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 + CO$_2$ Environmental Trackers**

- **CO$_2$** environmental + medical sensing based on Li$^+$
- Novel solid state Li battery with high capacities

**References:**
- I Garbayo et al. JLM Rupp, Advanced Energy Materials 2017
- 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

**Ionic memory and computing logics: memristors**

- Information storage + non-binary computing

**References:**
- S Schweiger et al. JLM Rupp, Advanced Materials 2017
- R Schmitt et al. JLM Rupp, ACS Nano 2017

**Renewable Solar Fuels (Hydrocarbons)**

- CO$_2$, H$_2$O -> reactor: new perovskites -> syngas Storage Or Chemicals
- Clean energy storage with no material’s capacity limitations

**References:**

**Micro-energy convertor designs**

- Grid-independent energy conversion for autonomous electronics

**References:**
- Y Shi et al. JLM Rupp, Adv Mat, 2016
Outline

Energy Storage: All Solid State Li\textsuperscript{+} Batteries
  • Cheap Ceramic Processing: Mass Storage
  • Low Temperature Microbatteries

Environmental Monitoring: CO\textsubscript{2} Sensing
  • Novel Li\textsuperscript{+}-Garnet-based CO\textsubscript{2} Sensor Architectures

Neuromorphic Computing: Memristors
  • Strained Memristor Concept
Today’s liquid-based Li-ion batteries have severe safety, stability and scaling limitations. New Material architectures and cell designs needed.
Young field, since 2012:
First macro ceramic Li-garnet electrolytes pellets: comparable Li conduction by one order to classic liquids $\rightarrow$ advantage: solid state nature

All Solid State Li\(^+\) batteries without Liquids

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

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

S Afyon, F Krumeich, JLM Rupp, J of Materials Chemistry A, 2015 - Featured in Green Car News
JLM Rupp, M Streiff, patent EP 15000536.1, 2015
Solid State Electrolyte Li-Garnet/Cathode Interfaces

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

What are suitable electrodes? Power?

young field: first battery in 2012

Li-Garnet Battery: Electrode Materials

Cathodes: LiCoO$_2$

Anode?

Discharge Voltage (V)

Discharge Capacity (mAh/g)

Ceramic processing and solid state battery engineering:
Electrodes compatible with Li-garnets needed
→ First cathodes reported (cells$^1$ + Ceder group MIT: MD modeling$^2$)

(2) LJ Miara, G Ceder et al,Chem of Materials, 27, 2015
(3) X Tong, V Thangadurai, E Wachsman, Inorganic Chemistry 54, 2015
Solid Li\(^+\) batteries the role of ceramic/interface manufacturing

Non-modified All Solid State Battery

Interface merged Solid State Battery

Model experiment:
Influence of solid-solid anode-electrolyte interface coagulation on electrochemistry?

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

Sb+3Li⁺+3e⁻ ⇌ Li₃Sb
(660 mAh g⁻¹, ΔV=135%)

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

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

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

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

Sb+3Li⁺+3e⁻ ⇌ Li₃Sb
(660 mAh g⁻¹, ΔV=135%)

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

S. Afyon, J. van den Broek, C. Haensel, S. Wang, K. Kravchik, M. Kovalenko, J. L. M. Rupp, in review 2017
Solid State Li⁺ Garnet Electrolyte Battery with Antimony Anode

Sb nanoparticles
liquid Li standard battery

Sb+3Li⁺+3e⁻⇄Li₃Sb
(660 mAh g⁻¹, ΔV=135%)

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

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

S. Afyon, J van den Broek, C Haensel, S Wang, K Kravchnik, M Kovalenko, JLM Rupp, in review 2017
What is next? A Fair and Green Solid State Li Battery

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

→ Amnesty International: violation of human rights
→ U.S. trade group Electronic Industry Citizenship Coalition: 60% world share of Co Congo are problematic

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
Outline

Energy Storage: All Solid State Li$^+$ Batteries
- Cheap Ceramic Processing: Mass Storage
- Low Temperature Microbatteries

Environmental Monitoring: CO$_2$ Sensing
- Novel Li$^+$-Garnet-based CO$_2$ Sensor Architectures

Neuromorphic Computing: Memristors
- Strained Memristor Concept
Microbattery: Energy Supply for Sensing and Transmitters

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

Si integrated

300 μm

Si integrated thin film battery

Oak Ridge “Bates” cell

Product: Thin Film Microbattery

Challenges

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


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-Li$_7$La$_3$Zr$_2$O$_{12}$ Films

$T_{dep}$

<table>
<thead>
<tr>
<th>$T_{dep}$</th>
<th>300°C</th>
<th>500°C</th>
<th>750°C</th>
</tr>
</thead>
</table>

(a) Au electrode

Thin film

50 nm

(b) Columnar grains

Crystalline La$_2$Zr$_2$O$_7$

FFT of grain 2

(c) Li garnet thin film

La$_2$Zr$_2$O$_7$ grains in Li-garnet amorphous network

50 nm

(d) Li garnet thin film

Li-garnet film

Pseudo-amorphous Li-garnet network

(e) Li garnet thin film

Li-garnet film

Crystalline La$_2$Zr$_2$O$_7$ dominates over amorphous Li-garnet

Si substrate

“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

Si-Chip with Li-garnet film

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

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

$\rightarrow$ new glass electrolytes
$\rightarrow$ unclear: integration?

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

Energy Storage: All Solid State Li\textsuperscript{+} Batteries
  • Cheap Ceramic Processing: Mass Storage
  • Low Temperature Microbatteries

Environmental Monitoring: CO\textsubscript{2} Sensing
  • Novel Li\textsuperscript{+}-Garnet-based CO\textsubscript{2} Sensor Architectures

Neuromorphic Computing: Memristors
  • Strained Memristor Concept
Relevance of CO$_2$ tracking for society and energy management

Needs for products:
- Power efficient
- Small
- Low cost
- Chip integration

M Struzik, JLM Rupp et al, to-be-submitted
Solid State Energy Storage and Tracking Devices Based on Li$^+$

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 CO$_2$ sensing

In-plane pellet based cell

Reference electrode Au paste

Auxiliary phase – Li$_2$CO$_3$+Au

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

M Struzik, JLM Rupp, in review 2017
Li-Garnet based in-plane structure for CO$_2$ sensing

First successful CO$_2$ sensor device with Li$_7$La$_3$Zr$_2$O$_{12}$-based solid electrolyte

**EMF:** Sensor detects changes in [CO$_2$], stable cyclability in a range 400-4000ppm

**Sensitivity:** $\sim$32 mV  **Response time:** <1 min at 280°C
Novel Li-Garnet CO\textsubscript{2} Sensors based on Battery Technology

Comparison to state-of-technology shows fastest response time < 60sec at lowest temperature >300°C for newly proposed CO\textsubscript{2} Sensors based on Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{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?

Memristor data storage chip
ETH Zurich

Example: first Pt-SrTiO$_{3-\delta}$-Pt-based memristor cross-bar arrays$^{1,3}$

Memristor = “Memory + Resistor“: the 4$^{th}$ 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 memristors$^{1-6}$ + new strained material building blocks as bit storage architectures$^4$

Memristor for Binary Information Storage

- Memristor computer storage: Hewlett Packard
- Memristor for Binary Information Storage: Ref. 1,2

<table>
<thead>
<tr>
<th></th>
<th>Memristor</th>
<th>Flash</th>
<th>DRAM</th>
<th>FeRAM</th>
</tr>
</thead>
<tbody>
<tr>
<td>write time (ns)</td>
<td>5</td>
<td>1000</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>write operation (V)</td>
<td>&lt;1.5</td>
<td>15</td>
<td>2.5</td>
<td>1.5</td>
</tr>
<tr>
<td>retention (yrs)</td>
<td>&gt;10</td>
<td>&gt;10</td>
<td>64ms</td>
<td>&gt;10</td>
</tr>
<tr>
<td>write cycles</td>
<td>$10^{16}$</td>
<td>$10^5$</td>
<td>$10^{16}$</td>
<td>$10^{14}$</td>
</tr>
<tr>
<td>smallest feature size F (nm)</td>
<td>25</td>
<td>36</td>
<td>50</td>
<td>180</td>
</tr>
<tr>
<td>cell area, F$^2$</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>22</td>
</tr>
</tbody>
</table>

Vision: Memristive Logics for Neuromorphic Computing

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

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

1) Peschkin and Ventra, Adv. in Physics 60, 2011
Example: 1st serial connection of 2-Bits based on bipolar switching CeO$_{2-x}$ oxide memristors. (ETH)

2 Bits (series): M1 (CeO$_{2-x}$)+M2 (CeO$_{2-x}$)

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

PhD Thesis Rafael Schmitt, Electrochemical Materials, MIT/ETH
State-of-the-art: Altering Strain Fields in “Electronics” and “Ionics”?

**Electronics**

*Electronic heterostructure oxide as building blocks for devices*

- LaAlO$_3$
- SrTiO$_3$
- insulator
- fast conducting electronic interface
- insulator

*Strained Transistor*

strain $\rightarrow$ enhances electronic mobility


**Ionics**

*Strain-ionic defect interaction: micro-devices*


* Ionic heterostructures*

- S Schweiger et al. and JLM Rupp, *Advanced Materials* (2016)
- Sanna, Esposito et al., Pryds *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)

Controlling strain patterns to modify transport

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 $\sigma_i$ due to strained multilayer $\varepsilon$ interfaces

No device integration so far!

<table>
<thead>
<tr>
<th>Material</th>
<th>T(K)</th>
<th>Relative change in conductivity</th>
<th>Remarks</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ/Y$_2$O$_3$</td>
<td>623 - 973</td>
<td>$10^1$</td>
<td>Multilayer</td>
<td>Korte et al.</td>
</tr>
<tr>
<td>Sm:CeO$_2$/YSZ</td>
<td>673 – 1073</td>
<td>$10^1$</td>
<td>Multilayer</td>
<td>Sanna et al.</td>
</tr>
<tr>
<td>YSZ/Gd$_2$Zr$_2$O$_7$</td>
<td>550 – 750</td>
<td>$10^2$</td>
<td>Multilayer</td>
<td>Li et al.</td>
</tr>
<tr>
<td>Gd:CeO$_2$ on MgO/STO</td>
<td>723 – 1123</td>
<td>$10^1$-$10^2$</td>
<td>Thin film</td>
<td>Kant et al.</td>
</tr>
<tr>
<td>YSZ on MgO</td>
<td>423 - 773</td>
<td>$10^3$</td>
<td>Thin film</td>
<td>Sillassen et al.</td>
</tr>
</tbody>
</table>

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

Metal electrodes
Electrolyte
Substrate

Electrolyte

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.

(1) J.L.M. Rupp, S.Schweiger, F. Messerschmitt; Patent WO2014170023

(2) S Schweiger, JLM Rupp et al., ACS Nano, 8, 5, 5032 (2014)
Successful manufacturing of strained multilayer microdot arrays for first devices.

S Schweiger, R Pfenninger, W Bowman, U Aschauer, JLM Rupp, Advanced Materials, 2017
• Compressive in-plane strain of -1.16% in conducting phase.
• Decreasing the film thickness from 280 nm to 7 nm (increasing number of interfaces) \( \rightarrow \) increase of \( E_a = \Delta 0.31 \text{ eV} \).
Influence of strain on memristance: Cyclic voltammetry

S Schweiger, R Pfenninger, W Bowman, U Aschauer, JLM Rupp, Advanced Materials, 2017
Strain relaxation in the $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ layers for 6 interfaces

→ in-plane compression $\Delta = 0.04\text{Å}$
→ out-of-plane tension $\Delta = 0.03\text{Å}$

Increasing anisotropy with decreasing $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ layer thickness
The strained memristor: defect transport model

\[ \sigma_{\text{tot}}(RT, \text{high } E, \text{total } V) = \mu_{e'} \cdot [e'] \cdot q + \mu_{V_0} \cdot [V_0^+] \cdot (2q) \]

S Schweiger, R Pfenninger, W Bowman, U Aschauer, JLM Rupp, Advanced Materials, 2017
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⁺
- Novel solid state Li battery with high capacities
- 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

**Ionic memory and computing logics: memristors**

- Information storage + non-binary computing
- S Schweiger et al. JLM Rupp, Advanced Materials 2017

**Renewable Solar Fuels (Hydrocarbons)**

- CO₂ → H₂O + reactor: new perovskites → syngasorage or chemicals
- Clean energy storage with no material’s capacity limitations

**Micro-energy convertor designs**

- Grid-independent energy conversion for autonomous electronics
- Y Shi et al. JLM Rupp, Adv Mat, 2016
What is next? Prof Rupp`s dream list

- 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

Socio-economic acceptable energy storage: Fair batteries

New Li circuits: storage, sensing, data computing

Solar fuel + plastics (cars, …)
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 energy harvesting device to convert sugar to energy as implant to human blood circuit to power e.g. sensor chips → study materials & power devices

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

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

confidential