



Engineering Ceramic and Glass-Materials for Energy Storage, Sensing and Computing

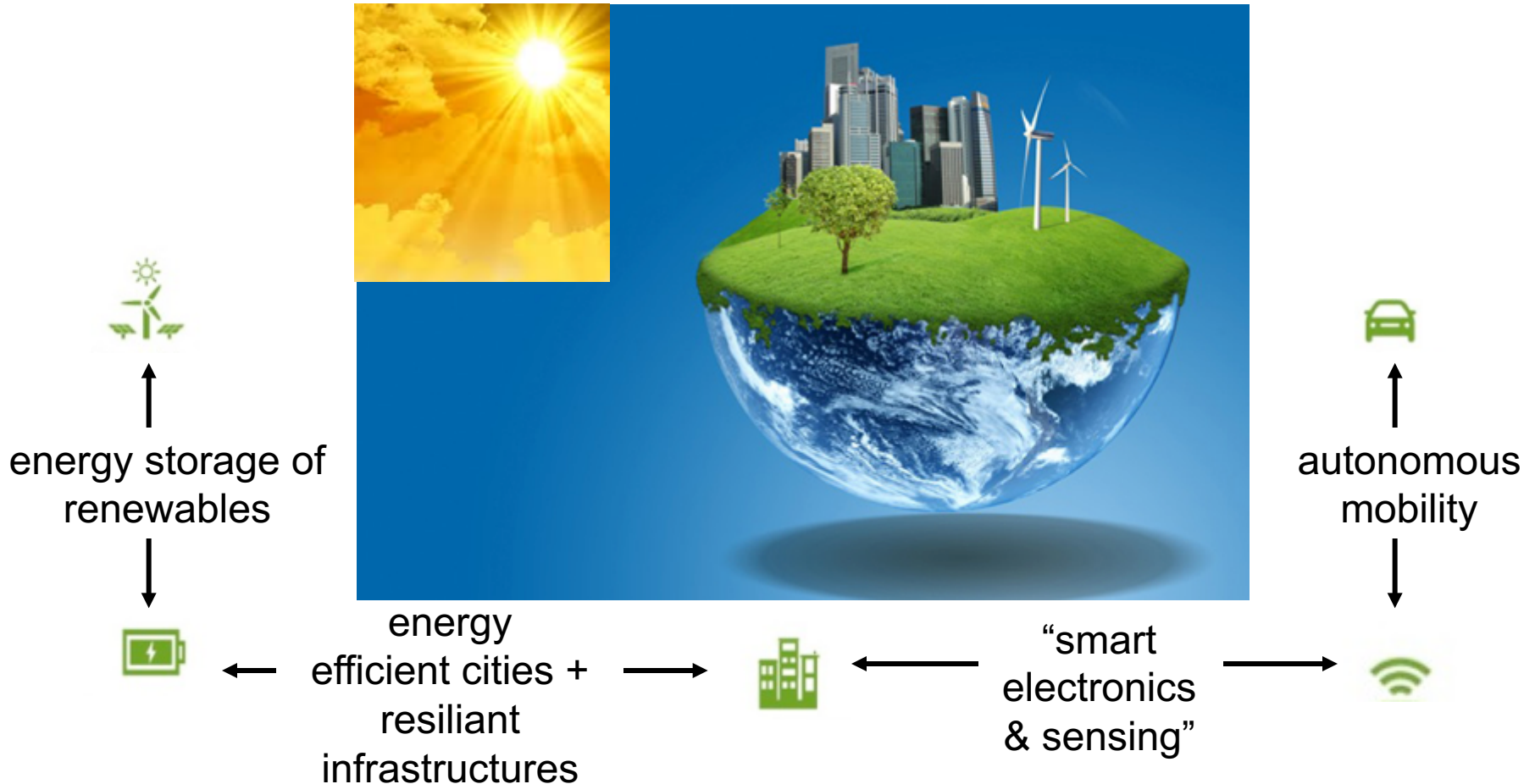
Jennifer L.M. Rupp

Electro-Chemical Materials Group



Massachusetts Institute of Technology, MIT

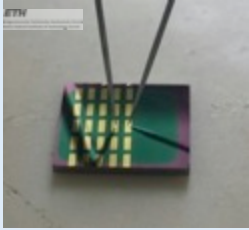
Green&Smart: Transfer and Storage of Energy and Information



Innovation for sustainable energy and information supply
.... is based on novel material and device concepts.

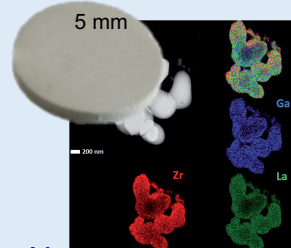
Rupp group: Solid State Materials for Energy & Information Devices

Novel All Solid State Li Batteries + CO₂ Environmental Trackers



CO₂ environmental + medical sensing based on Li⁺

I Garbayo et al. JLM Rupp, Advanced Energy Materials 2017
J Van den Broek et al. JLM Rupp, Advanced Energy Materials, 2016
C Haensel et al. JLM Rupp, Nanoscale 2016
M Rawlance et al. JLM Rupp, Nanoscale 2016
S Afyon et al. JLM Rupp, J of Materials Chemistry 2015



Novel solid state Li battery with high capacities

Ionic memory and computing logics: memristors



information storage + non-binary computing

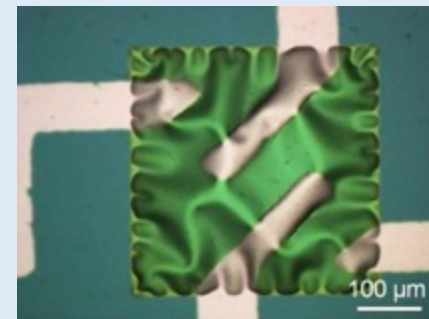
S Schweiger et al. JLM Rupp, Advanced Materials 2017
R Schmitt et al. JLM Rupp, ACS Nano 2017
M Kubicek, F Messerschmitt et al JLM Rupp, ACS Nano 9, 2015
F Messerschmitt, et al. JLM Rupp, Adv Funct Mater. 25, 2015
F Messerschmitt, et al. JLM Rupp, Adv Funct Mater. 24, 2014

Renewable Solar Fuels (Hydrocarbons) | Micro-energy convertor designs



clean energy storage with no material's capacity limitations

AH Bork et al., JLM Rupp, Advanced Energy Materials, 2016
AH Bork, et al. JLM. Rupp, J. of Mat Chem A, 2015



grid-independent energy conversion for autonomous electronics

Y Shi, AH Bork, S Schweiger, JLM Rupp, Nature Materials 14, 2015
Y Shi et al. JLM Rupp, Adv Mat, 2016

Outline

Energy Storage: All Solid State Li⁺ Batteries

- Cheap Ceramic Processing: Mass Storage
- Low Temperature Microbatteries

Environmental Monitoring: CO₂ Sensing

- Novel Li⁺-Garnet-based CO₂ Sensor Architectures

Neuromorphic Computing: Memristors

- Strained Memristor Concept

Energy Storage: Material Limitations of Liquid based Batteries

Renewable Energies



Solar



Wind



energy storage

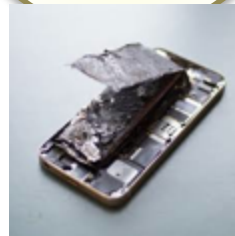


instable
electrolyte/electro
des
interfaces

challenges

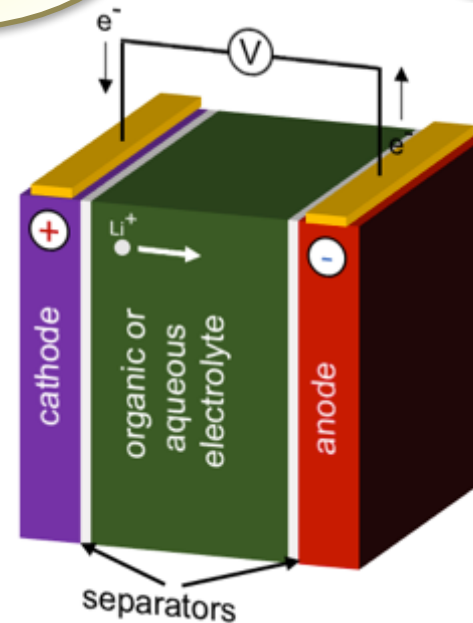
low temperature
window
($<120^{\circ}\text{C}$)

safety:
inflammable
batteries



limited
scalability
+
V-window

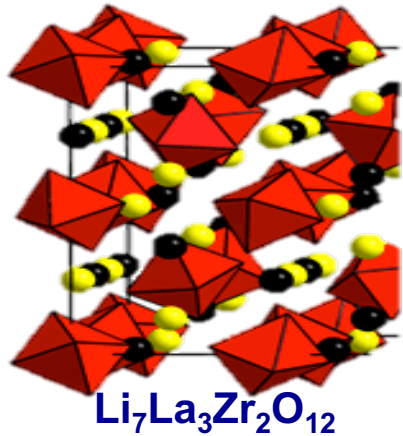
damage:
Li dendrites



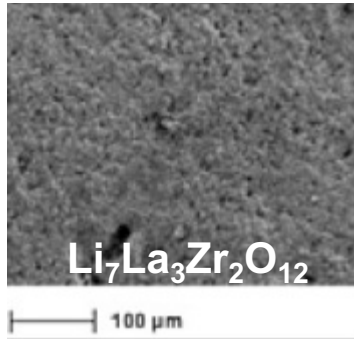
Today's liquid-based Li-ion batteries have severe safety, stability and scaling limitations. New Material architectures and cell designs needed.

Literature: All Solid State Battery Electrolytes based on Li-Garnets

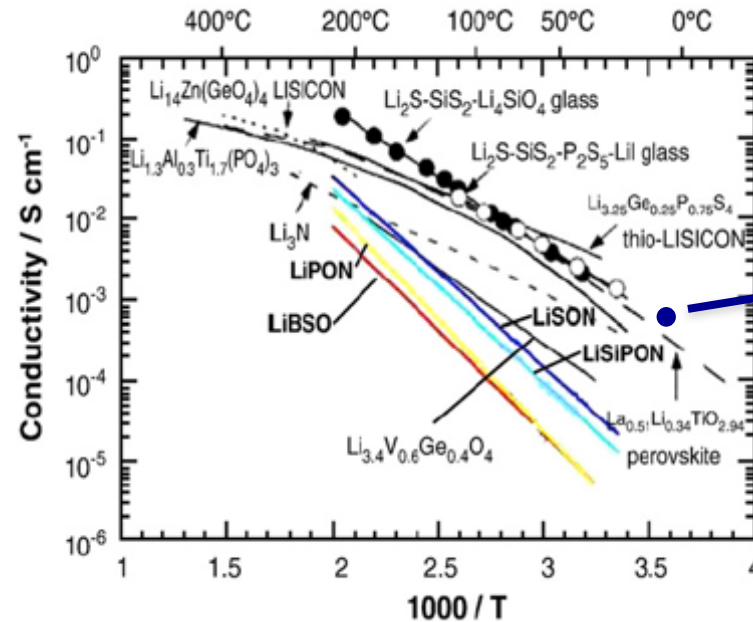
structure



dense ceramic

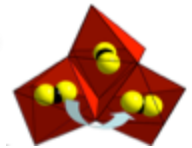


Li^+ ionic transfer



Li-Garnets
 $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$

structural Li^+
diffusion



Knauth et al., Solid State Ionics 180, 2009

H El Shiwari and J Janek, J. of Power Sources 2013

Young field, since 2012:

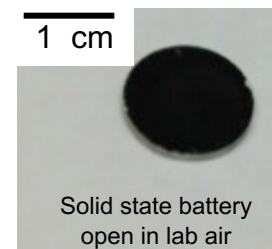
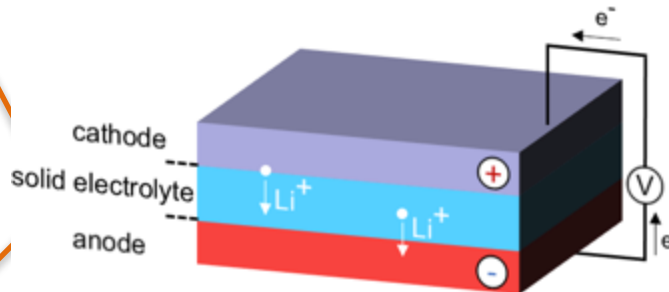
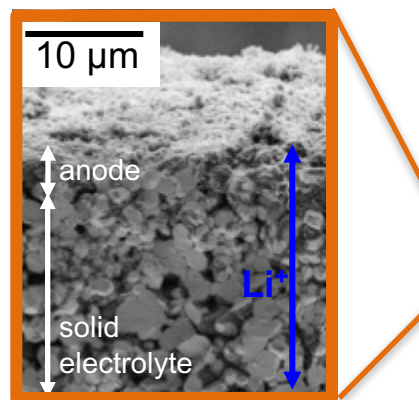
First macro ceramic Li-garnet electrolytes pellets: comparable Li conduction by one order to classic liquids → advantage: solid state nature

(1) Reviewed Li-garnet battery performance: J van den Broek, S Afyon, JLM Rupp, Advanced Energy Materials, 2016

(2) S Afyon et al. JLM Rupp, J. of Materials Chemistry A 3, 2015

All Solid State Li⁺ batteries without Liquids

Innovation: Non-inflammable Li⁺ battery up to 1000°C in air.



energy storage of renewables



electric vehicles



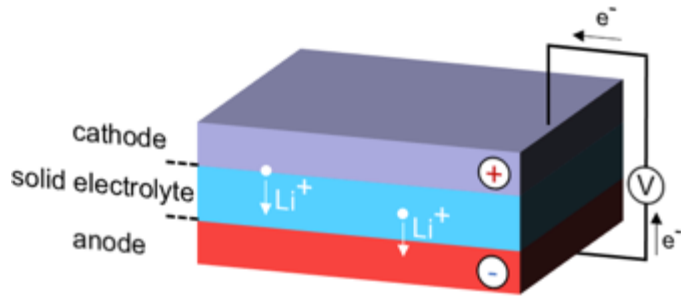
“smart electronics & sensing”



Rupp group research: All solid state batteries based on Li-Garnets. Cheap manufacturing, high V cathodes, understanding interface reactions, tuning power characteristics and charging.

Solid State Electrolyte Li-Garnet/Cathode Interfaces

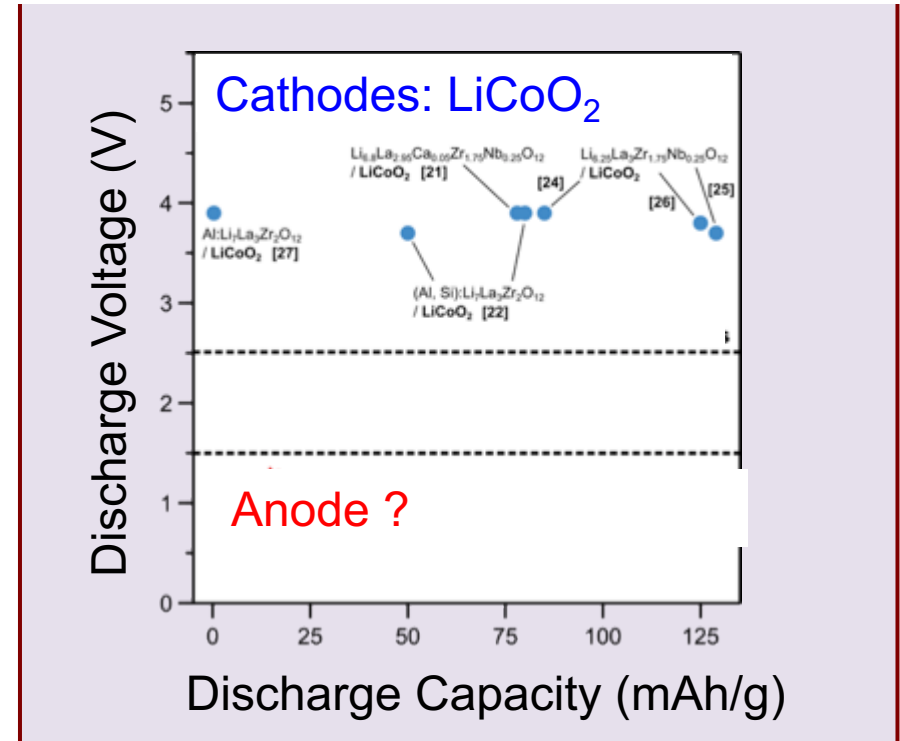
Integration of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ Solid Electrolytes to Batteries



What are suitable electrodes?
Power?

young field: first battery in 2012

Li-Garnet Battery: Electrode Materials



Ceramic processing and solid state battery engineering:

Electrodes compatible with Li-garnets needed

→ First cathodes reported (cells¹ + Ceder group MIT: MD modeling²)

(1) Reviewed Li-garnet battery performance: J van den Broek, S Afyon, JLM Rupp, Advanced Energy Materials, in press 2016

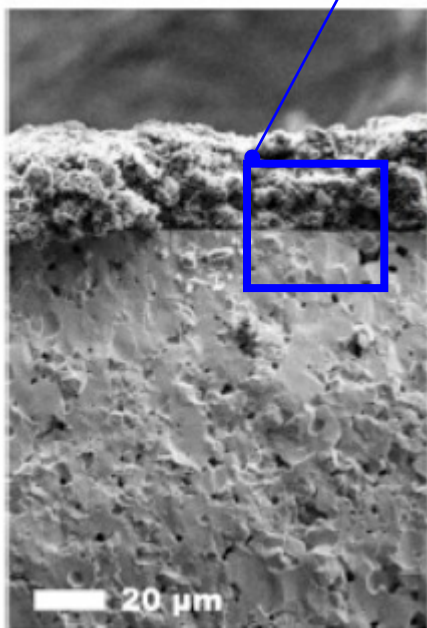
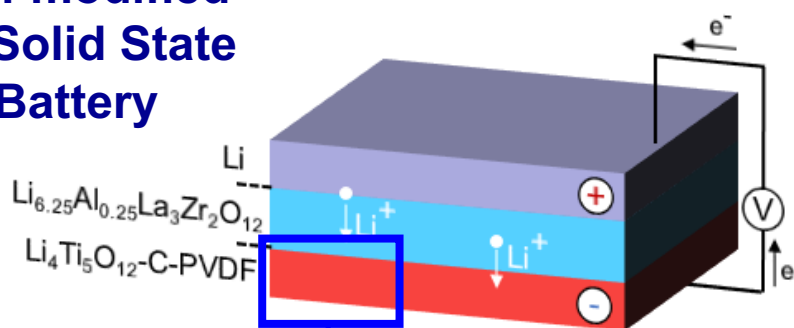
(2) LJ Miara, G Ceder et al, Chem of Materials, 27, 2015

(3) X Tong, V Thangadurai, E Wachsman, Inorganic Chemistry 54, 2015

(4) S Afyon et al. JLM Rupp, J. of Materials Chemistry A 3, 2015

Solid Li⁺ batteries the role of ceramic/interface manufacturing

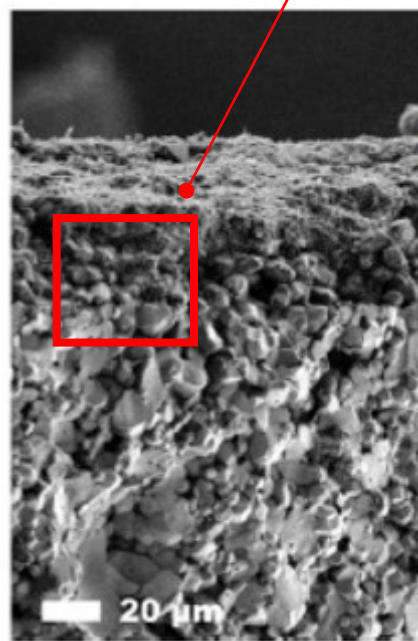
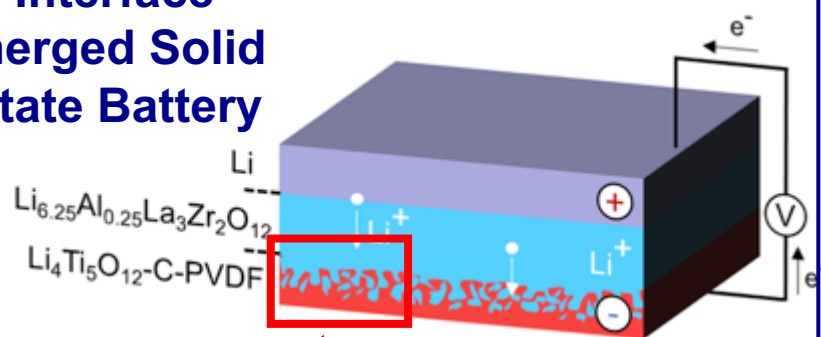
Non-modified All Solid State Battery



Li₄Ti₅O₁₂-C
anode

dense
electrolyte
Li₇La₃Zr₂O₁₂
ceramic

Interface merged Solid State Battery



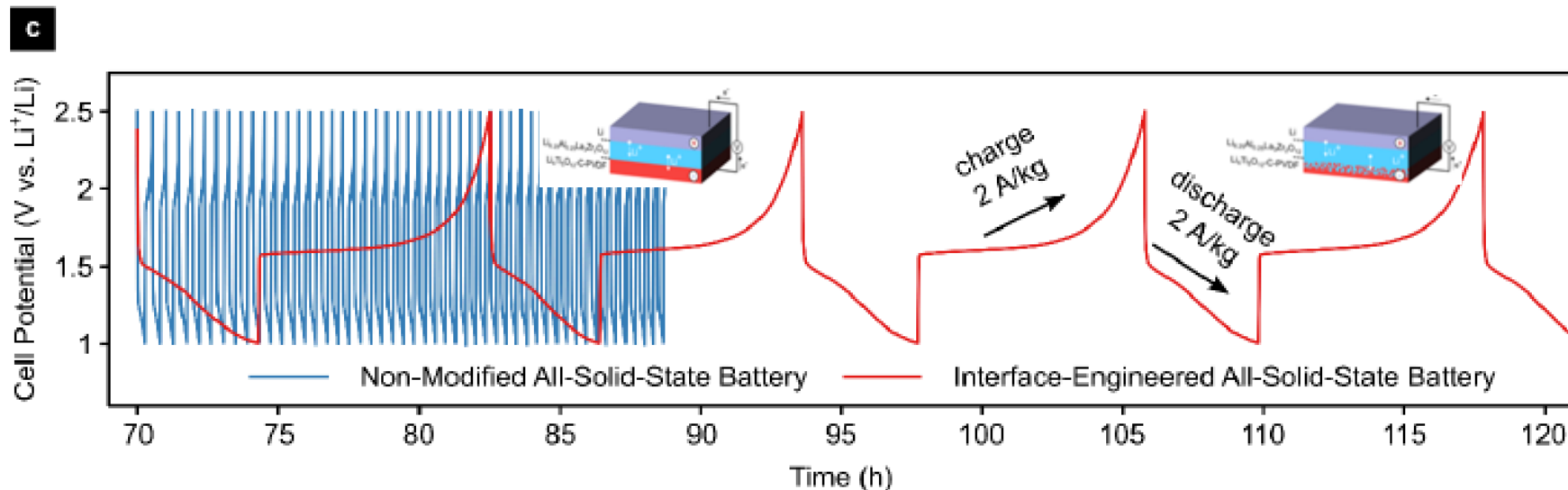
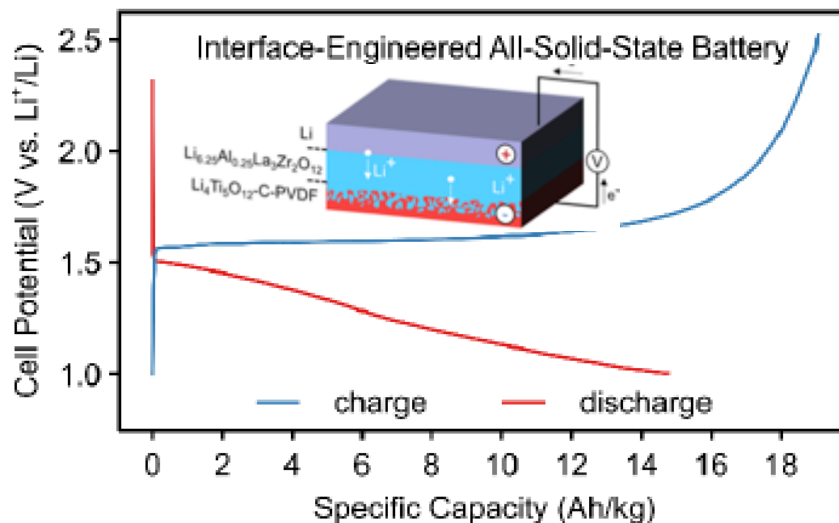
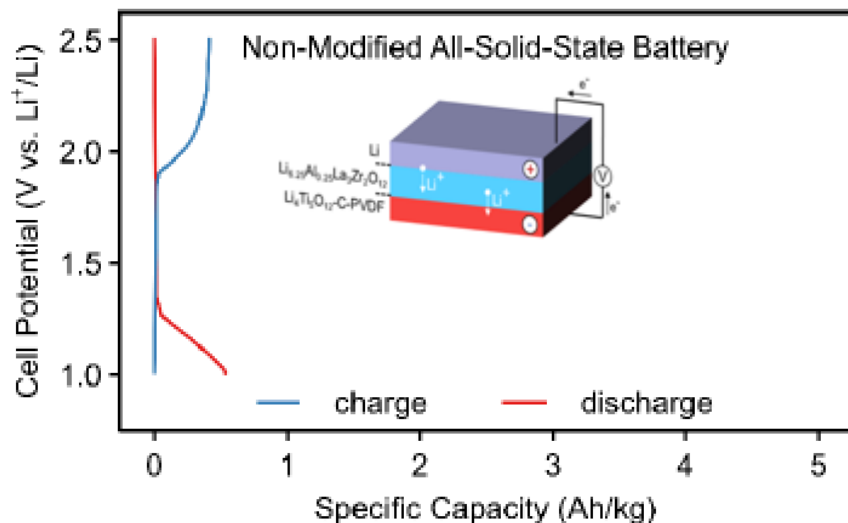
interface
merged
Li₄Ti₅O₁₂-C
anode

dense
electrolyte
Li₇La₃Zr₂O₁₂
ceramic

Model experiment:

Influence of solid-solid anode-electrolyte interface coagulation on electrochemistry?

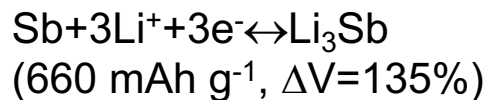
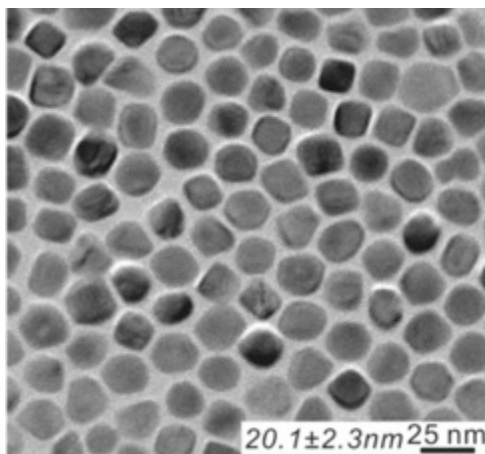
Solid Li⁺ batteries the role of ceramic/interface manufacturing



First metal oxide-based anode operated successfully in Li-Garnet battery cell.
Higher specific capacitances are reached for the interface engineered cells.

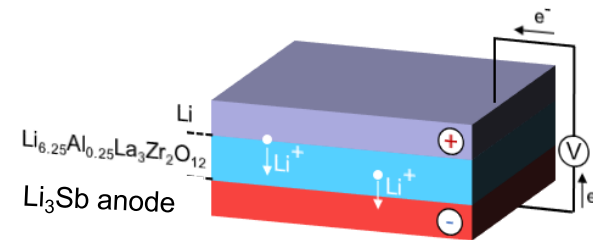
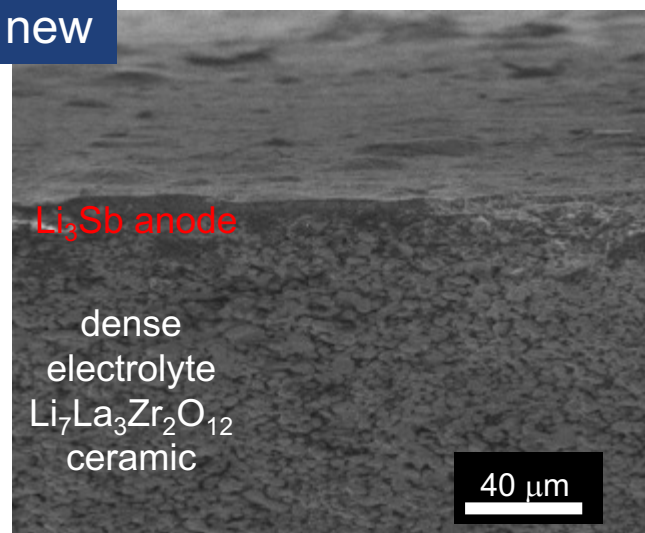
Solid State Li⁺ Garnet Electrolyte Battery with Antimony Anode

Sb nanoparticles
liquid Li standard battery

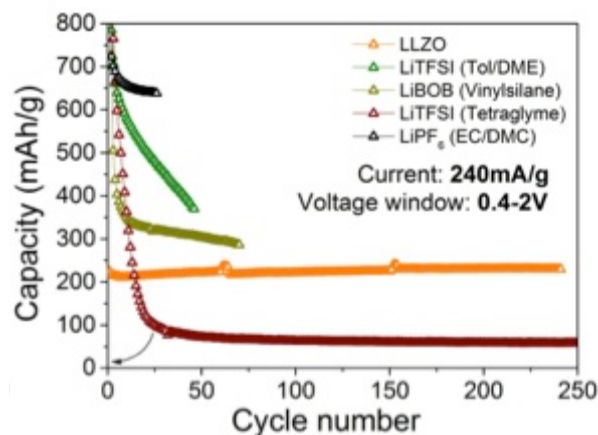


M. He, M Kovalenko et al, *Nano Letters*, 2014, 14, 1255

new



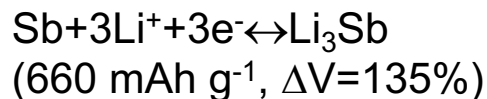
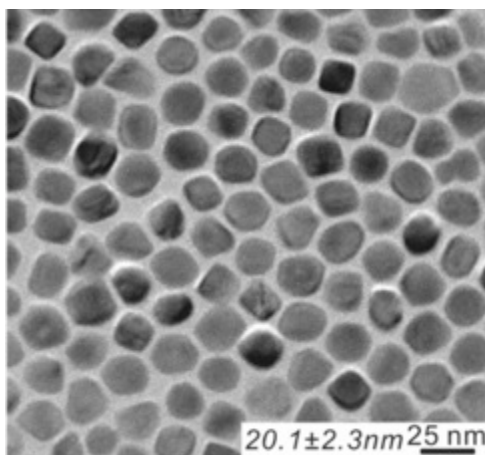
Sb anode + Li₇La₃Zr₂O₁₂
solid electrolyte ceramic
→ 230 mAh/g



High stability for solid state battery cell based on solid Li-garnet electrolyte compared to classic commercially available liquid electrolytes in batteries.

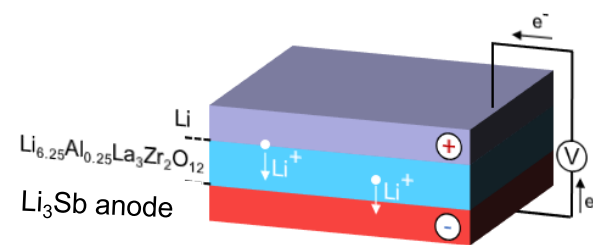
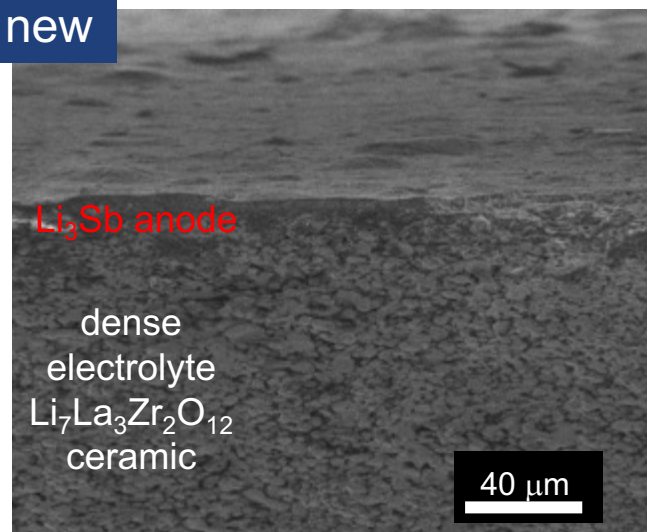
Solid State Li⁺ Garnet Electrolyte Battery with Antimony Anode

Sb nanoparticles
liquid Li standard battery

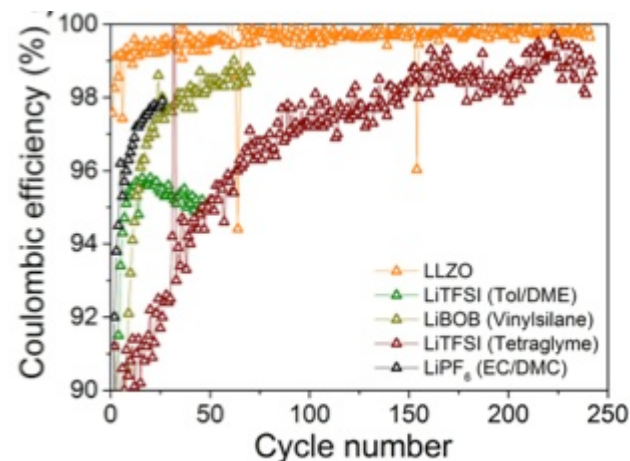
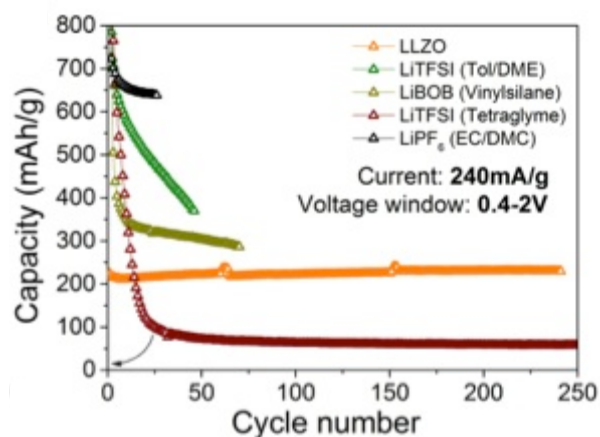


M. He, M Kovalenko et al, *Nano Letters*, **2014**, *14*, 1255

new



Sb anode + Li₇La₃Zr₂O₁₂
solid electrolyte ceramic
→ 230 mAh/g



High stability for solid state battery cell based on solid Li-garnet electrolyte compared to classic commercially available liquid type electrolytes in batteries.

What is next? A Fair and Green Solid State Li Battery



Co mines in Congo



Cathode of battery:
i.e. LiCoO_2 , LiMnNiCo (NMC) ...

90 % of today`s batteries are based on political and socio-economic critical elements such Co in their cathodes (i.e. Tesla, Duracell, ...)

→ Amnesty International: violation of human rights¹

→ U.S. trade group Electronic Industry Citizenship Coalition:
60% world share of Co Congo are problematic²

Innovation: Make a first solid state battery without politically critical elements

- 1) Amnesty International Report, Child labor behind smart phone and electric car batteries, retrieved 2016-01-19
- 2) Electronic Industry Citizenship Coalition, a practical approach to greening electronics supply chain, June 2010
- 3) African mineral Production, British Geological Survey, Retrieved 2009-0930

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Energy Storage: All Solid State Li⁺ Batteries

- Cheap Ceramic Processing: Mass Storage
- Low Temperature Microbatteries

Environmental Monitoring: CO₂ Sensing

- Novel Li⁺-Garnet-based CO₂ Sensor Architectures

Neuromorphic Computing: Memristors

- Strained Memristor Concept

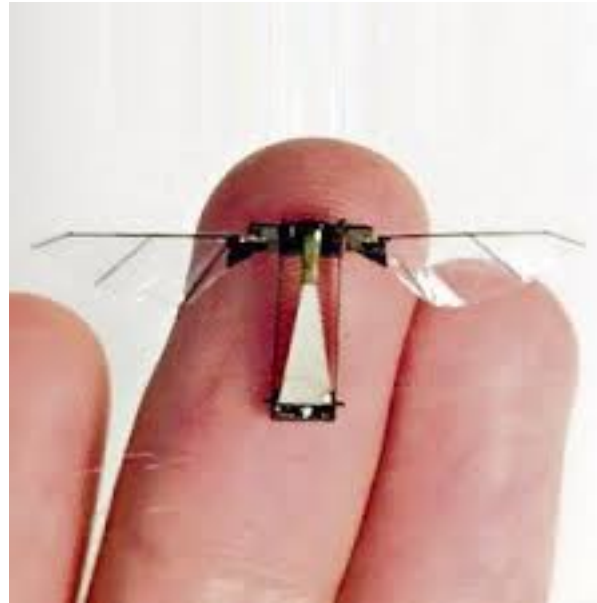
Microbattery: Energy Supply for Sensing and Transmitters



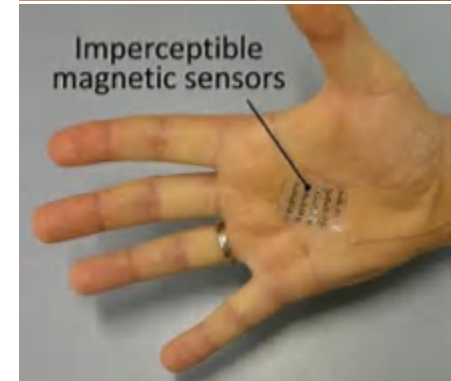
*sensing dust:
environmental monitoring*



*powered pills
controlled substance
release*



*miniaturized drones,
sensing,
transmitting devices,
reconnaissance technology*



*human
implants*



autonomous
energy
supply



“pre-
processing
sensing
data”



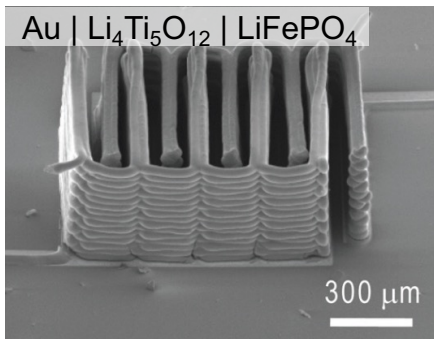
Autonomous sensors are required for future health and environmental sensing and sensing for efficient energy use:

→ thin film microbatteries required

State-of-Technology & Challenges: Thin Film Microbatteries

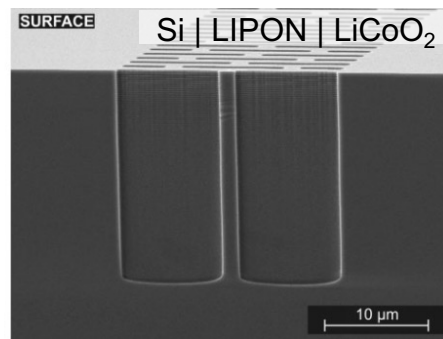
Academia: Microbattery Research

3D printed architectures



Sun, Lewis et al., *Adv. Mater.*, 25(33), 2013, 4539.

Si integrated



Notten et al., *Adv. Mater.*, 19(24), 2007, 4564.

Product: Thin Film Microbattery

Si integrated thin film battery



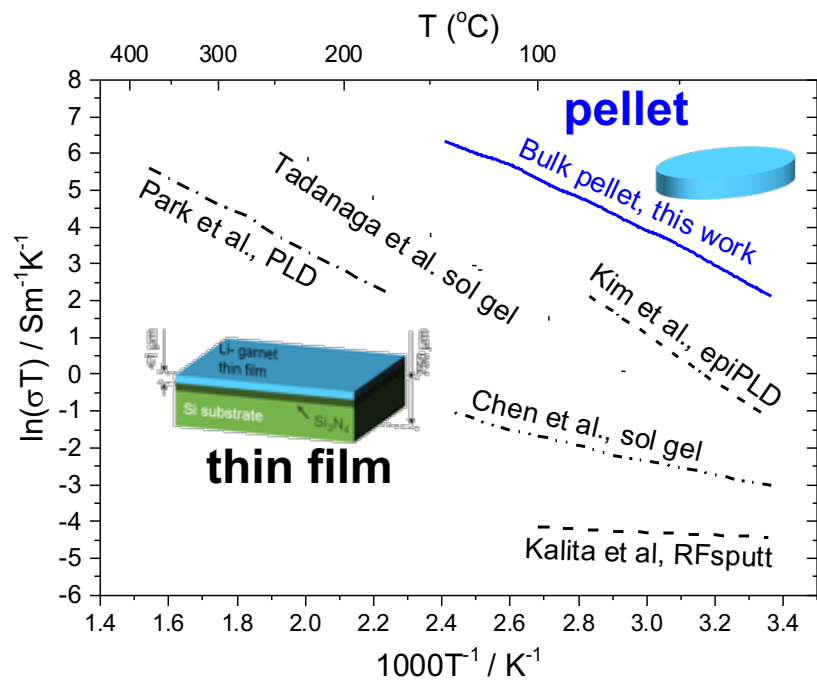
Oak Ridge "Bates" cell

Challenges

- Reduced Li conductivity electrolyte
- Limited T-operation window
- High V cathode integration challenging
- Safety & stability for high cycle life

Thin Films vs. Macro-Pellets of Li Garnet Electrolytes: $\text{Li}_7\text{La}_2\text{Zr}_3\text{O}_{12}$

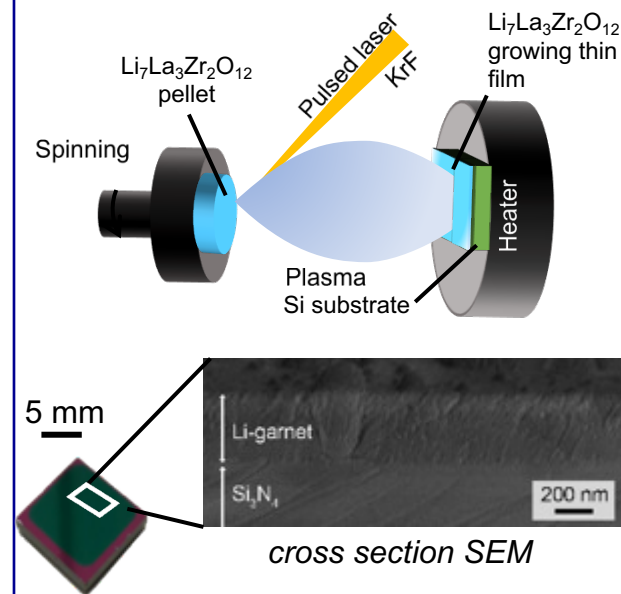
Literature: Al: $\text{Li}_7\text{La}_2\text{Zr}_3\text{O}_{12}$



Li-conductivity
variation
 10^{-7} - 10^{-3} S/cm !

- [1] Tan et al., ECS Solid State Letters 1(6), 2012.
- [2] Kim et al., Dalton Trans. 42, 2013.
- [3] Park et al., Thin Solid Films, 576, 2015.
- [4] Kalita et al., Solid State Ionics, 229, 2012.
- [5] Nong et al. Materials Letters 154: 167, 2015.
- [6] Tadanaga et al., J Power Sources, 273, 2015.
- [7] Chen et al., J Mater Chem A 2(33): 13277, 2015

Example MIT:
Pulsed Laser Deposition
 $\text{Ta}:\text{Li}_7\text{La}_2\text{Zr}_3\text{O}_{12}$



dense+crack-free electrolyte films

I Garbayo, JLM Rupp, to-be-submitted

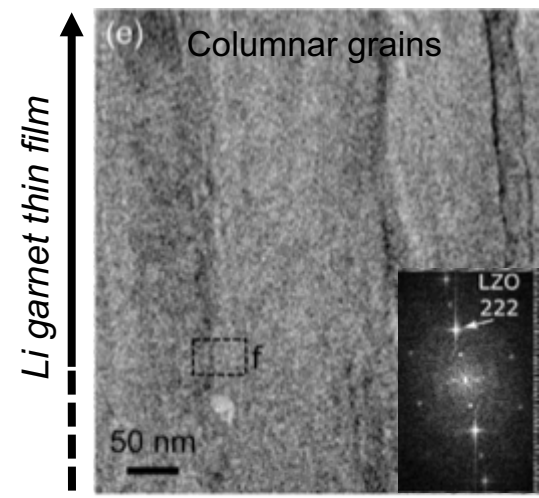
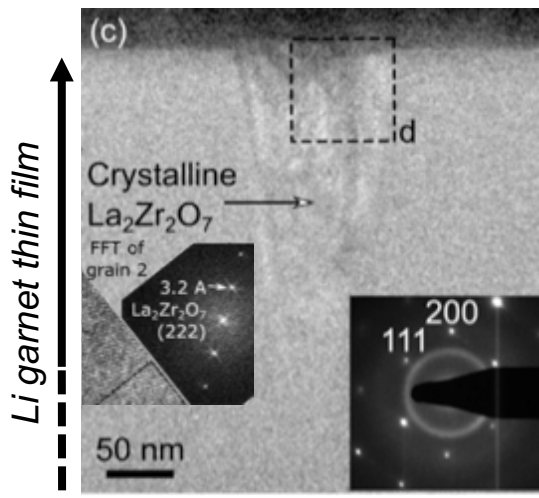
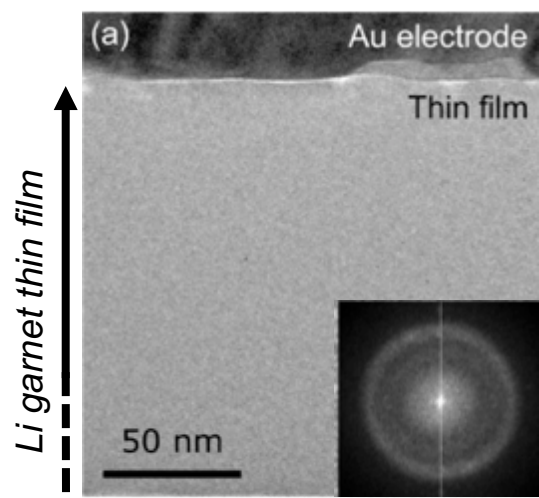
Open question for thin film electrolytes and future microbatteries:

How does processing affect the Li concentration, phase, density?

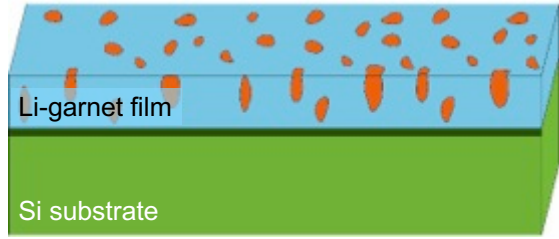
Ionic conductivity? Can we design low temperature microbattery processing?

TEM: Glassy to Crystalline Ta-Li₇La₃Zr₂O₁₂ Films

T_{dep} 300°C 500°C 750°C



Pseudo-amorphous
Li-garnet network



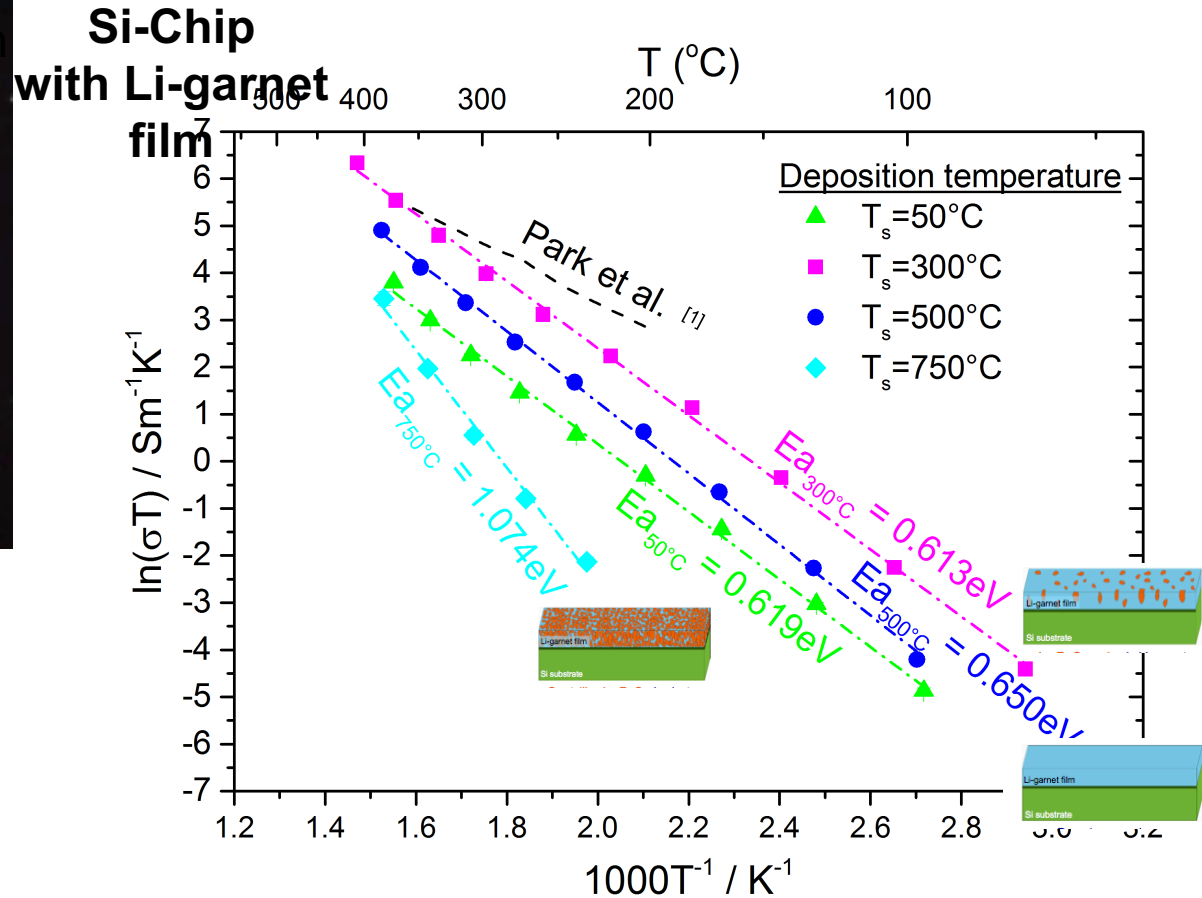
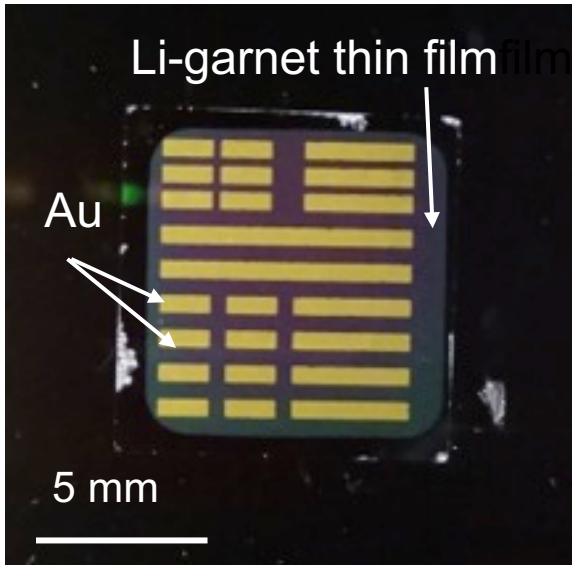
La₂Zr₂O₇ grains in Li-garnet
amorphous network



Crystalline La₂Zr₂O₇ dominates
over amorphous Li-garnet

“Glass-like” Li rich garnet films can be created: Cost reduction
→ low processing temperature → new strategy to avoid Li-dendrites

Li-transport Garnet Electrolyte Thin Films vs. Nanostructure



Highest Li^+ mobility at 300°C deposition temperature for glass-type Li garnet films.

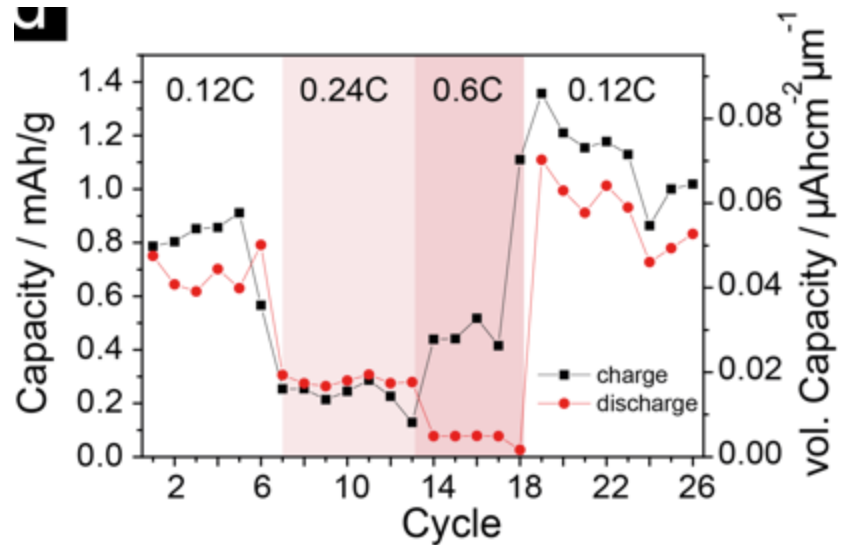
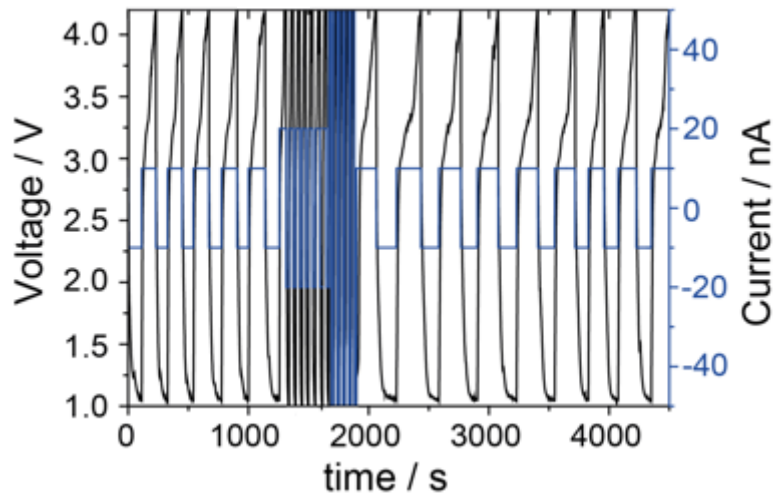
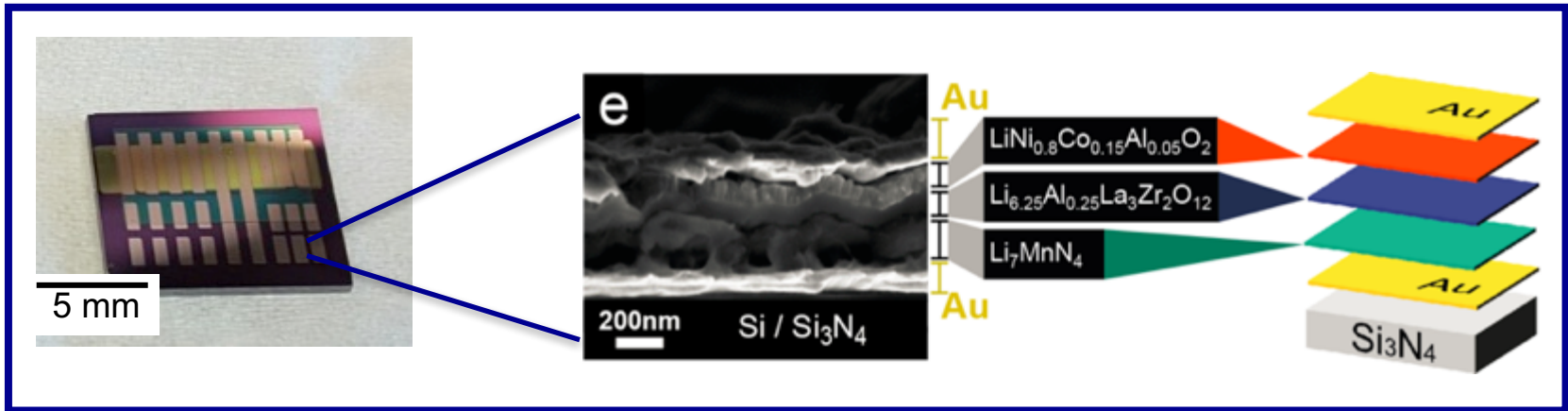
Opportunities:

- Low temperature processing
- Fast Li conductivity / increased T window

- new glass electrolytes
- unclear: integration?

[1] Park et al., Thin Solid Films, 576, 2015.

Low Temperature Processed Glassy Thin-Film Microbattery



➔ Stable Cycling Achieved for first Garnet-based All Solid State Thin-Film Microbattery. Whole cell stable in air and processed at low temperature.

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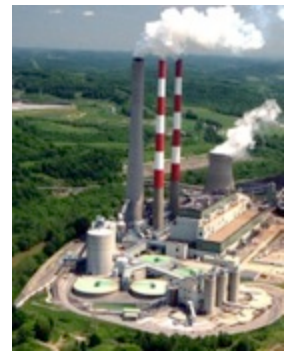
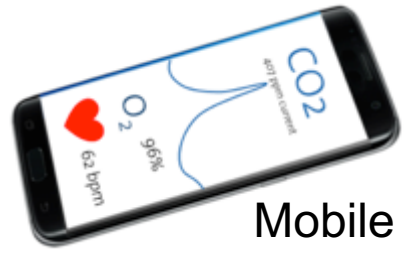
Relevance of CO₂ tracking for society and energy management



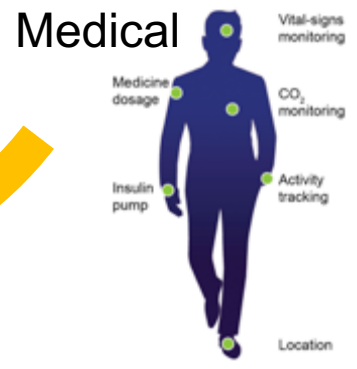
Electrochemical Sensor

Needs for products:

- Power efficient
- Small
- Low cost
- Chip integration

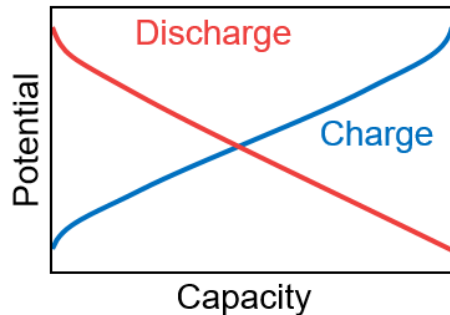
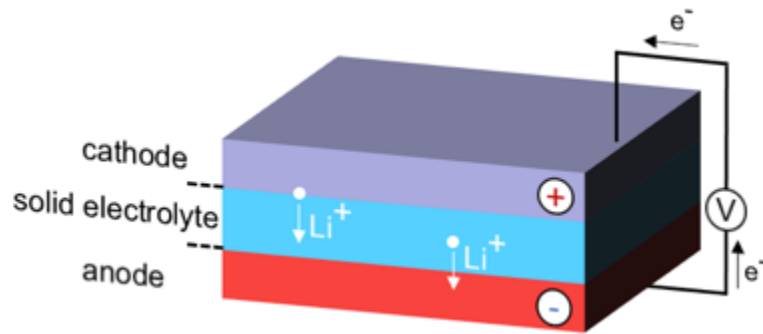


CO₂

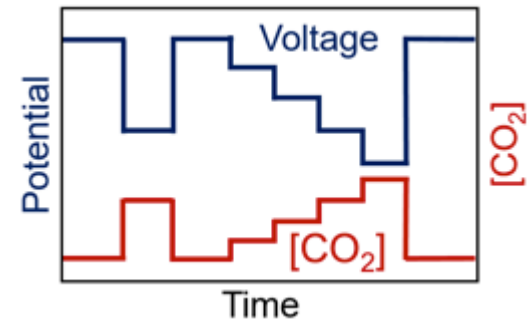
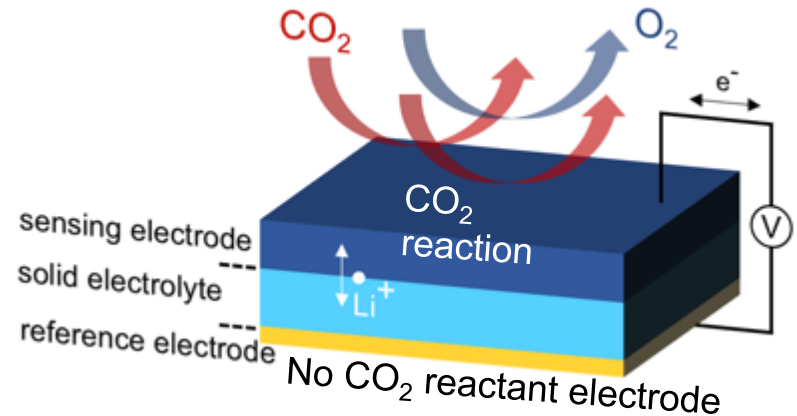


Solid State Energy Storage and Tracking Devices Based on Li^+

Energy Storage Devices



Electrochemical CO_2 sensors

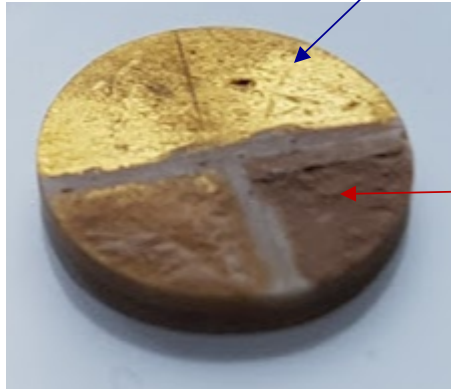
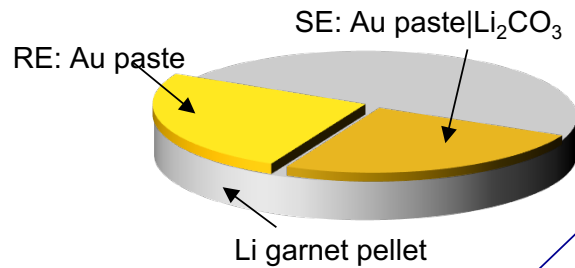


Replacing liquids by solid state electrolytes improves safety and stability

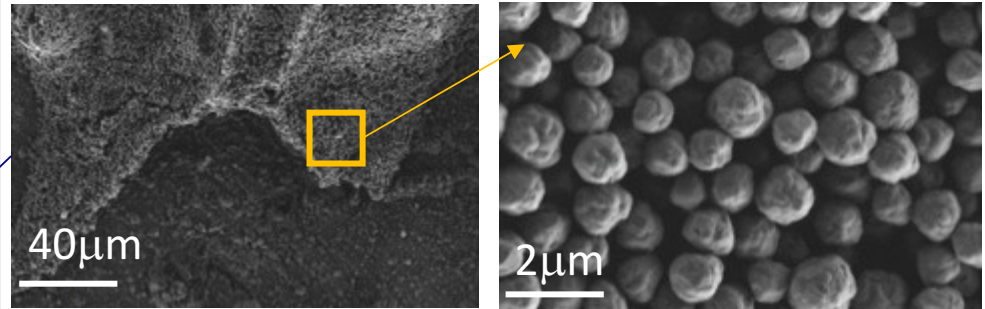
Challenges: fast, dense and thin Li-electrolytes needed with low interfacial resistances towards electrodes !

Li-Garnet based in-plane structure for CO₂ sensing

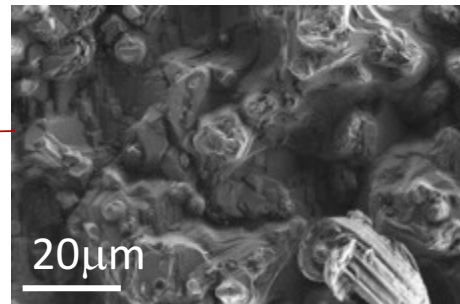
In-plane pellet based cell



Reference electrode Au paste



Auxiliary phase – Li₂CO₃+Au

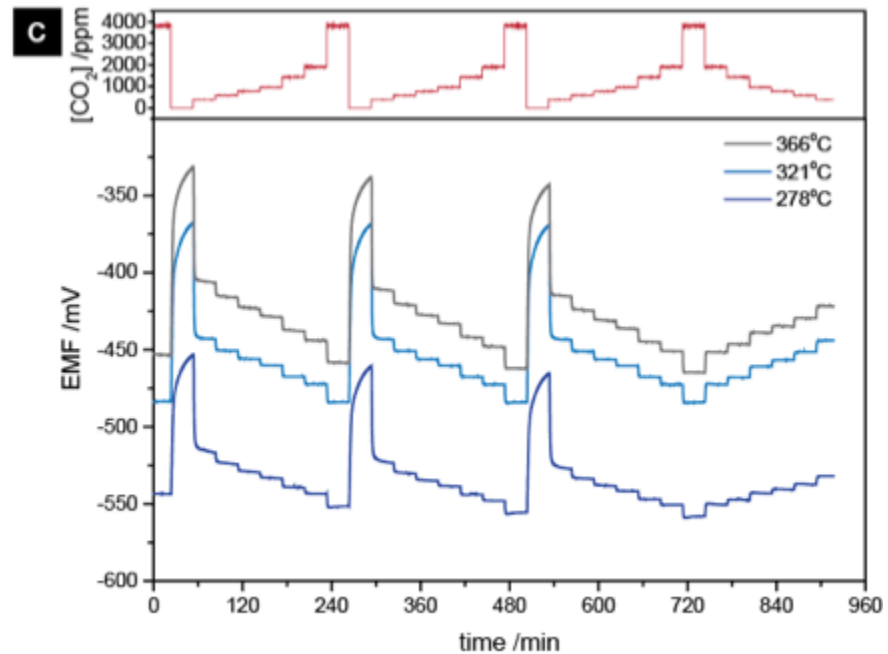
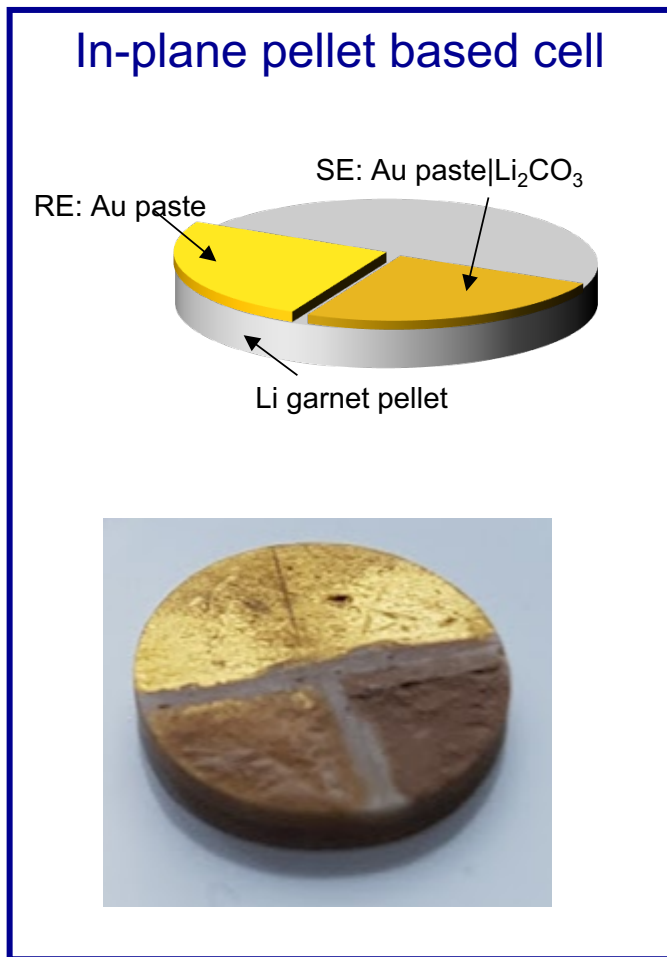


Porous morphology with access to the electrolyte

Good contact with LLZO

Successful integration of porous reference electrode and the auxiliary phase confirmed with SEM

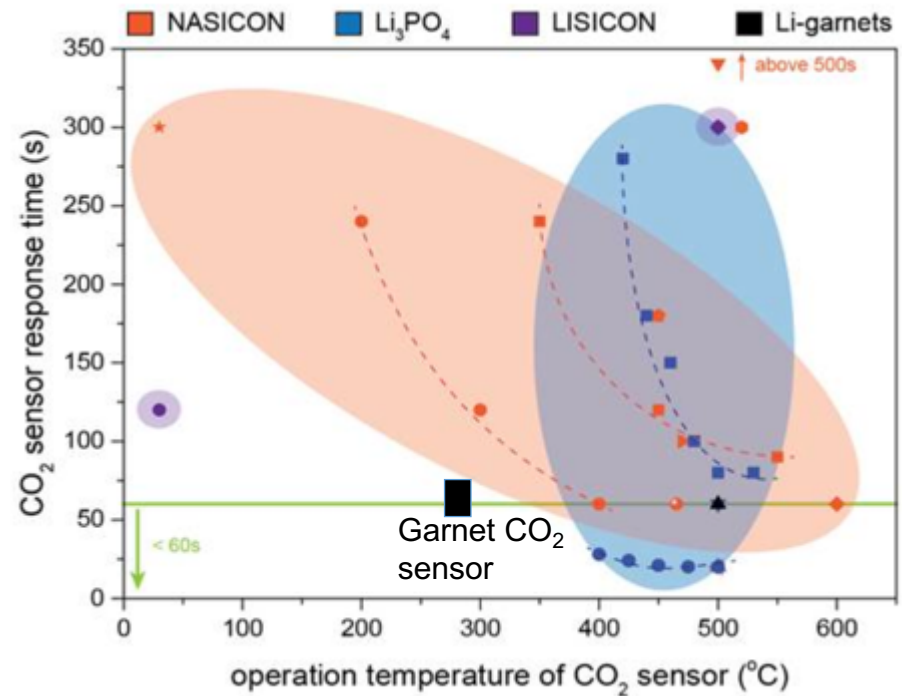
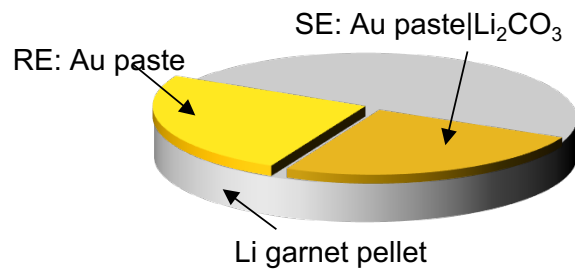
Li-Garnet based in-plane structure for CO₂ sensing



First successful CO₂ sensor device with Li₇La₃Zr₂O₁₂-based solid electrolyte
EMF: Sensor detects changes in [CO₂], stable cyclability in a range 400-4000ppm
Sensitivity: ~32 mV **Response time:** <1 min at 280°C

Novel Li-Garnet CO₂ Sensors based on Battery Technology

In-plane pellet based cell



Comparison to state-of-technology shows fastest response time < 60sec at lowest temperature >300°C for newly proposed CO₂ Sensors based on Li₇La₃Zr₂O_{12-d}

Outline

Energy Storage: All Solid State Li⁺ Batteries

- Cheap Ceramic Processing: Mass Storage
- Low Temperature Microbatteries

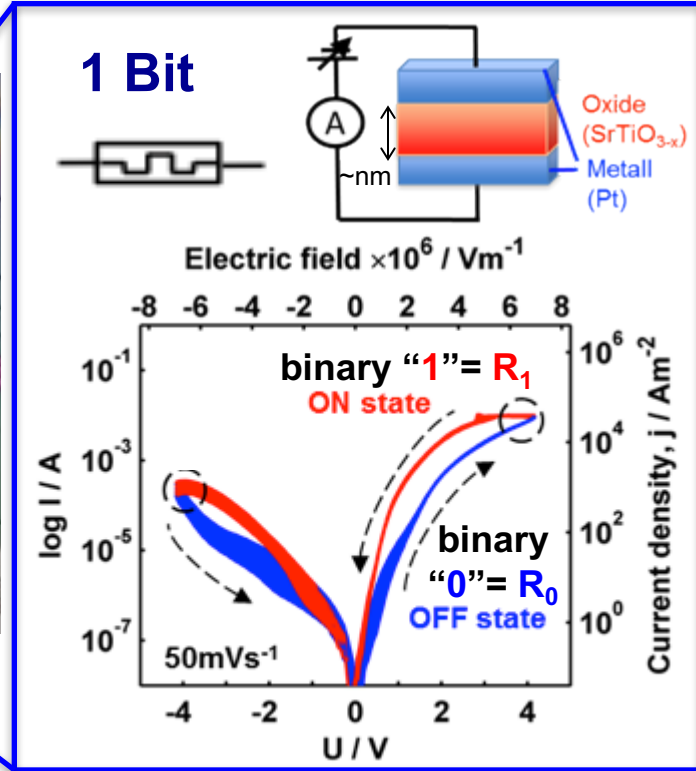
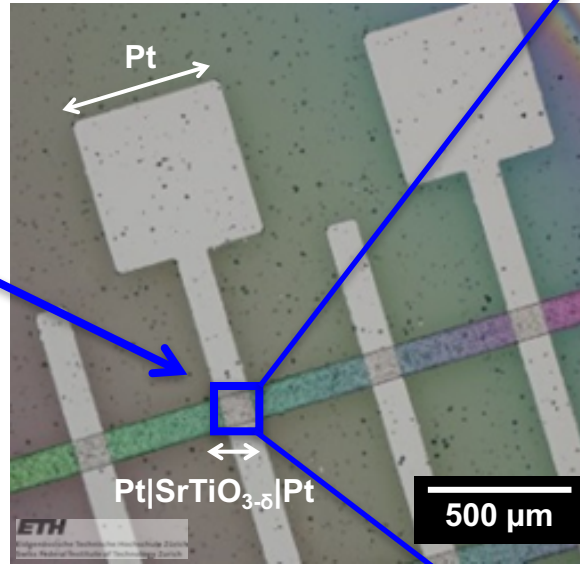
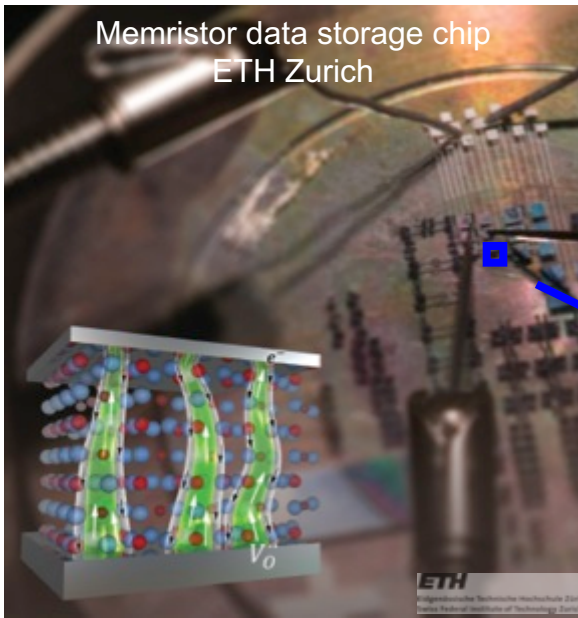
Environmental Monitoring: CO₂ Sensing

- Novel Li⁺-Garnet-based CO₂ Sensor Architectures

Neuromorphic Computing: Memristors

- Strained Memristor Concept

What is a Memristor / Resistive Switch?



Example: first Pt-SrTiO_{3-δ}-Pt-based memristor cross-bar arrays^{1,3}

Memristor = “Memory + Resistor“: the 4th basic circuit element

Potential application: data storage

Young field: active start 2008^{7,8}

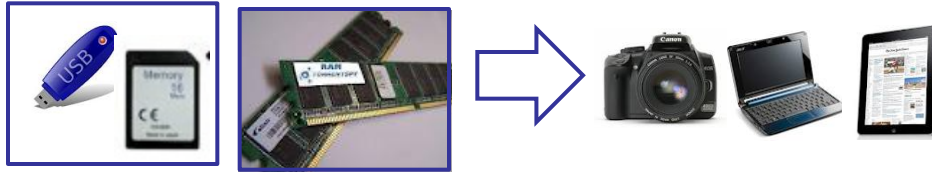
→ driven by electrical engineers

Team: oxide defect kinetic to device performances described for memristors¹⁻⁶ + new strained material building blocks as bit storage architectures⁴

1) Messerschmitt F, Rupp JLM, Advanced Functional Materials, 24, 2014
 2) Schweiger S, et al. Rupp JLM. ACS Nano, 8, 2014
 3) Messerschmitt F, Kubicek M, Rupp JLM, Advanced Functional Materials, 2015
 4) Schweiger S, Bowman W, Aschauer U, Rupp JLM, Advanced Materials, 2017

5) Schweiger et al. Rupp JLM, patent WO2014170023, 2014
 6) Kubicek M, et al. Rupp JLM, ACS Nano, 2015
 7) Yang et al. DB Strukov Nature Nanotechnology 3, 2008
 8) Waser et al., Advanced Functional Materials, 21, 2009

Memristor for Binary Information Storage

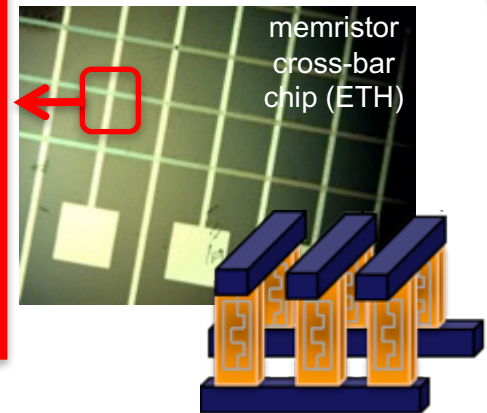
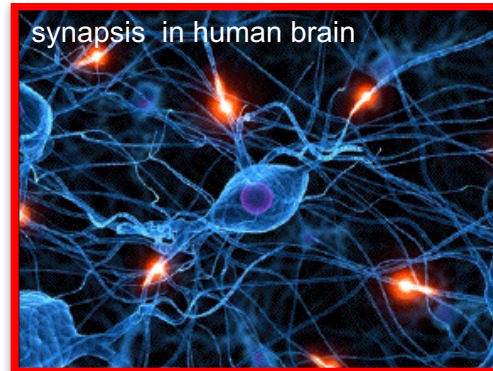


memristor computer storage:
Hewlett Packard

Ref. 1,2	Memristor	Flash	DRAM	FeRAM
write time (ns)	5	1000	10	10
write operation (V)	<1.5	15	2.5	1.5
retention (yrs)	>10	>10	64ms	>10
write cycles	10^{16}	10^5	10^{16}	10^{14}
smallest feature size F (nm)	25	36	50	180
cell area, F ²	4	5	6	22

Vision: Memristive Logics for Neuromorphic Computing

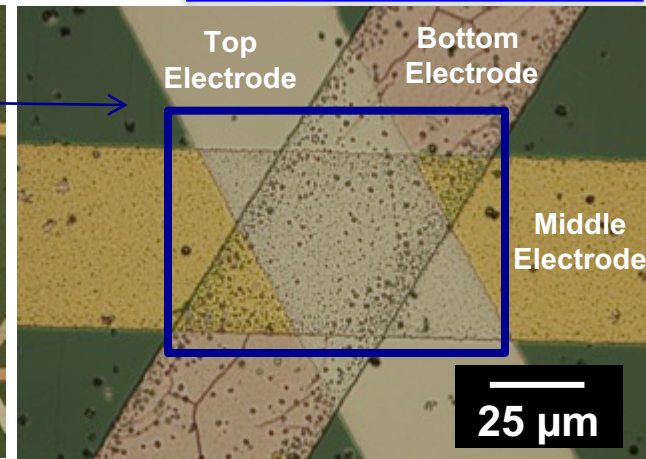
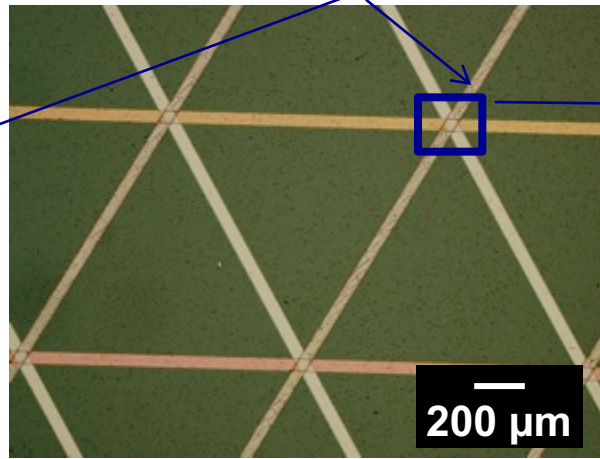
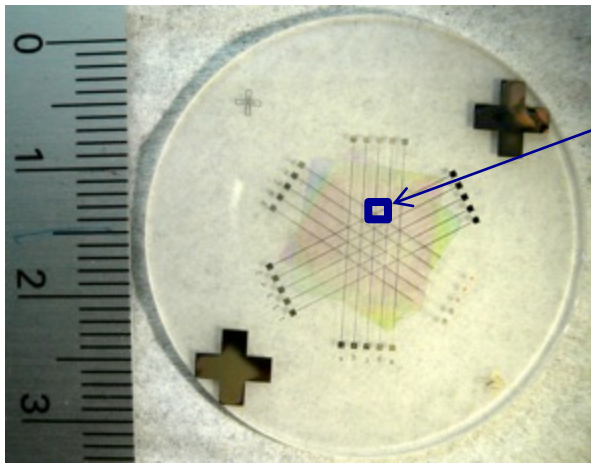
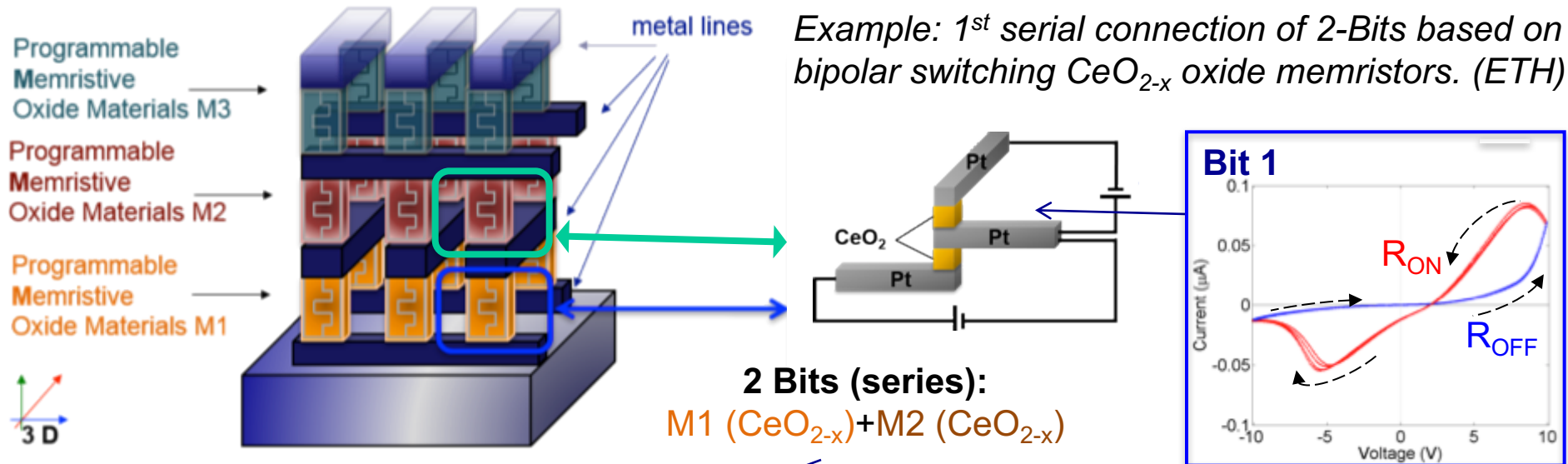
- synapsis (brain) ~ memristor bits (chip)
- similar density $10^{10}/\text{cm}^3$
- ionically controlled hysteretic response (e.g. synaptic time spike responses)
- multi-level: non binary-response



SNSF (ERC) Starting Grant, JLM Rupp 2015-2020

Material challenges: Defect chemical descriptions? Surface vs. bulk kinetics? Best oxide architecture? → base of memristor hardware

Let's design First Oxide-based Memristive Logics

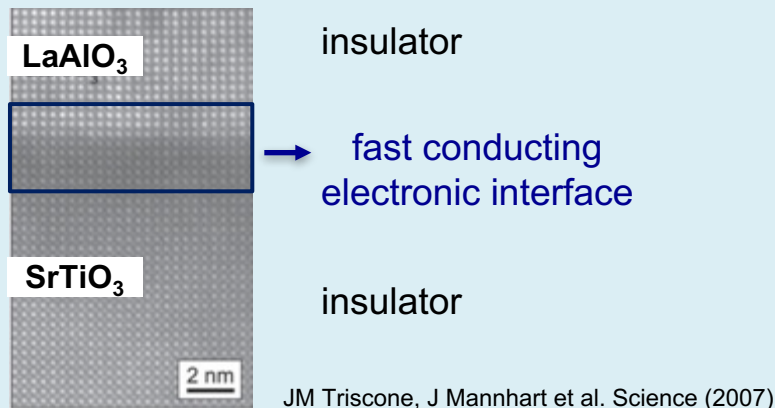


Make and study serial connections of the resistive switches
 Material engineering of new ionic controlled oxide computing hardware beyond binary.

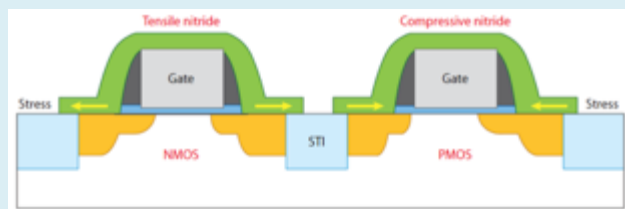
State-of-the-art: Altering Strain Fields in “Electronics” and “Ionics”?

Electronics

Electronic heterostructure oxide as building blocks for devices



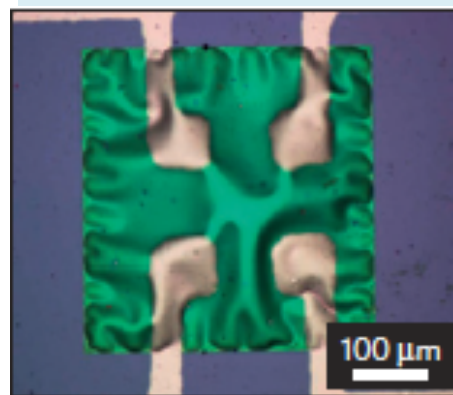
Strained Transistor



T Ghani, Intel Logic, www.intel.com 2009

Ionics

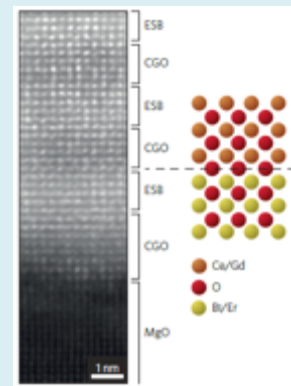
Strain-ionic defect interaction: micro-devices



Y Shi et al. and JLM Rupp, Nature Materials (2015)

Controlling strain patterns to modify transport

Ionic heterostructures

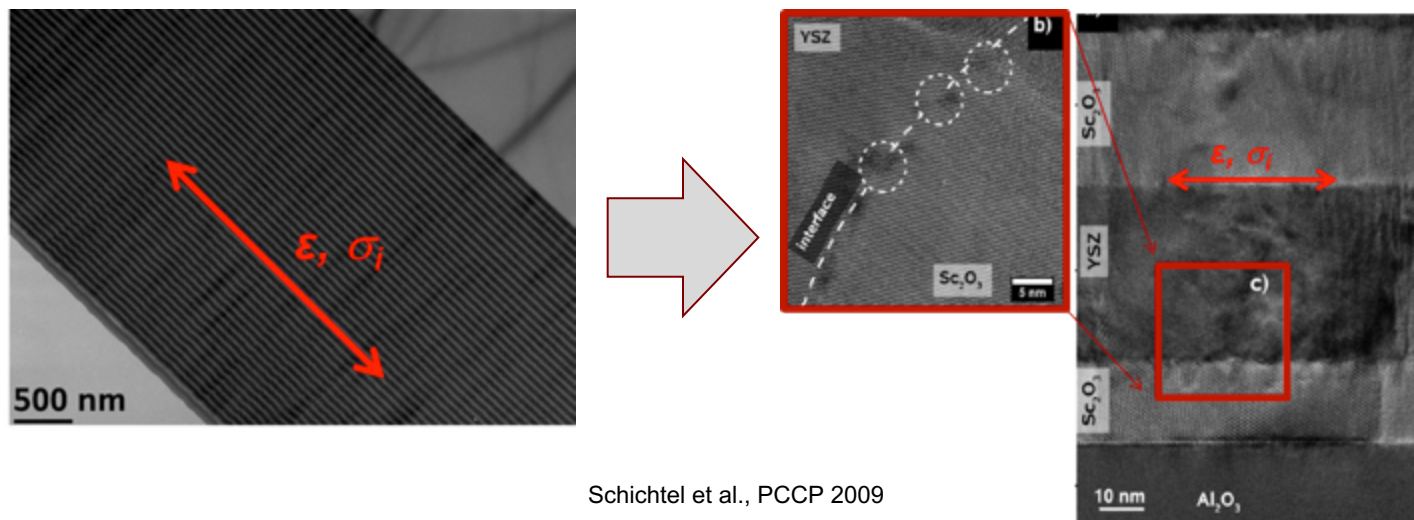


S Schweiger et al. JLM Rupp, ACS Nano (2014)
S Schweiger et al. JLM Rupp, Advanced Materials (2016)
Sata, Maier et al., Nature (2000)
Sanna, Esposito et al., Prys Nat Mat (2015)
Song, Gregori, Maier et al., APL Mat (2014)
Schichtel, Korte, Janek, PCCP (2009)
Korte, Janek et al., PCCP (2014)
Perkins, Kilner, McComb et al., AFM (2010)

Strain and space charges at interfaces

Strained oxide materials and concepts are needed for novel ionic devices !

What is known about strained oxide ionic heterostructures?



Schichtel et al., PCCP 2009

Changed conductivity σ_i due to strained multilayer ϵ interfaces
 No device integration so far!

Material	T(K)	Relative change in conductivity	Remarks	Authors
YSZ/Y ₂ O ₃	623 - 973	10 ¹	Multilayer	Korte et al.
Sm:CeO ₂ /YSZ	673 - 1073	10 ¹	Multilayer	Sanna et al.
YSZ/Gd ₂ Zr ₂ O ₇	550 - 750	10 ²	Multilayer	Li et al.
Gd:CeO ₂ on MgO/STO	723 - 1123	10 ¹ -10 ²	Thin film	Kant et al.
YSZ on MgO	423 - 773	10 ³	Thin film	Sillassen et al.

Reviews:

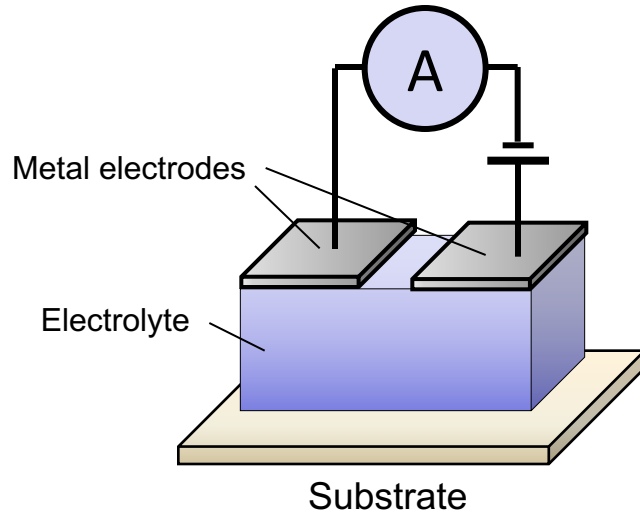
JLM Rupp, SSI 2012
 B Yildiz, MRS Bulletin 2014

Theory:

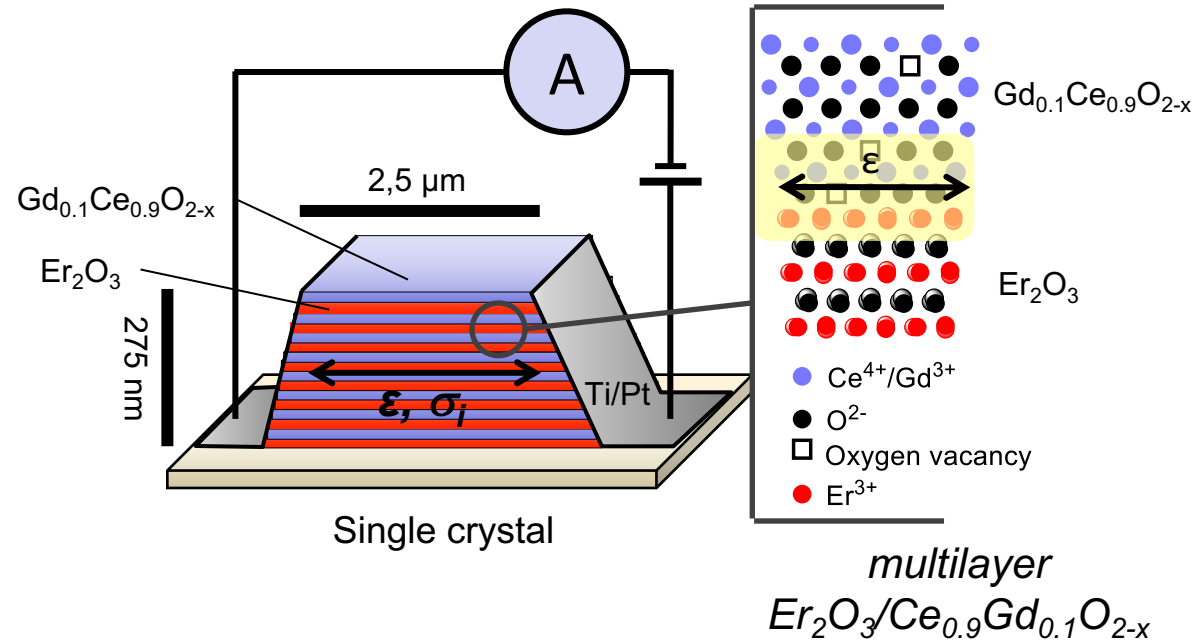
A Kushima and B Yildiz, J of Mat Chem 2010
 RA DeSouza et al. PRL, 2013

Strained multilayers - alternative to doping in resistive switches?

State-of-the-art



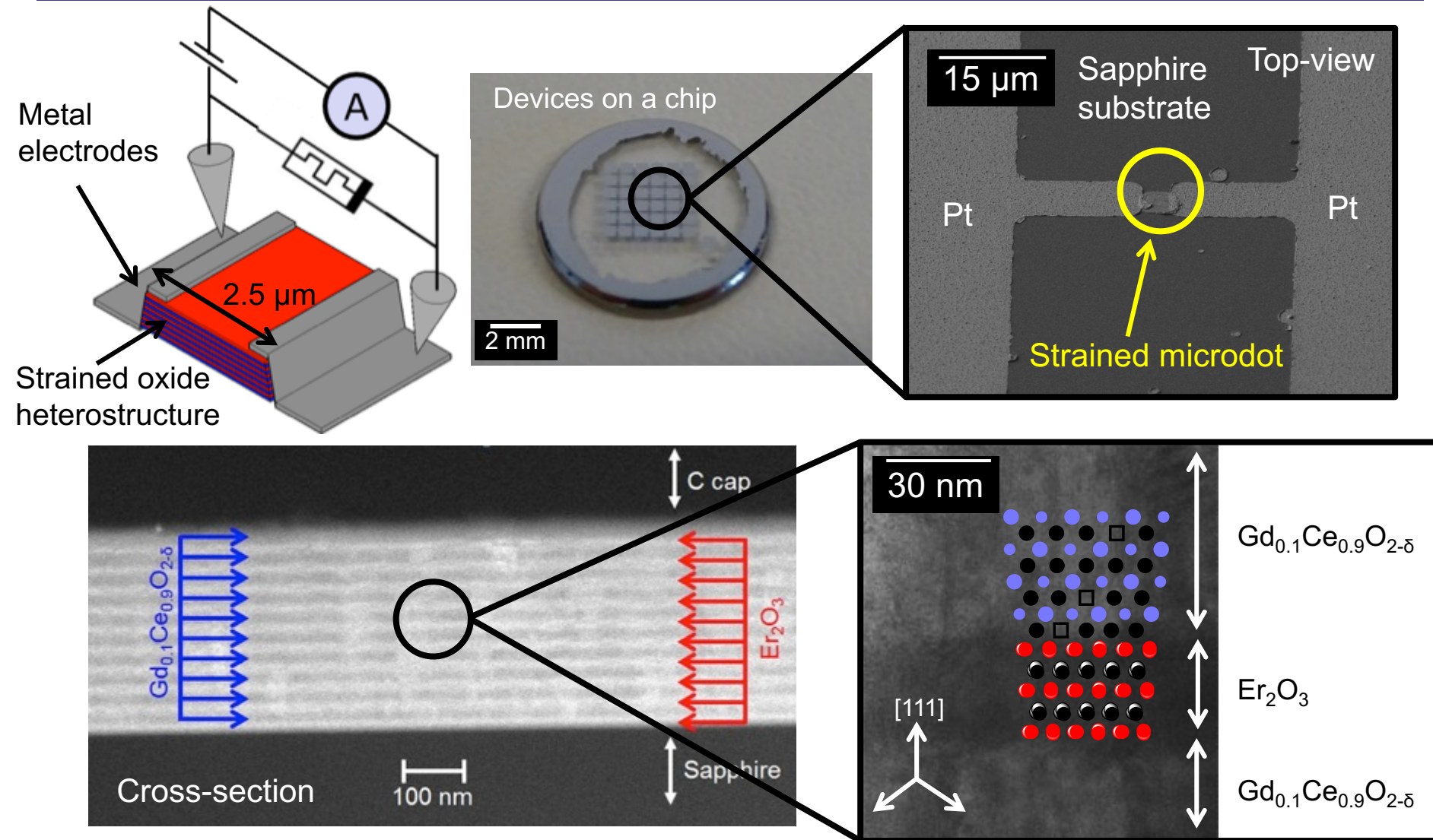
New micro-dot electrode concept



Change in classic top-electrode contacting: sideways electrode micro-dot contacting for strained oxides?

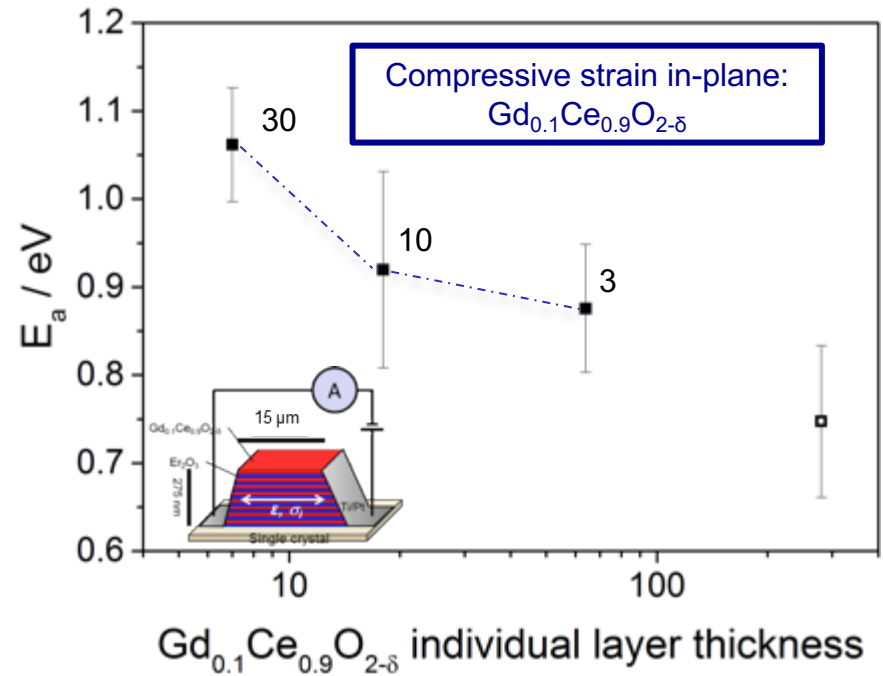
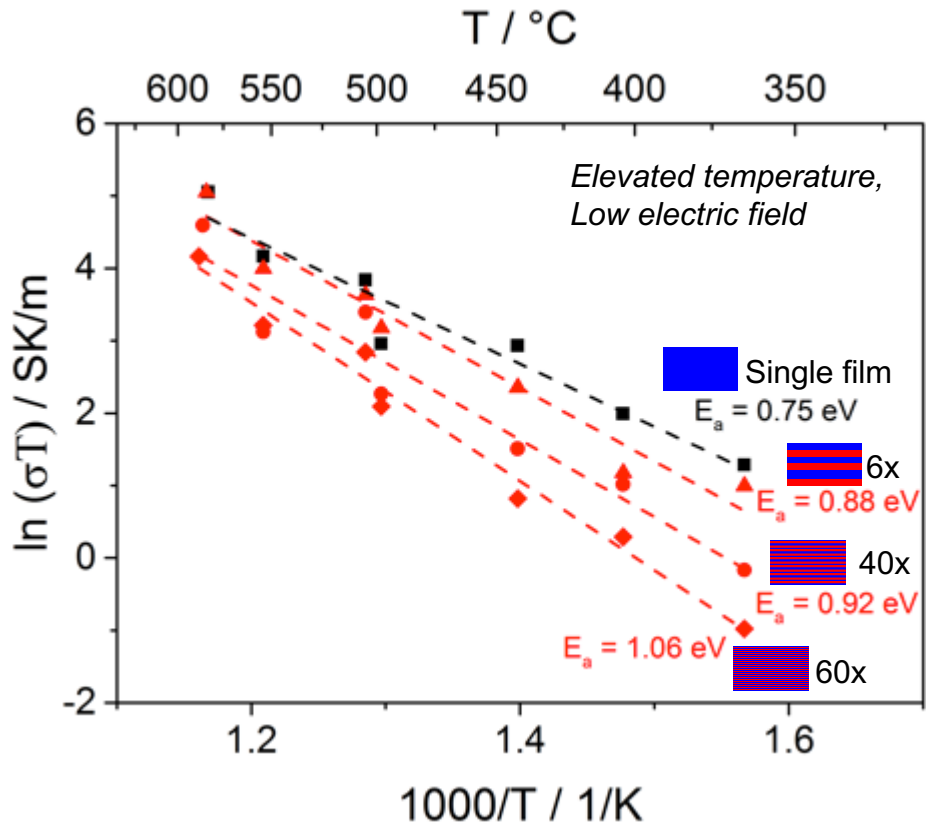
- Replace top-electrode contacting of single oxide films
- Electric conductivity of multilayers is variable by far more than pure monolayer characteristics. No device integration so far.

Strained ionic heterostructure microdots



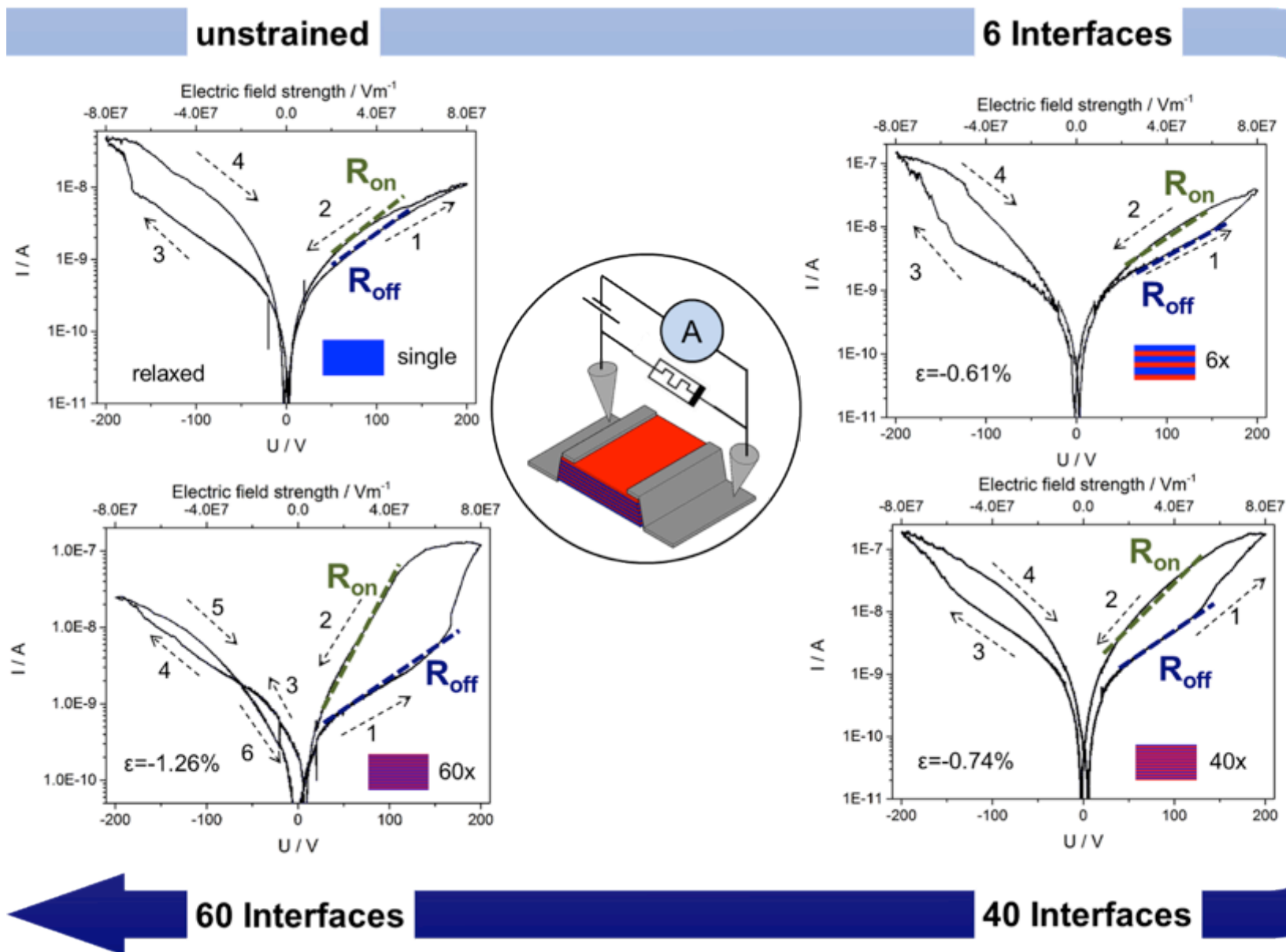
Successful manufacturing of strained multilayer microdot arrays for first devices.

Transport properties of microdot device

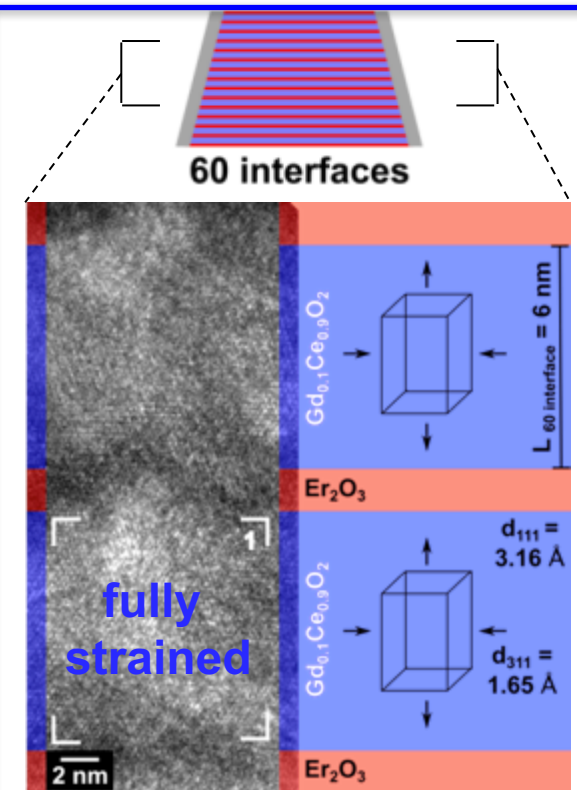
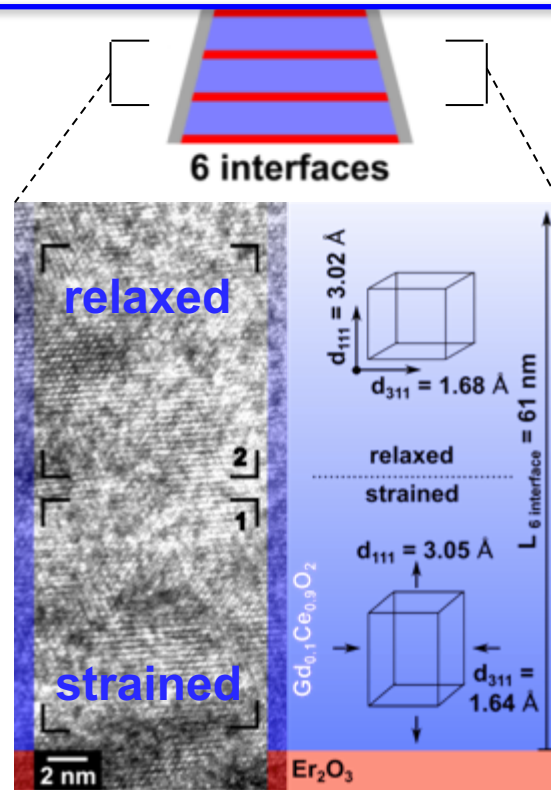
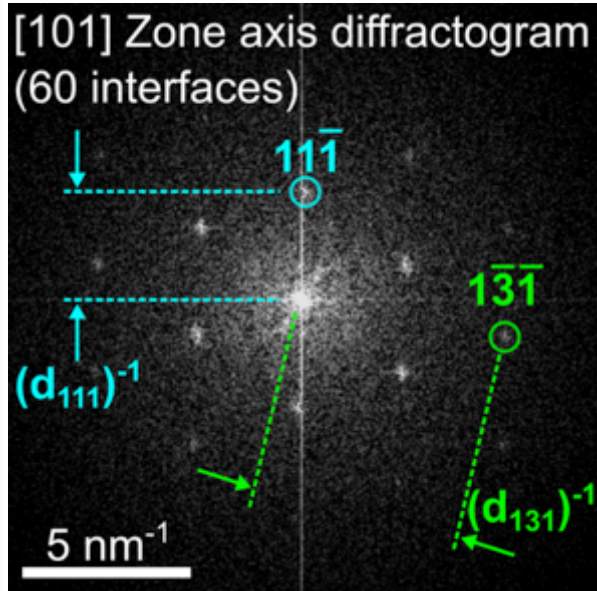


- Compressive in-plane strain of **-1.16%** in conducting phase.
- Decreasing the film thickness from 280 nm to 7 nm (increasing number of interfaces) → **increase of $E_a = \Delta 0.31$ eV.**

Influence of strain on memristance: Cyclic voltammetry



Heterostructure oxide thin films: TEM investigations



Strain relaxation in the Gd_{0.1}Ce_{0.9}O_{2-δ} layers for 6 interfaces

- in-plane compression
- out-of-plane tension

$$\Delta = 0.04 \text{ \AA}$$

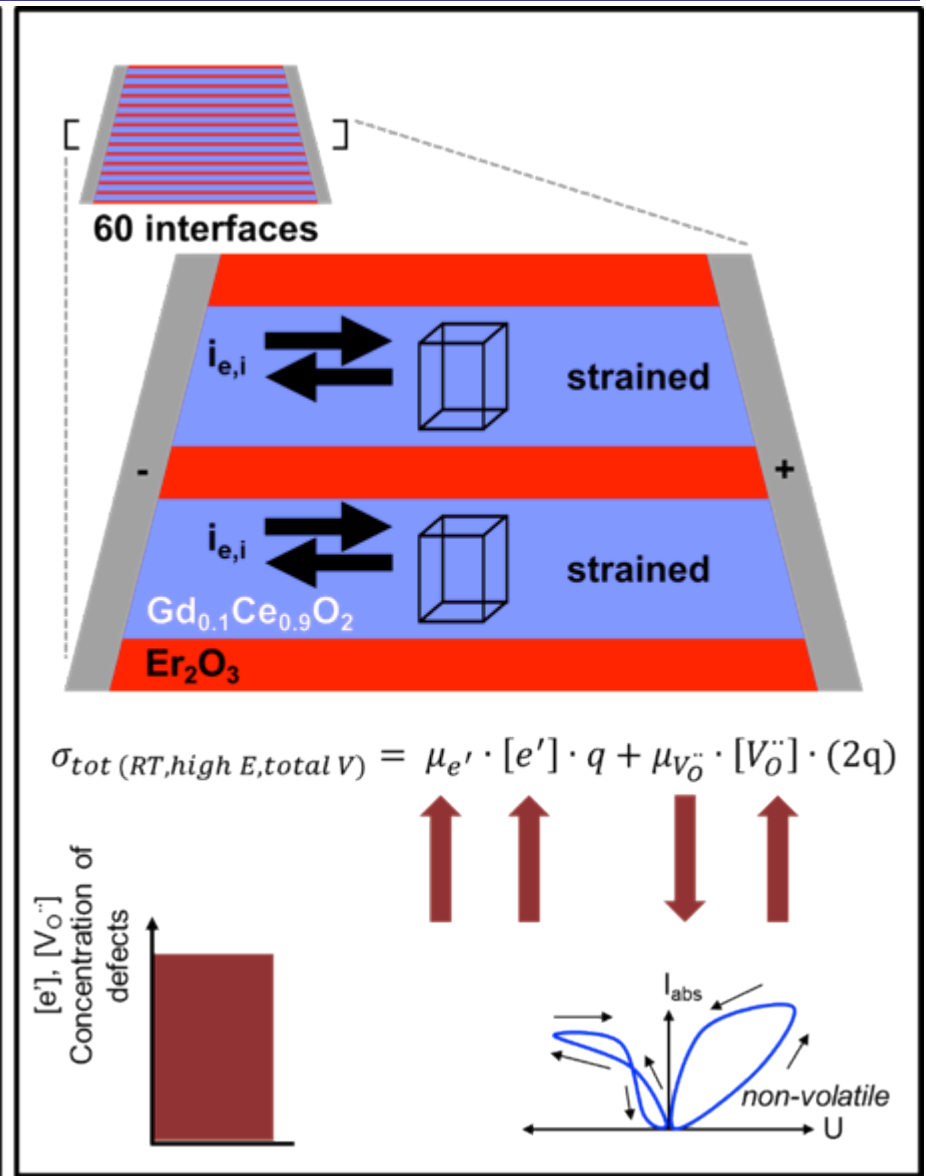
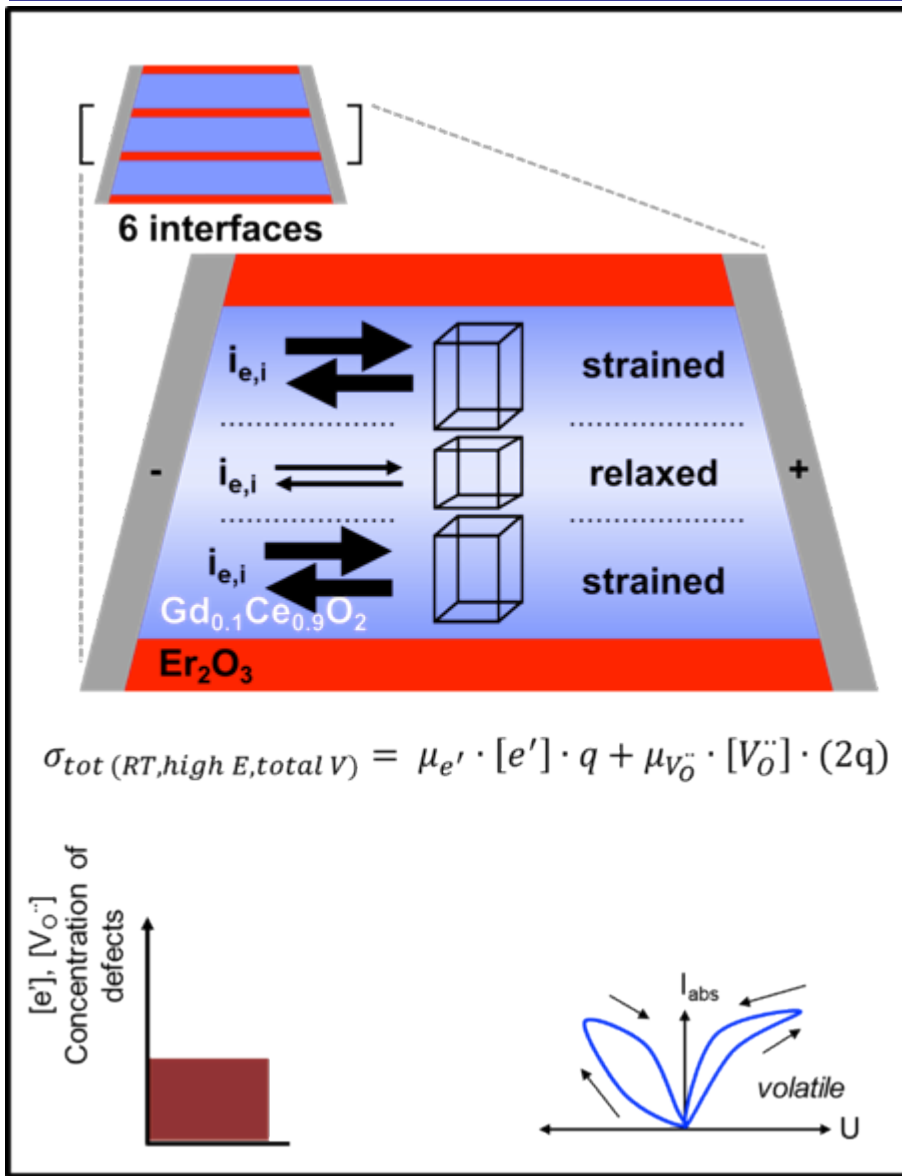
$$\Delta = 0.03 \text{ \AA}$$

Fully strained

Gd_{0.1}Ce_{0.9}O_{2-δ} layers for 60 interfaces no relaxation,
 $\Delta_{\text{out-of-plane}} = 0.14 \text{ \AA}$

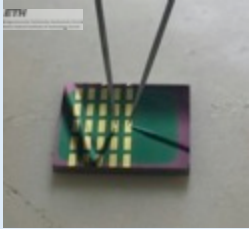
Increasing anisotropy with decreasing Gd_{0.1}Ce_{0.9}O_{2-δ} layer thickness

The strained memristor: defect transport model



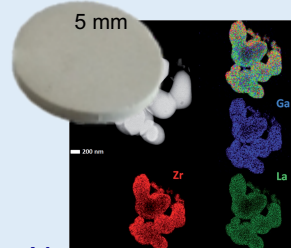
Rupp group: Solid State Materials for Energy & Information Devices

Novel All Solid State Li Batteries + CO₂ Environmental Trackers



CO₂ environmental + medical sensing based on Li⁺

J Van den Broek et al. JLM Rupp, Advanced Energy Materials, 2016
C Haensel et al. JLM Rupp, Nanoscale 2016
M Rawlance et al. JLM Rupp, Nanoscale 2016
S Afyon et al. JLM Rupp, J of Materials Chemistry 2015



Novel solid state Li battery with high capacities

Ionic memory and computing logics: memristors



information storage + non-binary computing

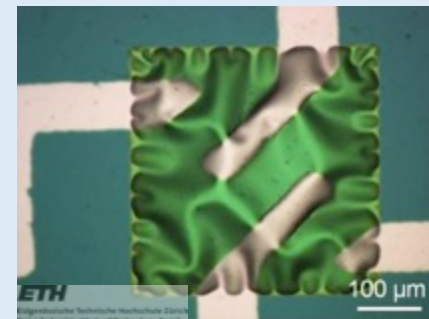
S Schweiger et al. JLM Rupp, Advanced Materials 2017
M Kubicek, F Messerschmitt et al JLM Rupp, ACS Nano 9, 2015
F Messerschmitt, et al. JLM Rupp, Adv Funct Mater. 25, 2015
F Messerschmitt, et al. JLM Rupp, Adv Funct Mater. 24, 2014

Renewable Solar Fuels (Hydrocarbons) | Micro-energy convertor designs



clean energy storage with no material's capacity limitations

AH Bork et al., JLM Rupp, Advanced Energy Materials, 2016
AH Bork, et al. JLM. Rupp, J. of Mat Chem A, 2015



grid-independent energy conversion for autonomous electronics

Y Shi, AH Bork, S Schweiger, JLM Rupp, Nature Materials 14, 2015
Y Shi et al. JLM Rupp, Adv Mat, 2016



Electrochemical Materials MIT USA

Memristive Information Storage & Logics



Dr. Andreas
Nenning



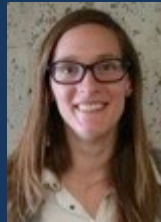
Dr. Felix
Messerschmitt



Dr. Juan Carlos
Gonzalez Rosillo



Thomas
Defferriere



Eva
Sediva



Prof. Dr.
Jennifer Rupp

Fuel Cells



Philipp Simons

Solid State Li-Ion Batteries + Sensors



Dr. Michal
Struzik



Michael
Rawlence



Reto
Pfenninger

Solar-to-Fuel Materials



Dr. Alexander
Bork



Dr. Kunjoong
Kim

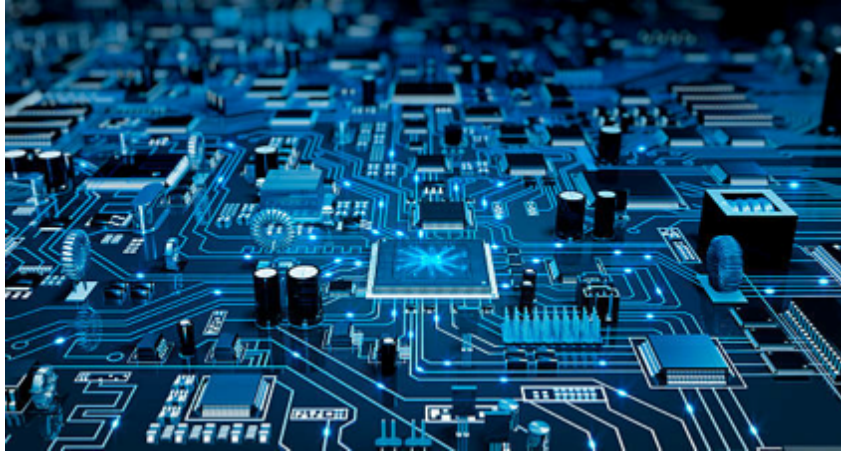


Dr. Alfonso
Carrillo

What is next ? Prof Rupp`s dream list



*Socio-economic
acceptable energy
storage: Fair batteries*



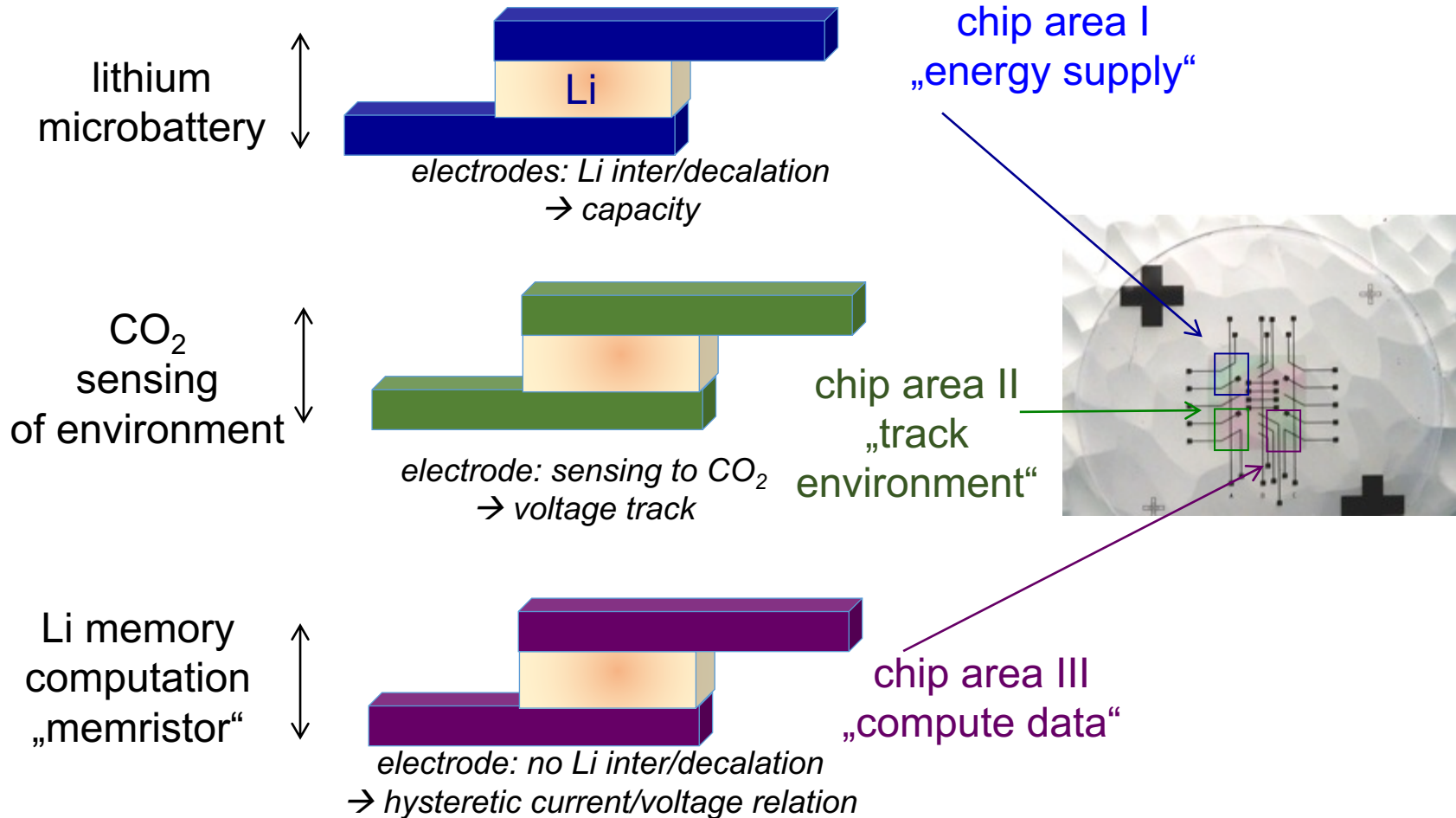
New Li circuits: storage, sensing, data computing



*Solar fuel + plastics
(cars, ...)*

- Make 1st Solid State Fair Trade Battery Concepts
- Lithium Oxide Circuits for Energy Storage, Sensing and Computing Units: Lithium are the next electrons 😊
- Make fully Glass-Type Batteries
- Power Efficiently Human Implants

What's next? "Lithionic Emulator Chips"



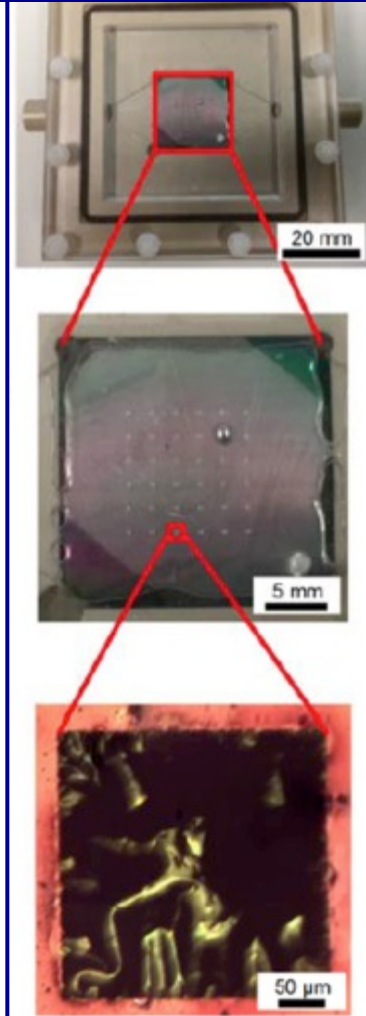
One Li-electrolyte thin film material enables by electrode choice superior functions:
→ Use Li motion to sense, store energy and compute data

A Sugar Fuel Cell to Power Implants in Humans

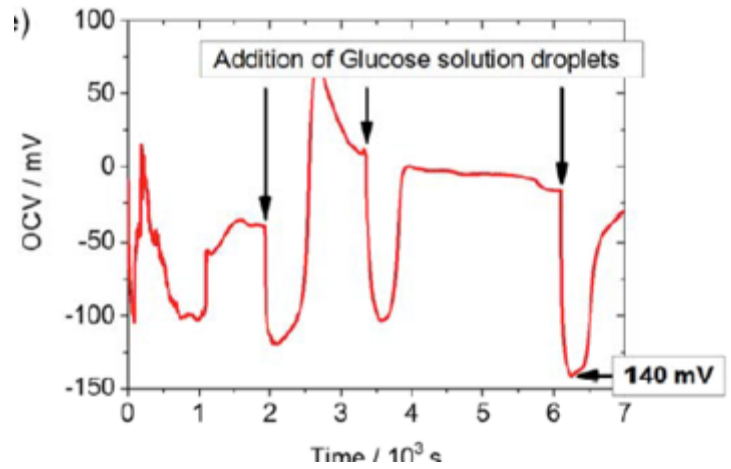
new device concept



human body requires on-board power supply ...
... to power sensors, pacemakers, ...
... to connect wirelessly for monitoring...



1st solid state sugar-to-power converting chip for human blood flow



Examples: 1st Si-chips with integrated glucose fuel cell membranes + proof-of-principle operation for solid state materials, developed by Rupp team MIT

New energy harvesting device to convert sugar to energy as implant to human blood circuit to power e.g. sensor chips → study materials & power devices

confidential