Nové materiály pre výrobu a uskladnenie energie – prehľad o aktivitách na Ústave geotechniky SAV.

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Elektroenergetika 2019

Basic Research Needs:
Electrical Energy Storage

- Portable Electronics (Cell phones, laptops, PDA, digital cameras)
- Medical Devices

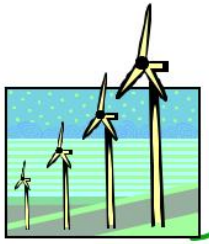


Low Power (high energy)

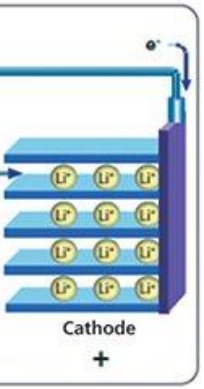
- Portable tools
- Back-up power (UPS)

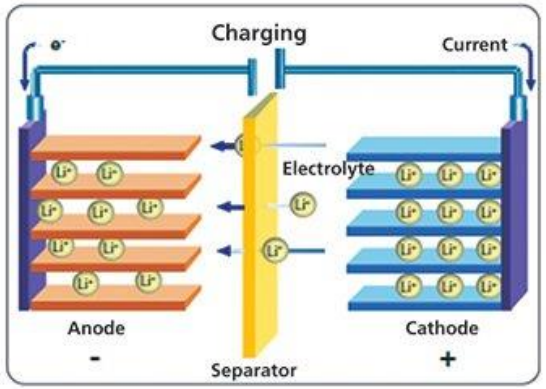
- Power Storage for Renewable Energy
- EVs and HEVs
- Electric bikes/scooters
- "Industrial" EV, forklifts

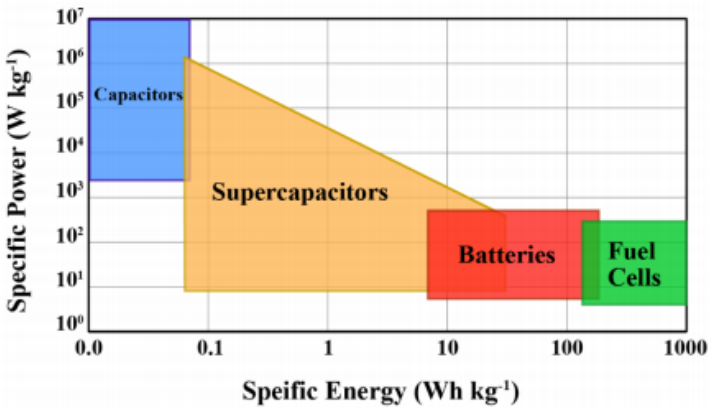
golf carts

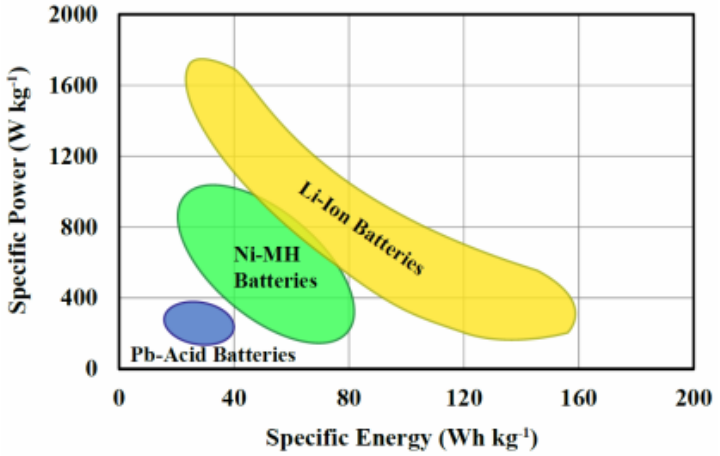




High Power



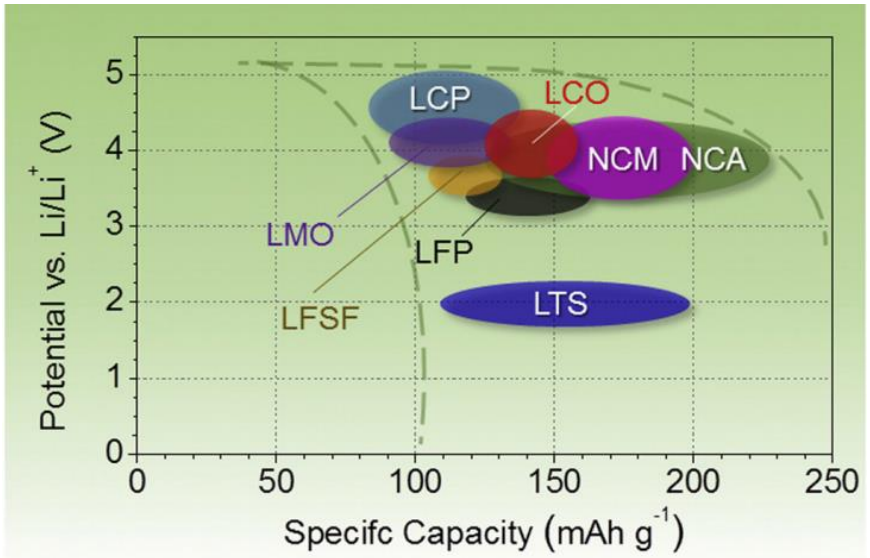


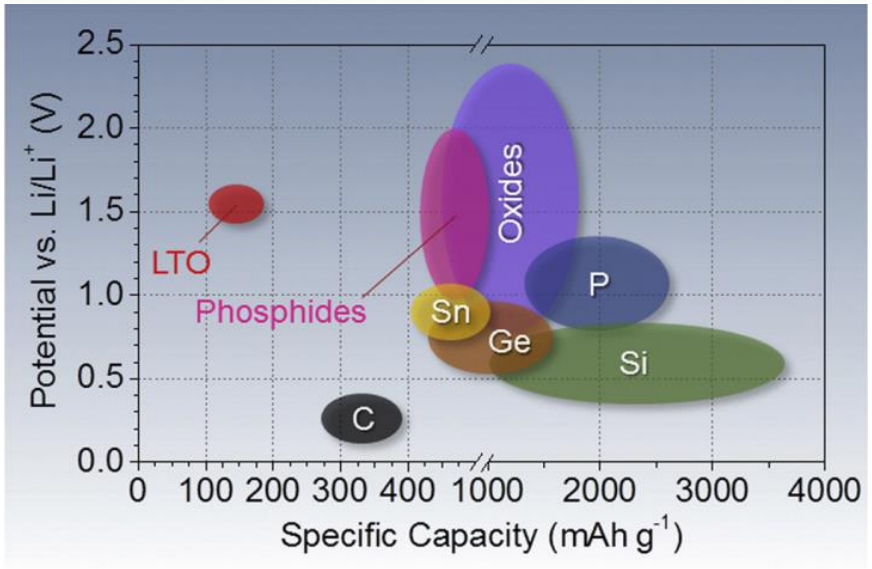




Adapted from: E.K. Heidari et al., JUFGNMS 51 (2018) 1

Basic Research Needs:
Electrical Energy Storage





Improving battery performance will be driven by:

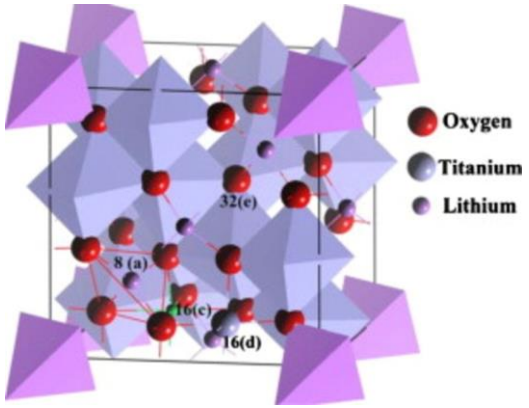
- New/modified materials
- Understanding how the systems function
- and why they fail -characterization (diagnostics)

Energy density:
Need to increase the amount of charge stored per unit of material

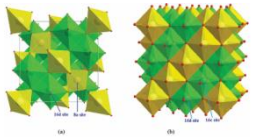
Power (rate):
Need to increase Li+ diffusion (and electronic conductivity)
Engineering of cell design

Adapted from: Y. Wang et al., J. Power Sources 286 (2015) 330

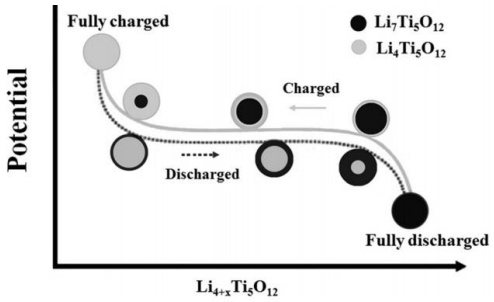
$Li_4Ti_5O_{12}$ spinel as anode material



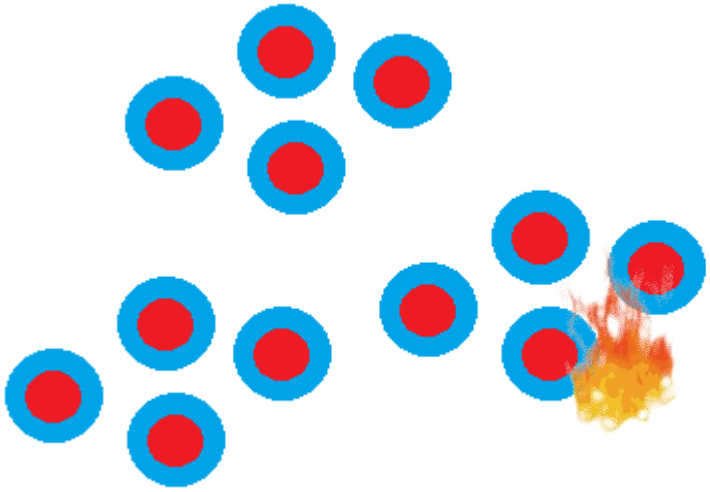
Long lifetime
Minimum strain
High rate capabilities
Th. Capacity (175 mAh/g)

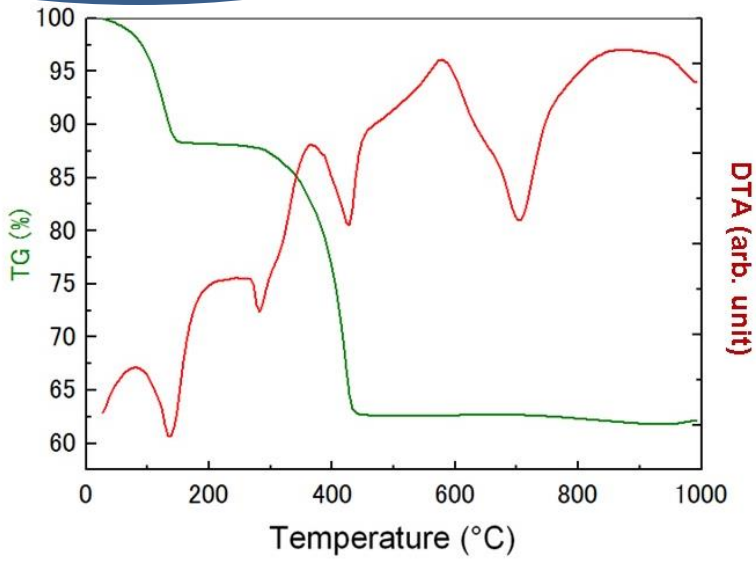


$$Li_{3(8a)}[LiTi_5^{4+}]_{(16d)}O_{12(32e)} + 3e^- + 3Li^+ \leftrightarrow Li_{6(16c)}[LiTi_3^{3+}Ti_2^{4+}]_{(16d)}O_{12(32e)}$$



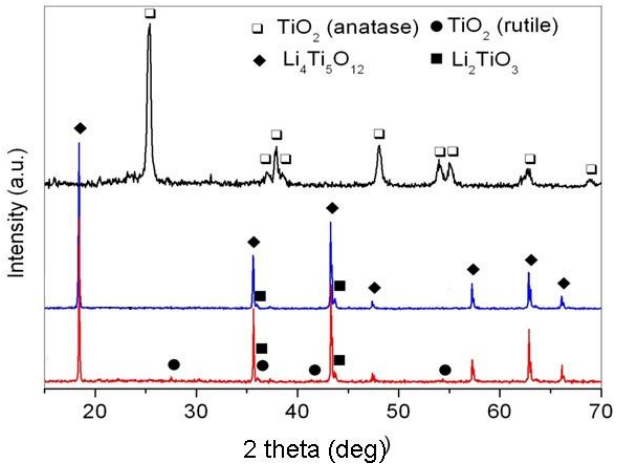
$CH_3COOLi + TiO_2 + EtOH \equiv$ Precursor + 600°C = LTO

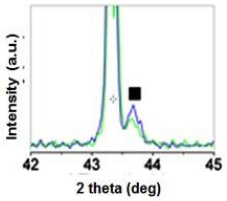


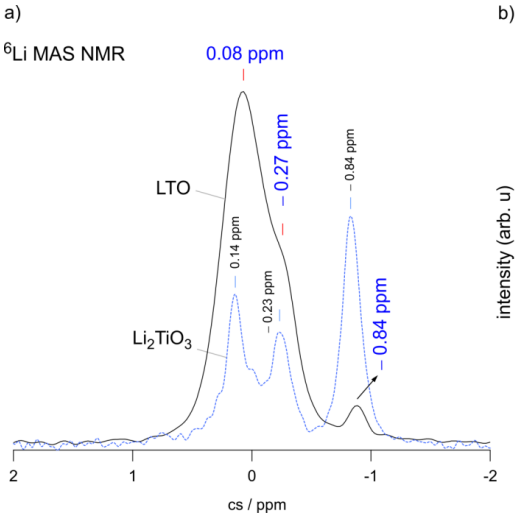


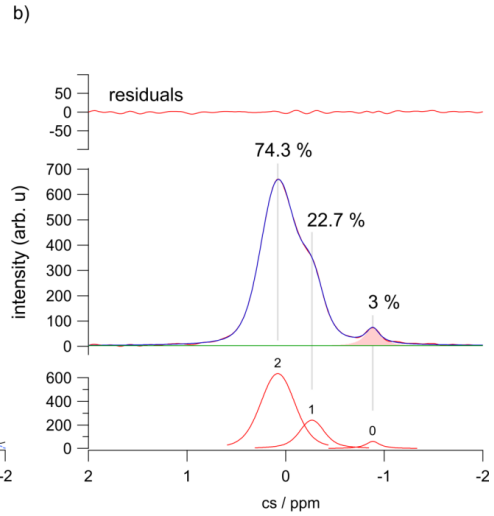
Zaghib et al., J. Power Sources 81 (1999) 300. 800°C/12 h!!!

$Li_4Ti_5O_{12}$ spinel as anode material



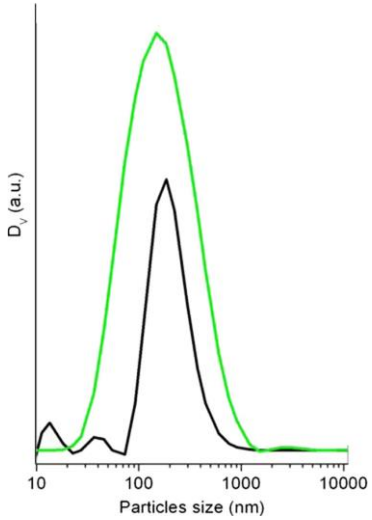


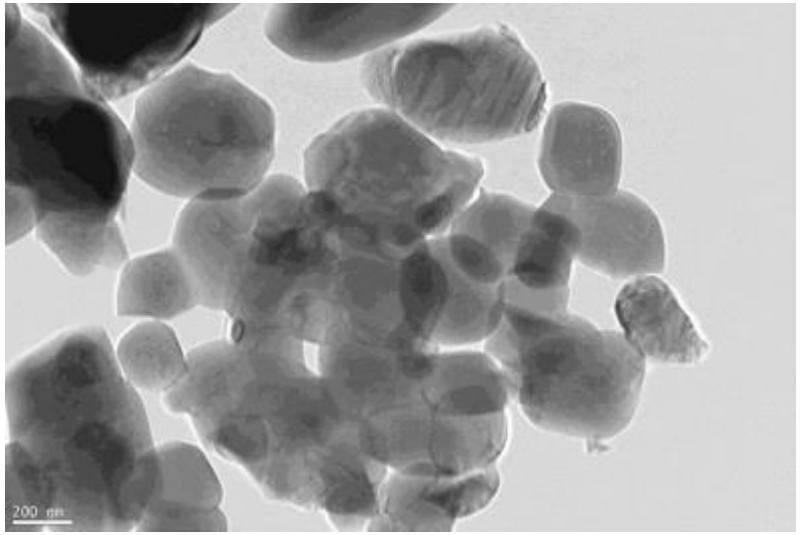




High phase purity !!!

MAP s-LTO a-LTO



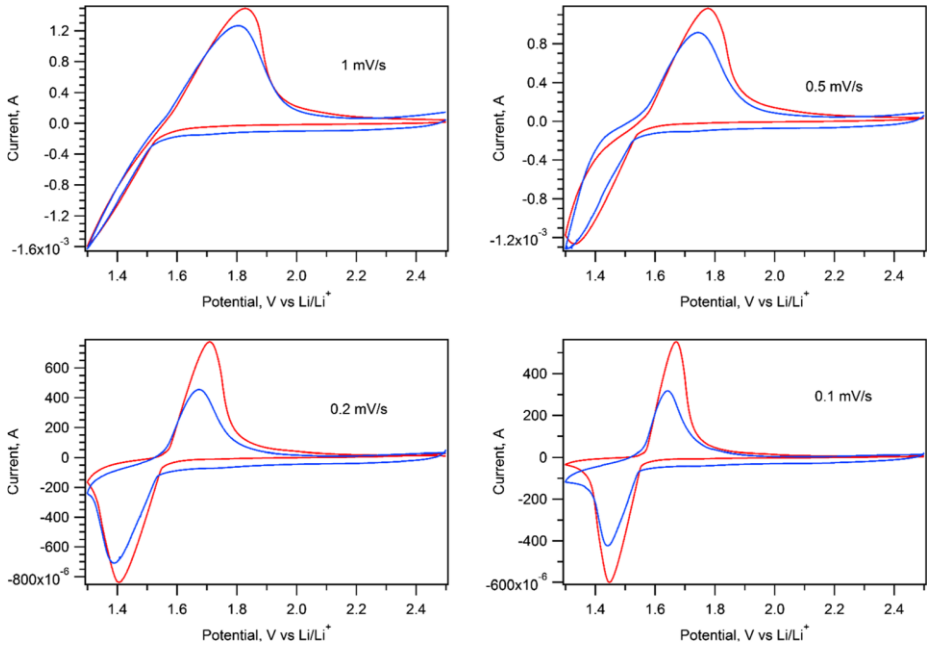


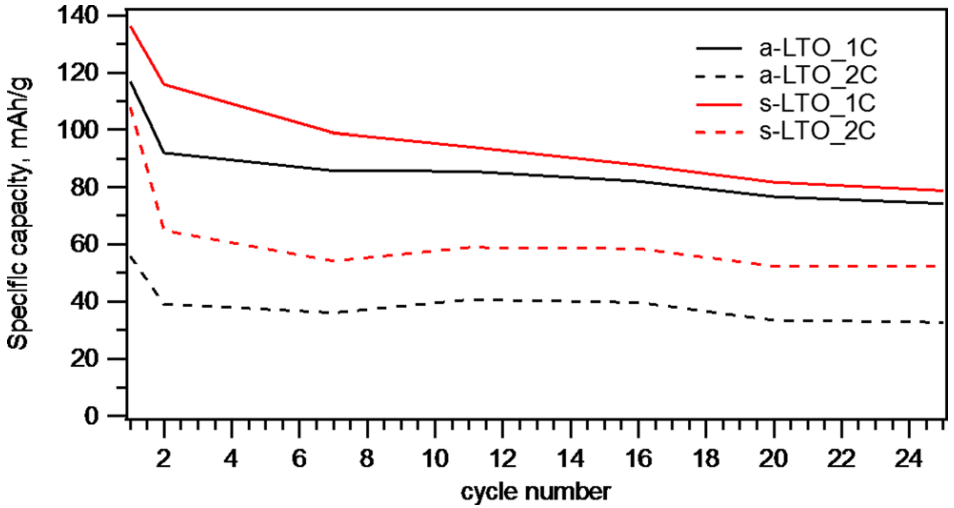
a-LTO a = 8.33 - 8.36 Å, s-LTO a = 8.363(4) Å

Oxygen defects and/or Ti^{4+}/Ti^{3+} reduction?

D ~ 180 nm (Rietveld refinemnt, DLS)

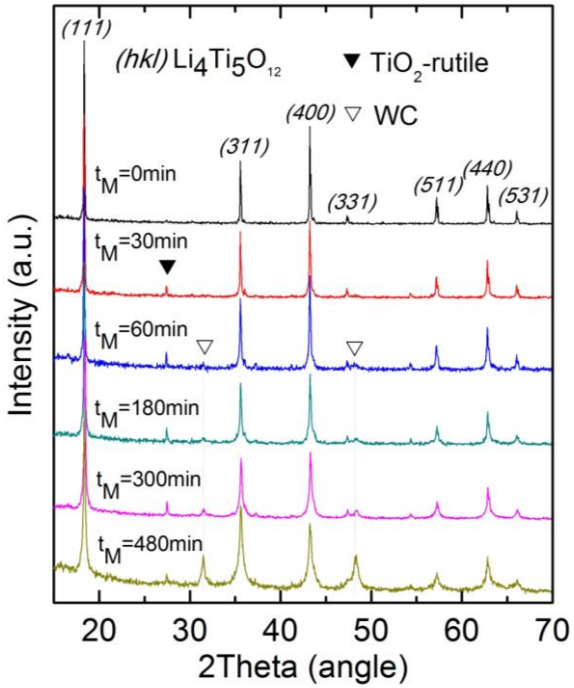
$Li_4Ti_5O_{12}$ spinel as anode material

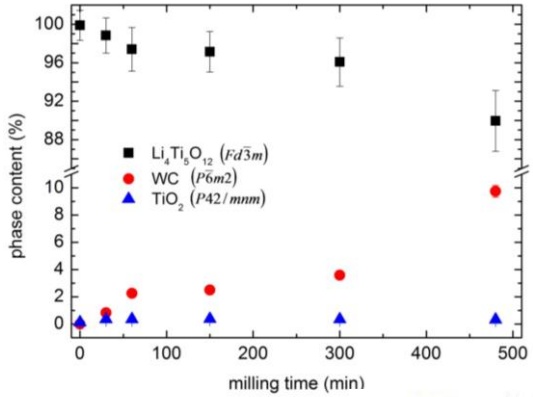




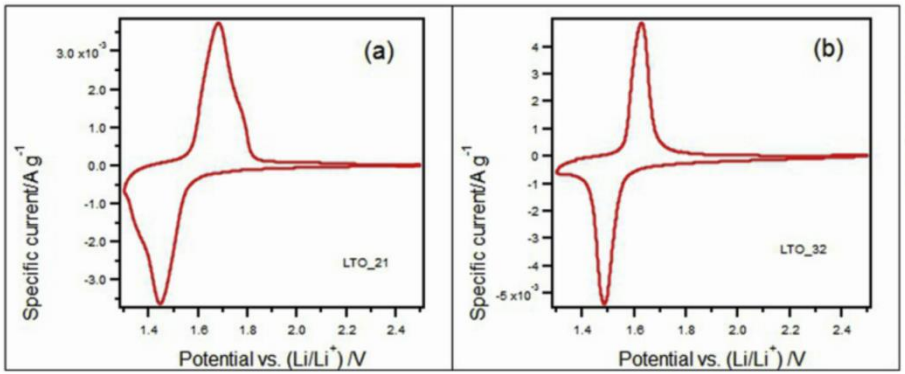
Theoret.	a-LTO	LTO
175 mAh/g	95 mAh/g (54 %)	142 mAh/g (80 %)
	12.5 m^2/g	1.4 m^2/g
1C and 2C	20 % (1C), 16 % (2C) CTR 609 Ωcm^2	30 % (1C), 9 % (2C) CTR 319 Ωcm^2

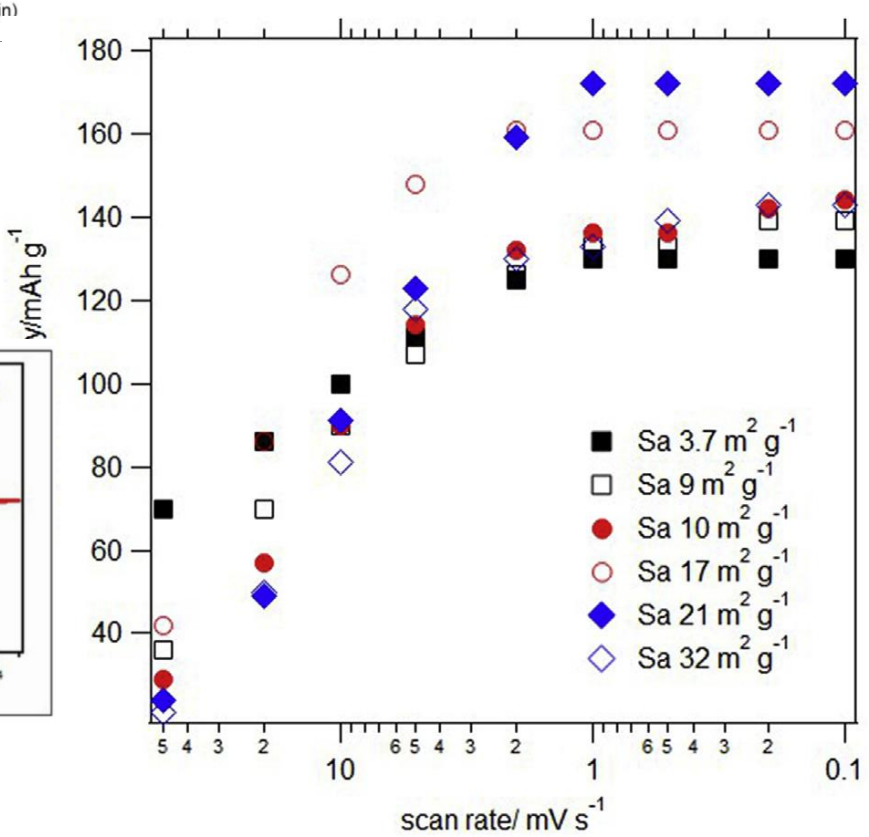
$Li_4Ti_5O_{12}$ spinel as anode material



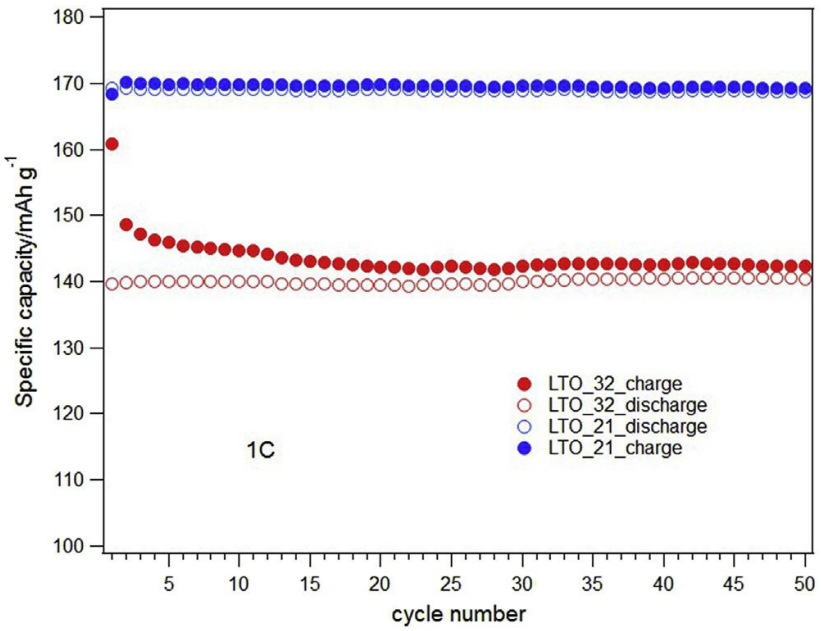


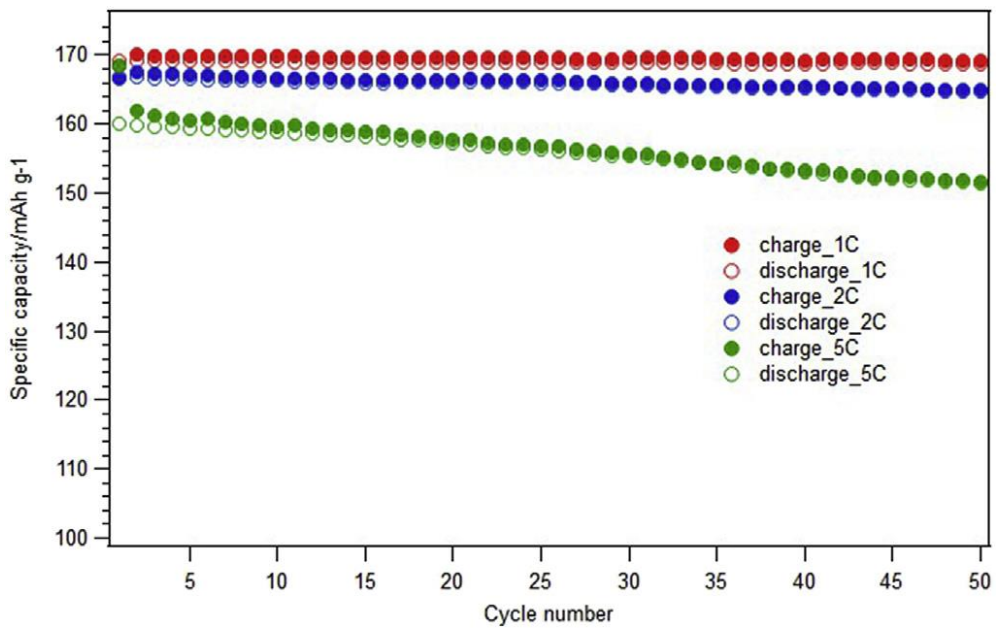
t_M (min)	B.E.T. S_a (m^2/g)
0	3.7
30	9.0
60	10.0
150	17.0
300	21.0
480	32.0





$Li_4Ti_5O_{12}$ spinel as anode material



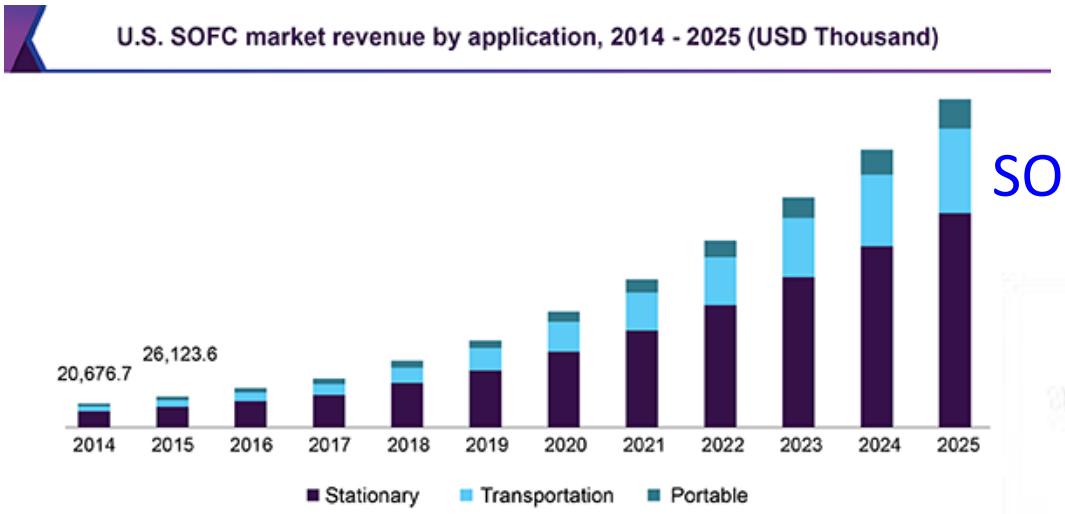


1. ZUKALOVÁ, Markéta - **FABIÁN, Martin** - KLUSÁČKOVÁ, Monika - KLEMENTOVÁ, M. - PITŇA LÁSKOVÁ, Barbora - DANKOVÁ, Zuzana - **SENNA, M.** - KAVAN, Ladislav. ***Li insertion into Li4Ti5O12 spinel prepared by low temperature solid state route: Charge capability vs surface area***. In Electrochimica Acta, 2018, vol. 265, p. 480-487.

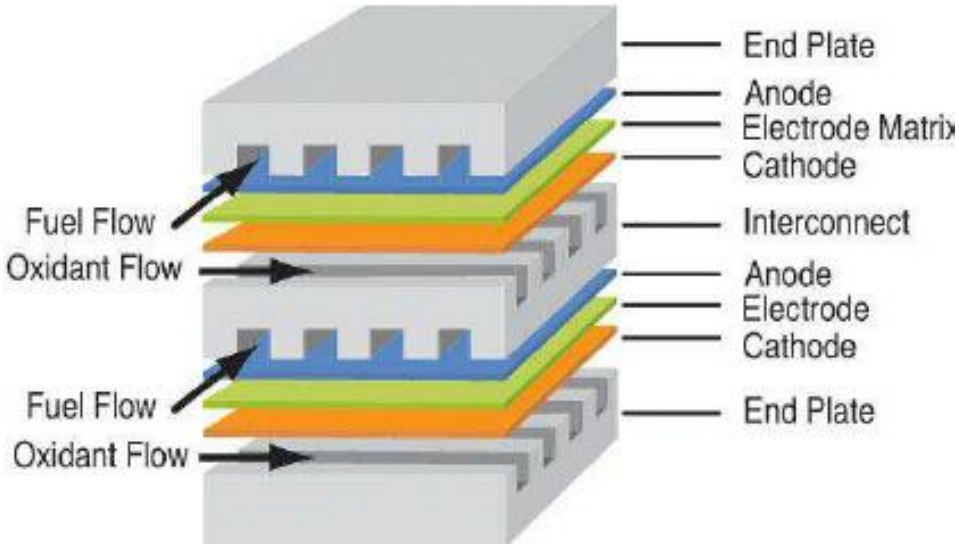
2. SENNA, M. - FABIÁN, Martin - KAVAN, Ladislav - ZUKALOVÁ, Markéta - BRIANČIN, Jaroslav - **TÓTHOVÁ, Erika** - BOTTKE, Patrick - WILKENING, Martin - **ŠEPELÁK, Vladimír**. ***Electrochemical properties of spinel Li4Ti5O12 nanoparticles prepared via a low-temperatúre solid route***. In Journal of Solid State Electrochemistry, 2016, vol. 20., no. 10, p. 2673-2683.

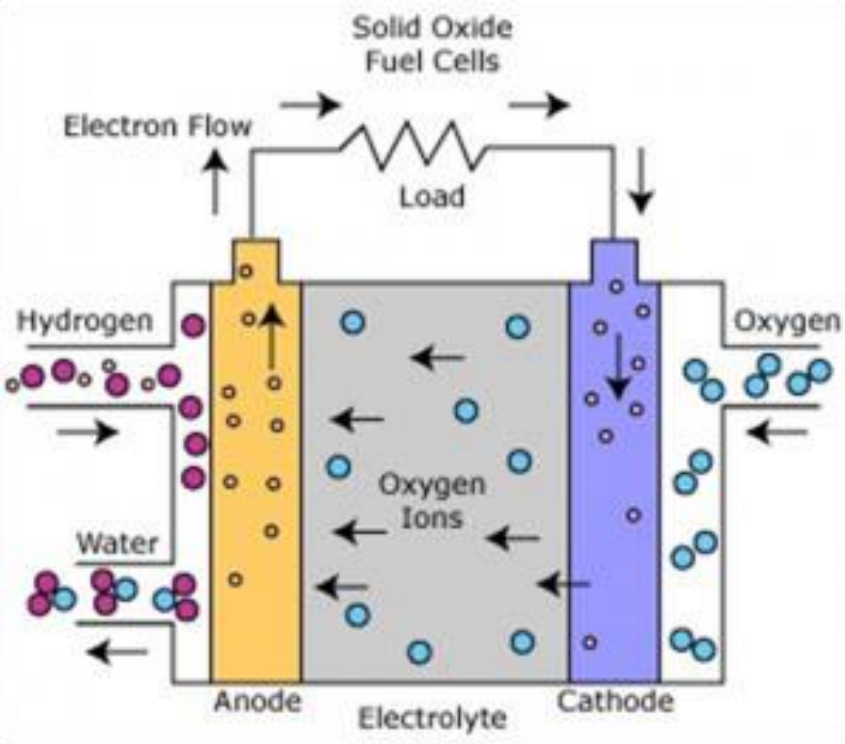
- Target materials of further interest:
  $Li_7La_3Zr_2O_{12}$ (Ta^{5+}, Ga^{3+}, ...) (electrolyte)
  $K_2Ti_6O_{13}$, solid solutions (Na, K) of $Li_4Ti_5O_{12}$ (anode)
  $Li(Na)_3V_2(PO_3)_3$ (cathode)
  Implementation of carbon source: graphite, graphene, organic sources of carbon,....

Motivation



SOFC = **S**olid **O**xide **F**uel **C**ells





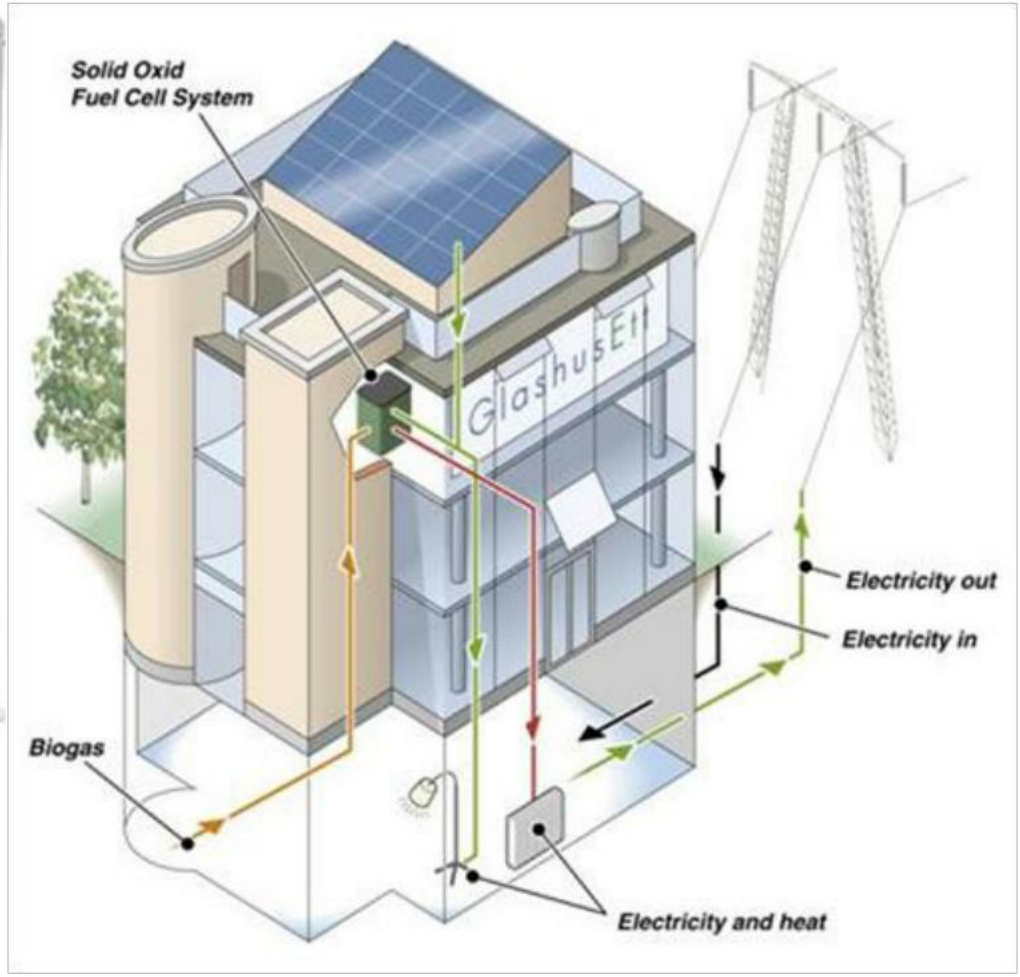
C: ½ O_2 + 2 e^- = O^{2-}

A: H_2 + ½ O^{2-} = H_2O + 2 e^-

H_2 + ½ O^{2-} = H_2O + 2 e^-

Motivation


SOFC
FC-5A


Solid Oxid
Fuel Cell System
GlashusEtt
Electricity out
Electricity in
Biogas
Electricity and heat

Motivation

SOFC Hardware Material Alternatives

Electrolytes

Zirconia Materials
YSZ
SSZ
CaSZ

Ceria Materials
GDC
SDC
YDC
CDC

Lanthanum Materials
LSGM
LSGMC
LSGMF
LSGMCF
$LaAlO_3$ based

Other Materials
BCY
YSTh
YSHa
Bismuth oxide-based
Pyrochlorores-based
Barium and strontium brownmillerites

Anodes

Nickel Materials
Ni-O/YSZ
Ni-O/SSZ
Ni-O/GDC
Ni-O/SDC
Ni-O/YDC

Copper Materials
$CuO_2/CeO_2/YSZ$
CuO_2/YSZ
Cu/YZT
$CuO_2/CeO_2/SDC$

Lanthanum Materials
$La_{1-x}Sr_xCrO_3$
$La_{1-x}Sr_xCr_{1-y}M_yO_3$
LST
LAC

Other Materials
CeO_2/GDC
TiO_2/YSZ
Cobalt-based
Platinum-based
Ru/YSZ

Cathodes

Lanthanum Materials
LSM
LSF
LSC
LSCF
LSMC
LSMCr
LCM
LSCu
LSFN
LNF
LSCN
LBC
LNC
LSAF
LSCNCu
LSFNCu
LNO

Gadolinium Materials
GSC
GSM

Praseodymium Materials
PCM
PSM
PBC

Strontium Materials
SSC
NSC
BSCCu

Yittria Materials
YSCF

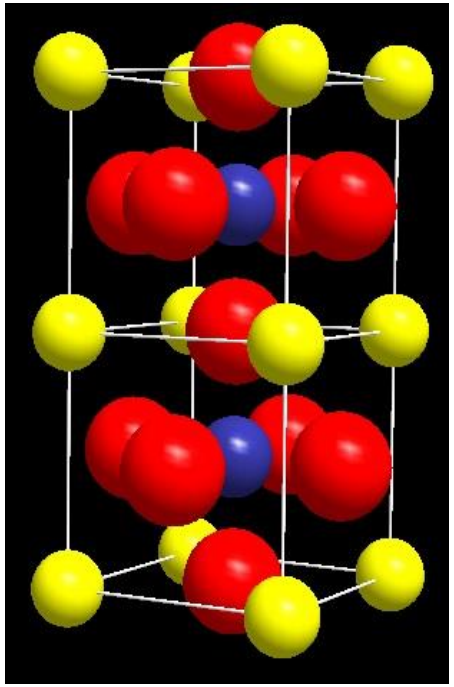
Interconnects

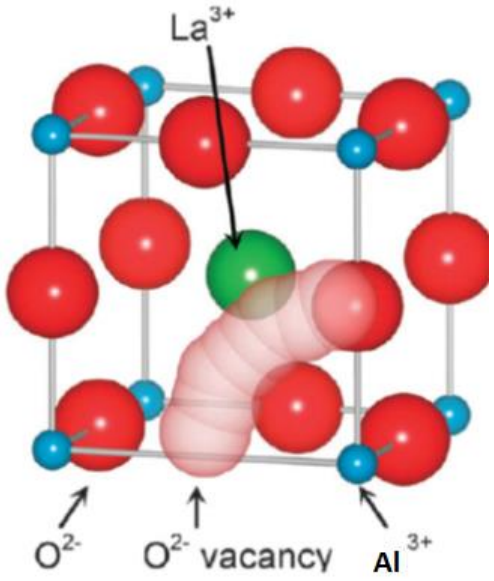
Metals
*base materials
chromium alloys
ferritic stainless steels
austenitic stainless steels
iron super alloys
nickel super alloys
*coatings
LSM
LCM
LSC
LSFeCo
LSCr
LaCoO3

Ceramics
Lanthanum chromites

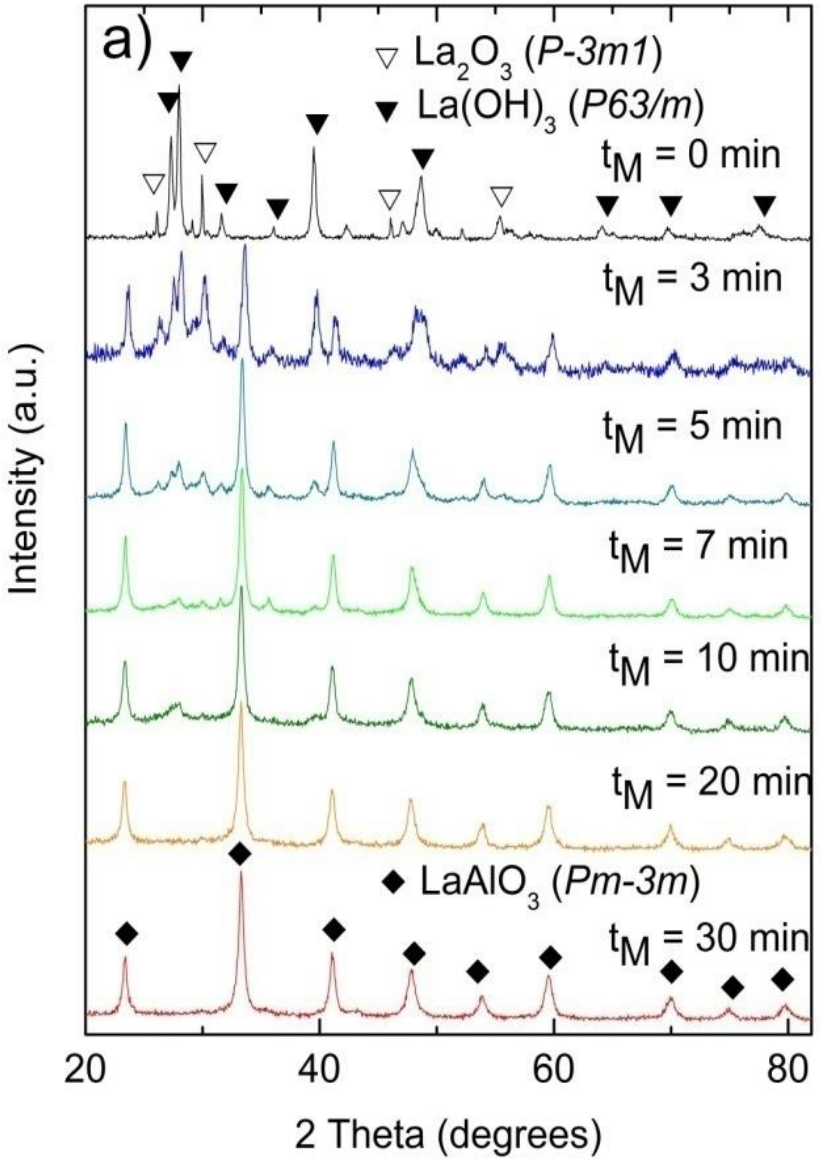
Seals

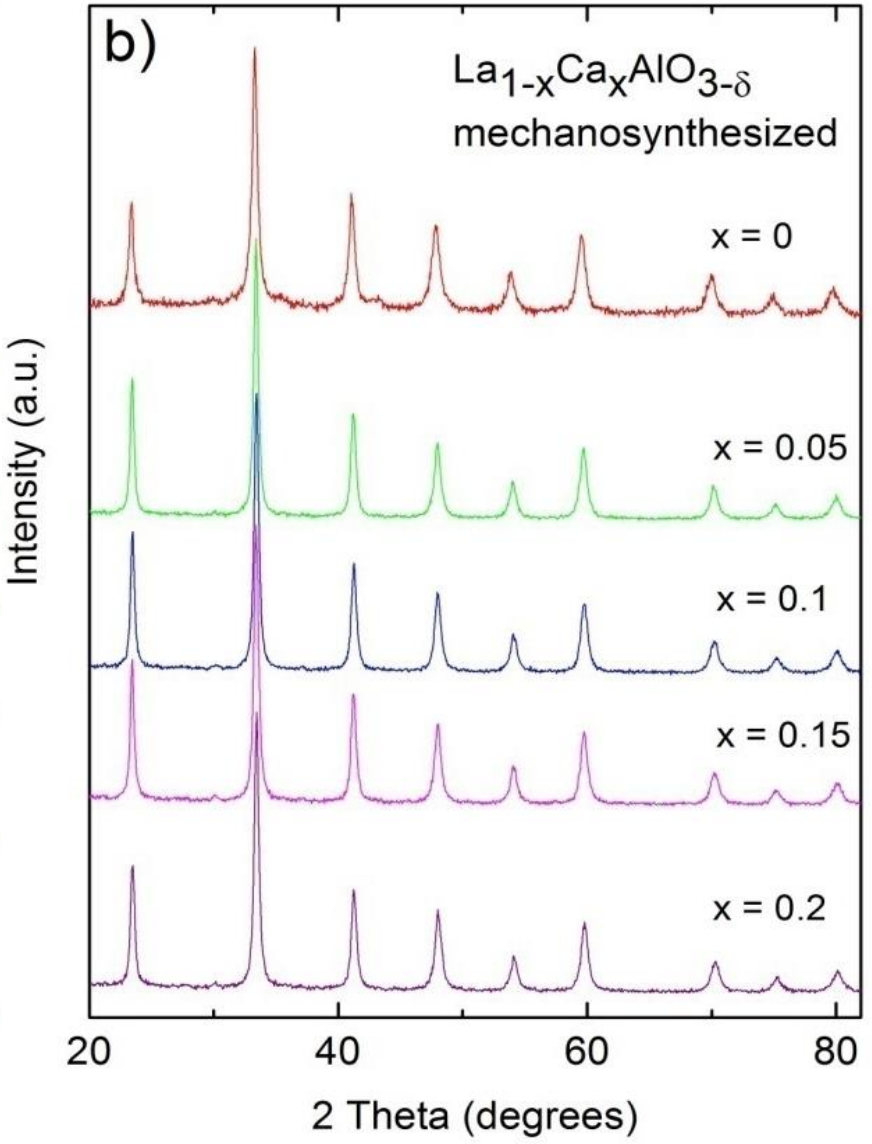
glass or glass-ceramic materials
mica-based composites



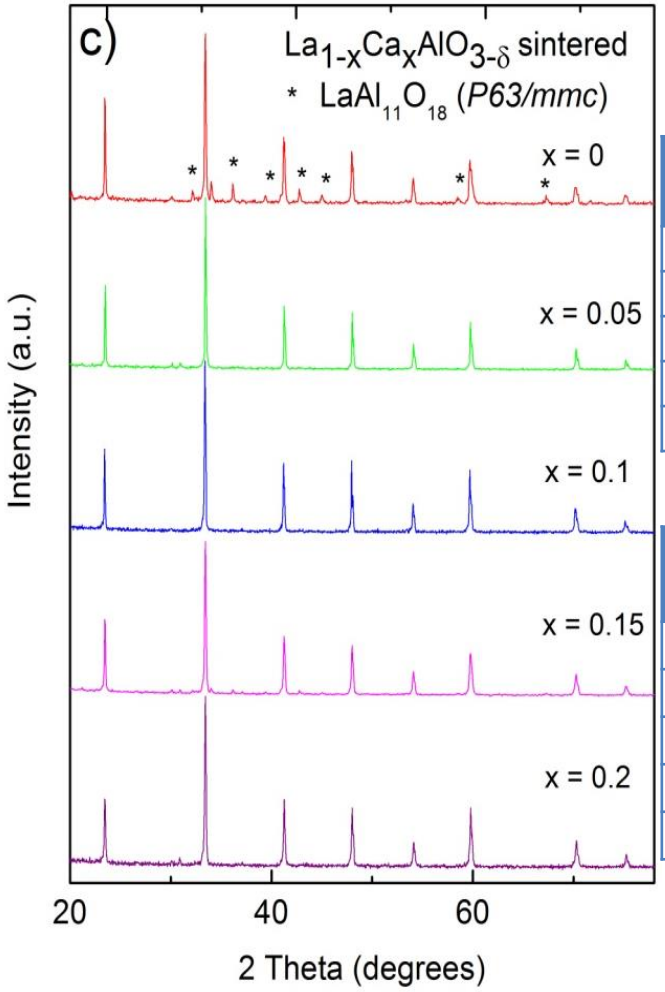


$La_{1-x}Ca_xAlO_{3-d}$ - synthesis





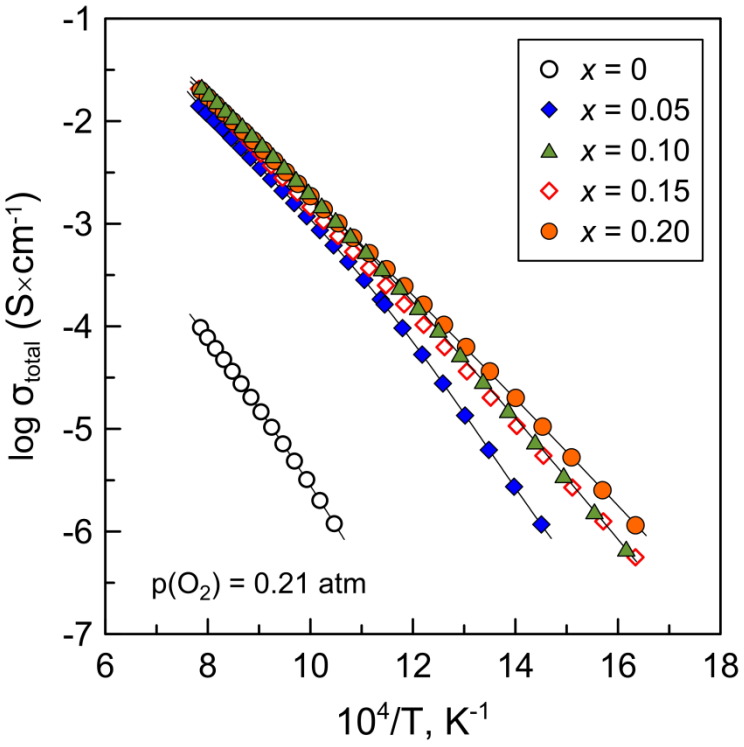
$La_{1-x}Ca_xAlO_{3-d}$ - synthesis

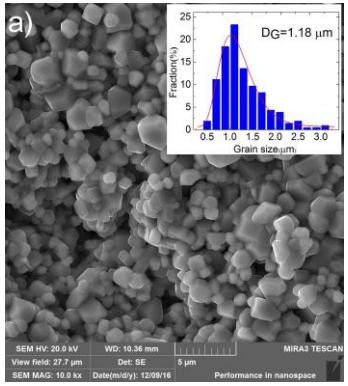


x	Lattice parameter (Å)	Volume (Å^3)	Crystallite size, D (nm)	Strain (×10^{-4})
0	3.80339(12)	55.019	11	19
0.05	3.79312(6)	54.578	30	39
0.1	3.79065(7)	54.468	33	52
0.15	3.79008(7)	54.443	39	57
0.2	3.78879(6)	54.388	34	70

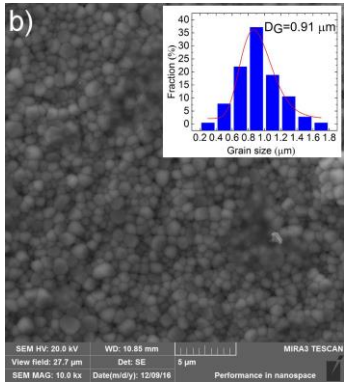
x	Lattice parameter (Å)	Volume (Å^3)	Grain size, D_G (μm)
0	3.79171(5)	54.514	1.18
0.05	3.79122(5)	54.493	0.91
0.1	3.78904(7)	54.399	0.70
0.15	3.78774(11)	54.343	0.59
0.2	3.78739(6)	54.328	0.22

$La_{1-x}Ca_xAlO_{3-d}$ – functional properties

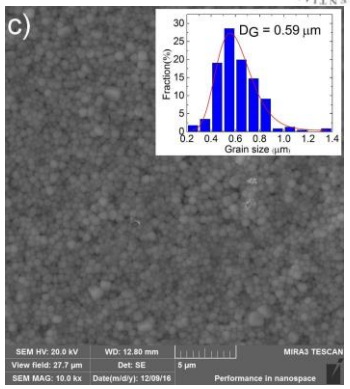




$LaAlO_3$



$La_{0.95}Ca_{0.05}AlO_{2.975}$

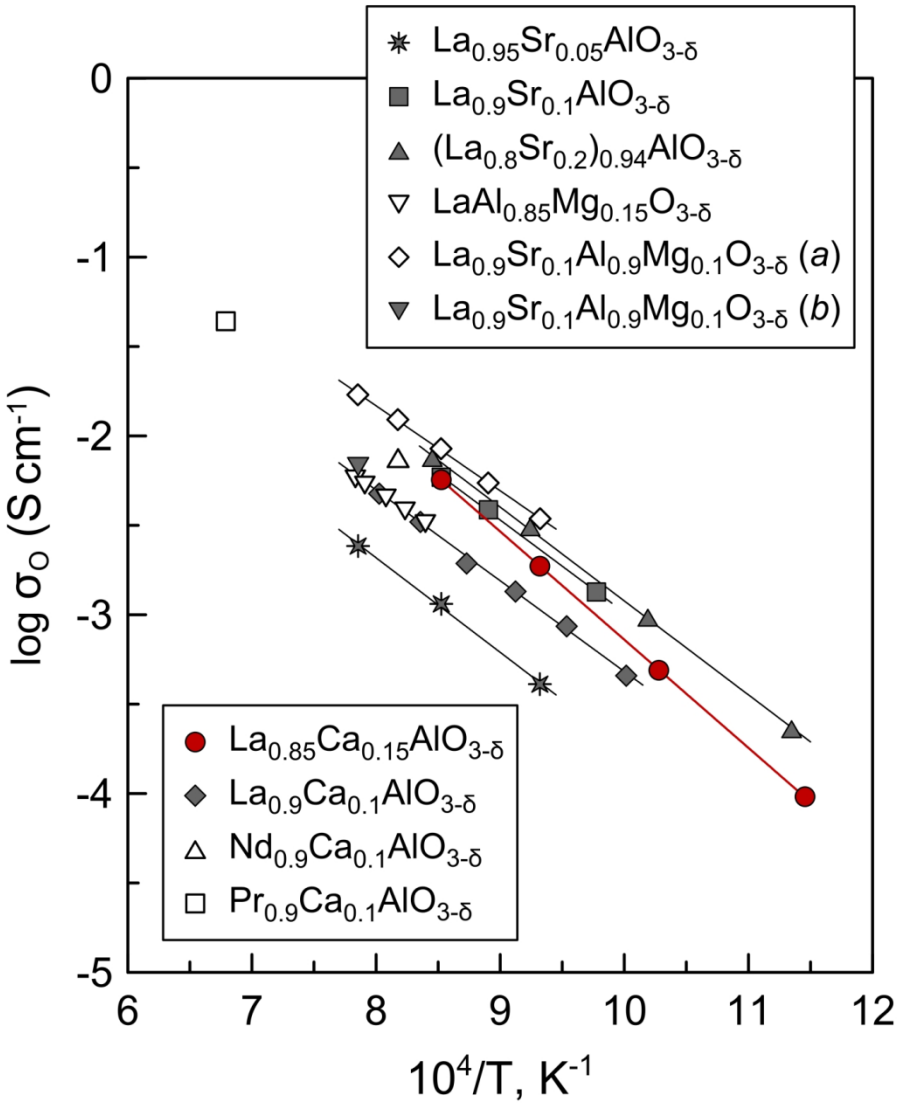


$La_{0.85}Ca_{0.15}AlO_{2.925}$

Temperature dependence of total electrical conductivity of $La_{1-x}Ca_xAlO_{3-\delta}$ ceramics in air.

x	T, ° C	E_A, kJ/mol
0	680-1000	148.4 ± 1.0
0.05	630-1000	109.3 ± 0.4
	415-630	140.1 ± 0.9
0.10	630-1000	104.7 ± 0.4
	370-630	115.5 ± 0.5
0.15	340-1000	109.5 ± 0.2
0.20	340-1000	102.0 ± 0.3

$La_{1-x}Ca_xAlO_{3-d}$ – functional properties



Composition	Sintering		Relative density, %
	T, ° C	Time, h	
$La_{0.85}Ca_{0.15}AlO_{3-\delta}$	1450	12	96
$La_{0.90}Ca_{0.10}AlO_{3-\delta}$	1600	12	-
$Nd_{0.90}Ca_{0.10}AlO_{3-\delta}$	1500	12	-
$Pr_{0.90}Ca_{0.10}AlO_{3-\delta}$	1650	-	87
$La_{0.95}Sr_{0.05}AlO_{3-\delta}$	1675	4	77
$La_{0.90}Sr_{0.10}AlO_{3-\delta}$	1400<T<1600	4-7	72
$(La_{0.8}Sr_{0.2})_{0.94}AlO_{3-\delta}$	1500	10	90
$LaAl_{0.85}Mg_{0.15}O_{3-\delta}$	1950	0.25	-
$La_{0.90}Sr_{0.10}Al_{0.90}Mg_{0.10}O_{3-\delta}$ (*a*)	1650	4	98
$La_{0.90}Sr_{0.10}Al_{0.90}Mg_{0.10}O_{3-\delta}$ (*b*)	1700	8	92.5

Thank you for your attention!