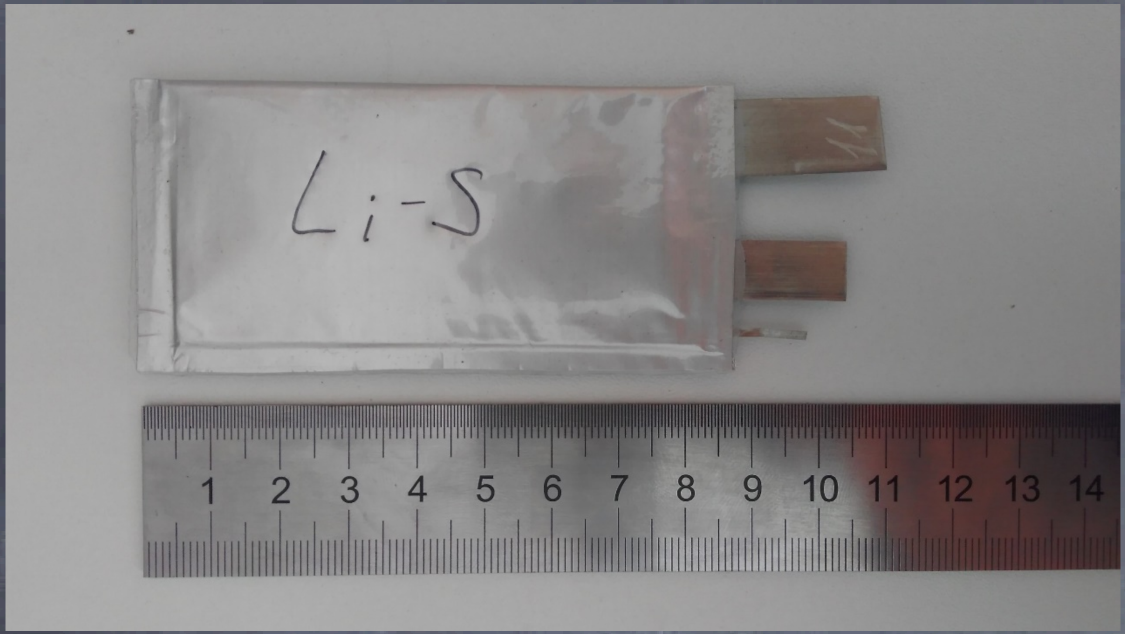
Polymeric separator

NATO OTAN

This project is supported by: The NATO Science for Peace and Security Programme

NATO SPS project No. 985148

Safety tests - Li-S prototype after overcharging and nail penetration test.

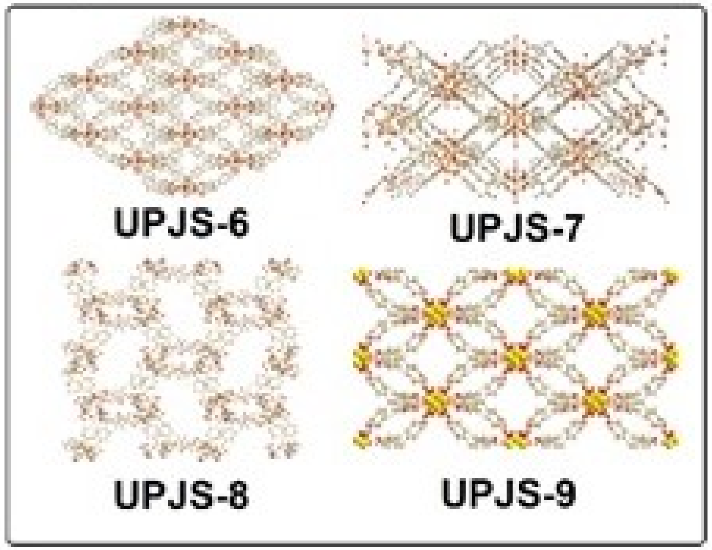


EU Patents:

1. Advanced Pre-Lithiated Heterofibrous Monolithic Wafer-Like Silicon Anode (2021)
2. Advanced monolithic sulphur wafer-like cathode based on hyper-branched super-structures and method of manufacture thereof (2020)
3. Alkali and/or alkaline earth ion - monoclinic sulfur allotrope battery with self-supporting electrodes (2018)

Metal Organic Frameworks

Pripravené MOF zlúčeniny:



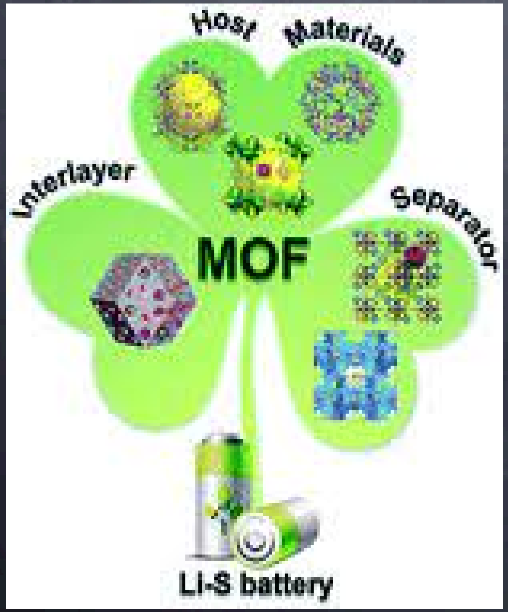
Chemické zloženie:

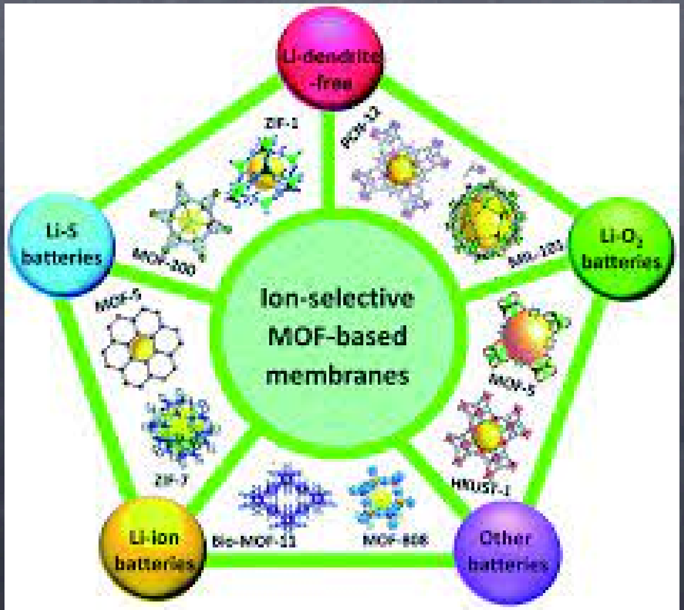
UPJS-6 = $\{[Ca_4(\mu_8\text{-}C_{29}H_{16}O_8)_2]\cdot 2C_3H_7N_1O_1\cdot 4H_2O\}_n$

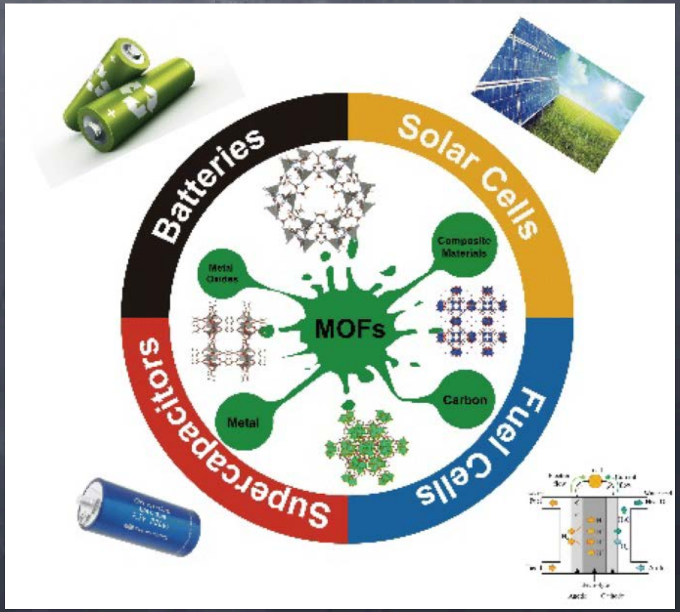
UPJS-7 = $\{[Ca_4(\mu_4\text{-}O)(\mu_8\text{-}C_{29}H_{16}O_8)_{3/2}(H_2O)_4]\cdot 4C_3H_7N_1O_1\cdot 4H_2O\}_n$

UPJS-8 = $\{[Sr_3(\mu_7\text{-}C_{29}H_{16}O_8)_{3/2}]\cdot 4C_3H_7N_1O_1\cdot 7H_2O\}_n$

UPJS-9 = $\{[Ba_3(\mu_7\text{-}C_{29}H_{16}O_8)_{3/2}(H_2O)_6]\cdot C_3H_7N_1O_1\cdot 4H_2O\}_n$





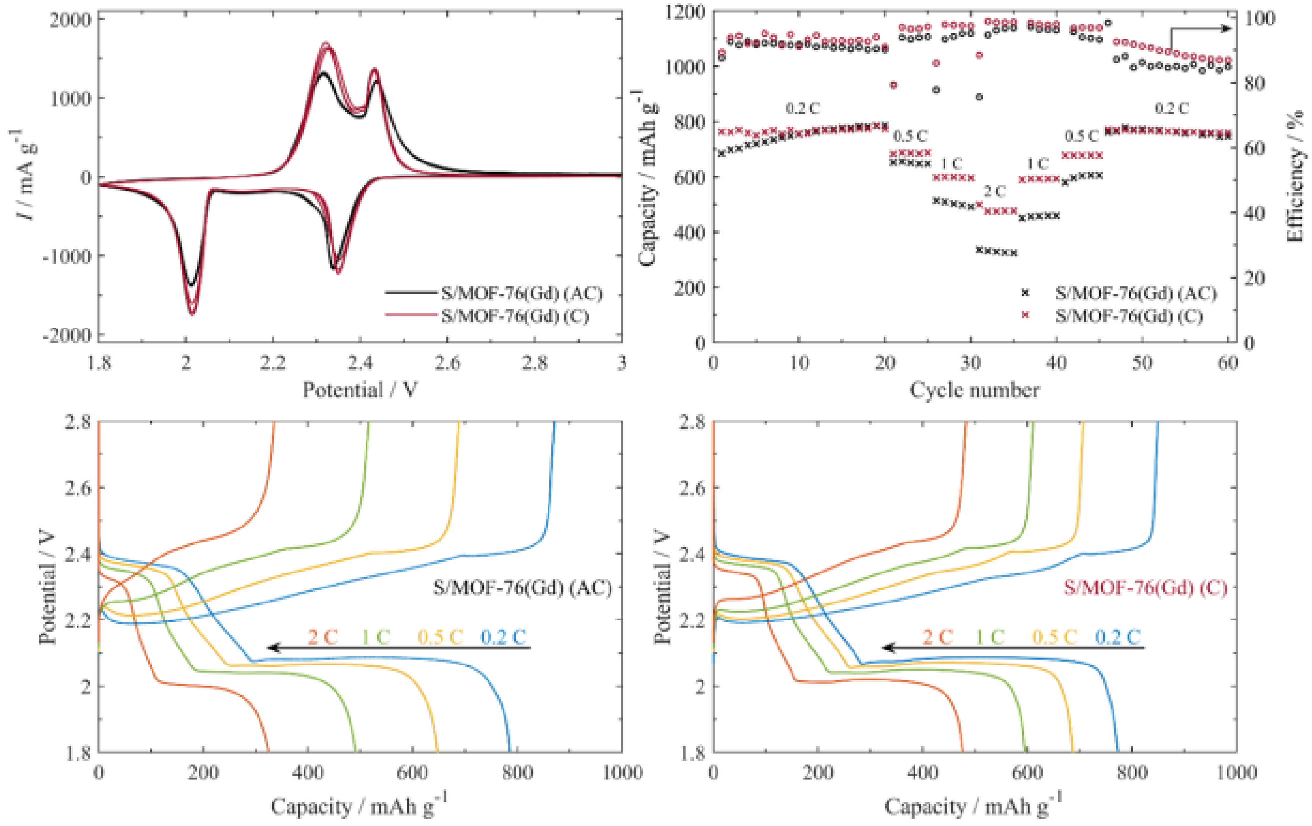


MOF-76(Gd) (AC)/(C)

- The current density of activated MOF-76(Gd) is lower compared to carbonized MOF

Multi-current cycling:

- As the C-rate increases, the difference between the achieved capacities increases
- Reduced plateaus at 2 C for S/MOF-76(Gd)(AC)

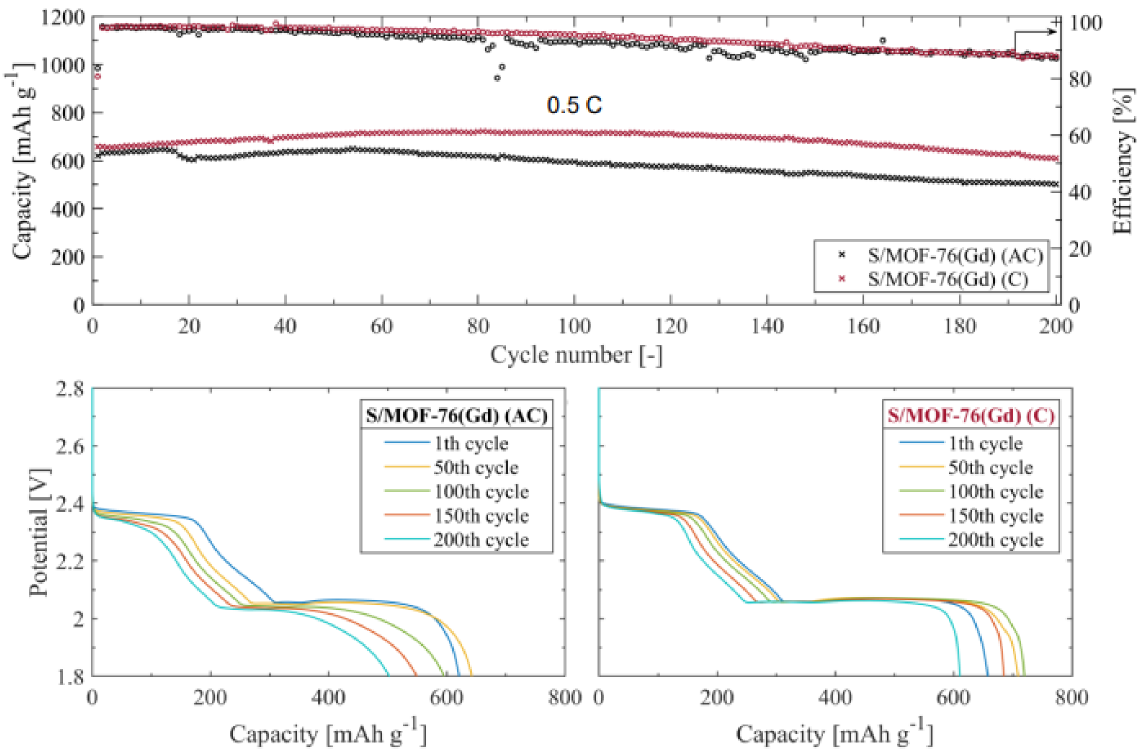


D. Capkova et al., *Journal of Energy Storage,* **51**, 104419, 2022.

MOF-76(Gd) (AC)/(C)

Long-term cycling (0.5 C) :

- The initial discharge capacity is higher for MOF-76(Gd) (C)
- Highly stable cycle performance for the S/MOF-76(Gd)(C)
- Change in the shape of the lower plateau of S/MOF-76(Gd) (AC), which is accompanied by a decrease in capacity
- Capacity retention:
  - S/MOF-76(Gd) (AC) 81 %
  - S/MOF-76(Gd) (C) 93 %



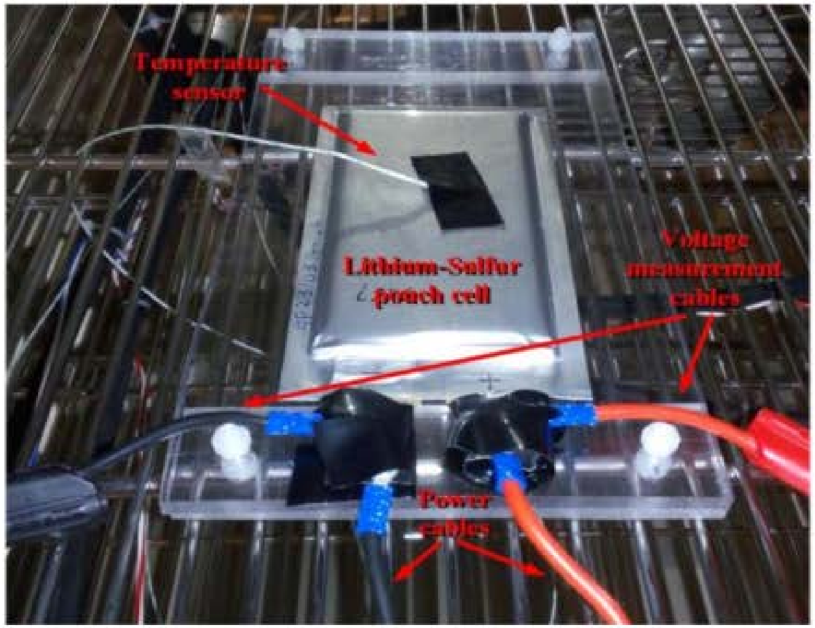
D. Capkova et al., *Journal of Energy Storage,* **51**, 104419, 2022.

- The modification of MOF with Ni^{2+} ions may increase the capacity
- Carbonization process may improve electrochemical properties

Material	Sulfur content [%]	C-rate	Capacity [mAh g-1] 1st cycle	Capacity [mAh g-1] 200th cycle	Fading rate per cycle [%]
S/GaTCPP(AS)	60	0.5 C	601	517	0.07
S/GaTCPP(Co)	60	0.5 C	524	374	0.14
S/GaTCPP(Ni)	60	0.5 C	610	479	0.11
S/MOF-76(Gd)(AC)	60	0.5 C	621	502	0.10
S/MOF-76(Gd)(C)	60	0.5 C	658	610	0.04
S/MIL(C)	60	0.5 C	705	476	0.16

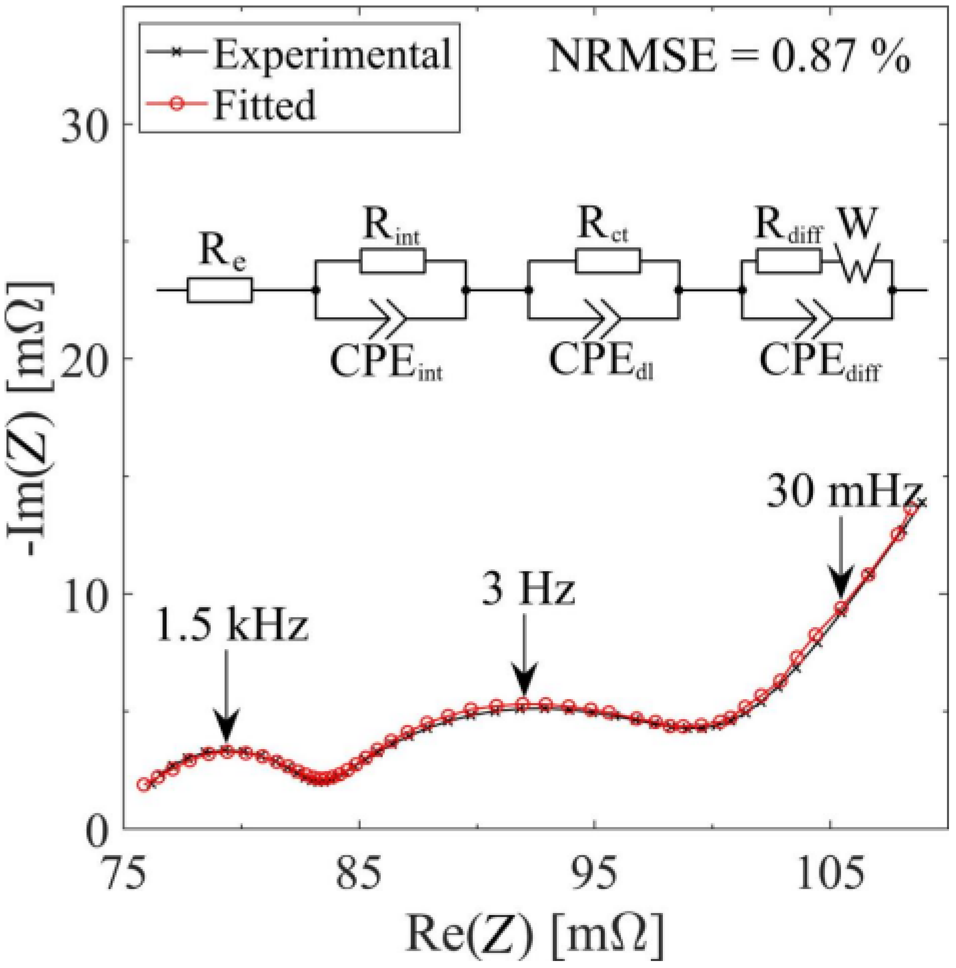
Investigated Li-S pouch cells

Nominal capacity (30 °C)	3.4 Ah
Nominal voltage	2.05 V
Charge cutoff voltage	2.45 V
Discharge cutoff voltage	1.5 V
Nominal charging current	0.34 A (0.1 C)
Nominal discharging current	0.68 A (0.2 C)
Ambient temperature operation range	5 – 80 °C



Measurement of EIS

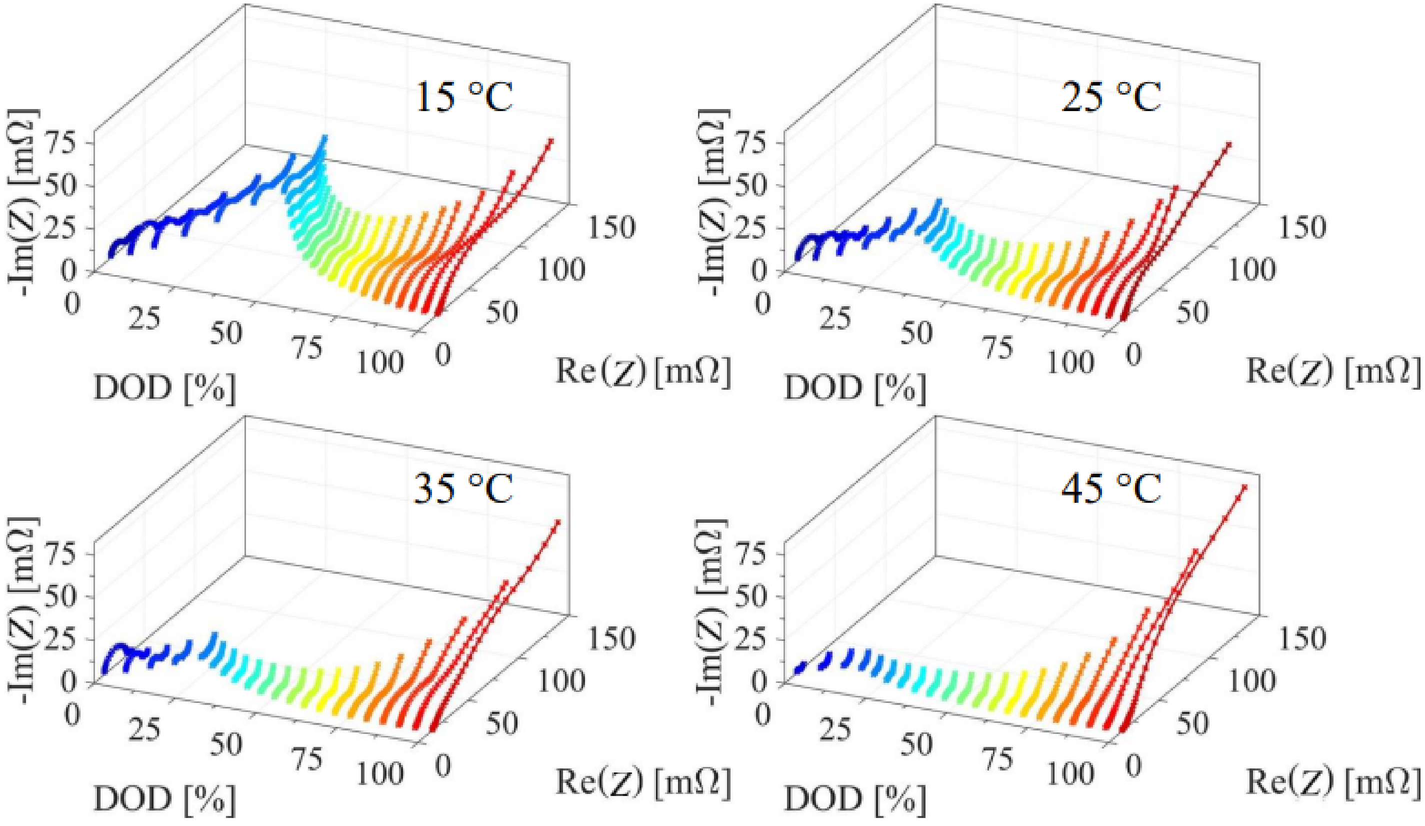
- The voltage amplitude was set to 3 mV
- The frequency range 6.5 kHz − 10 mHz (for temperature testing), 6.5 kHz − 1 Hz (for steady and dynamic EIS)
- EIS spectra were fitted in Matlab – Zfit function (NRMSE = 1.8 %)



D. Capkova et al., *Journal of Energy Chemistry,* **72**, 318-325, 2022.

Variation of EIS spectra with DOD and temperature

- EIS spectra vary depending on DOD and temperature
- The impedance spectra exhibit two semicircles and an inclined line

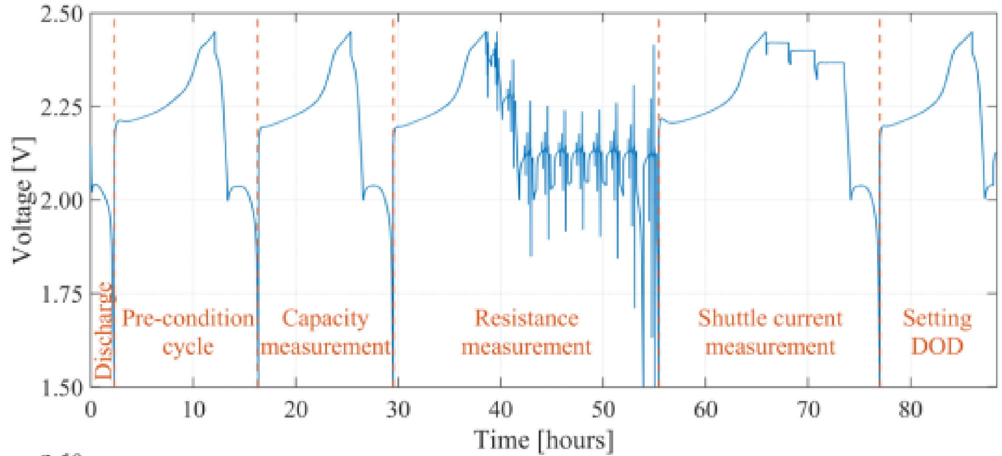


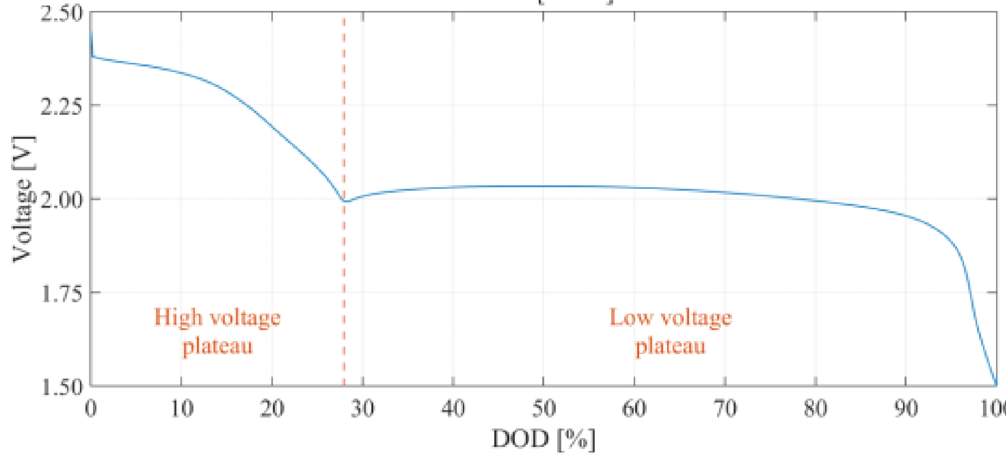
D. Capkova et al., *Journal of Energy Chemistry,* **72**, 318-325, 2022.

Calendar aging of 3.4 Ah Li-S pouch cells

Reference performance test (RPT) was performed periodically every month:

1. Discharging of the cell to obtain the remaining capacity after storage;
2. To reset 'the cumulative history' of the cell a precondition cycle was performed;
3. The measurement of actual charge and discharge capacity;
4. A set of charging and discharging pulses were applied at various DOD/DOC levels to obtain the resistance of the cell;
5. For every even RPT measuring of the shuttle current or EIS;
6. Charging followed by discharging of the cell to target DOD level





D. Capková et al., *Applied Energy* **332** (2023) 120543

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- ✓ Dr. Václav Knap, ČVUT Praha
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- ✓ prof. Elena Shembel, Ukrainian State University of Chemical Technology, Dnipro, UA
- ✓ prof. Martin Winter, Westfalische Wilhelms University, Münster, DE
- ✓ Dr. Dominika Capková PhD., Dr. Veronika Niščáková, Dr. Katarína Benková PhD.

- NATO SPS project No. 985148 (2016-2020)
- APVV-20-0138 a APVV-20-0111
- DSV projekt iCoTS - Inovatívne riešenia pohonných, energetických a bezpečnostných komponentov dopravných prostriedkov
- IPCEI_IE_FLOW_BESS_012021 Redoxné prietokové batérie (InoBat Enegry)
- IPCEI REBATT 313012BUN5 Regenerácia použitých batérií z elektromobilov (ZŤS Výskum a Vývoj)

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