International Symposium on Electrical Fatigue in Functional Materials
September 15, 2014
Sellin, Rügen, Germany

Design and fabrication of all-solid-state rechargeable lithium batteries using ceramic electrolytes

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Outline

1. Introduction

> Why all-solid-state?

> Tasks in the development of all-solid-state batteries

2. Strategy (cell design)

> 3D structured solid electrolyte

> Sol-gel technique to construct a good electrode/electrolyte interface

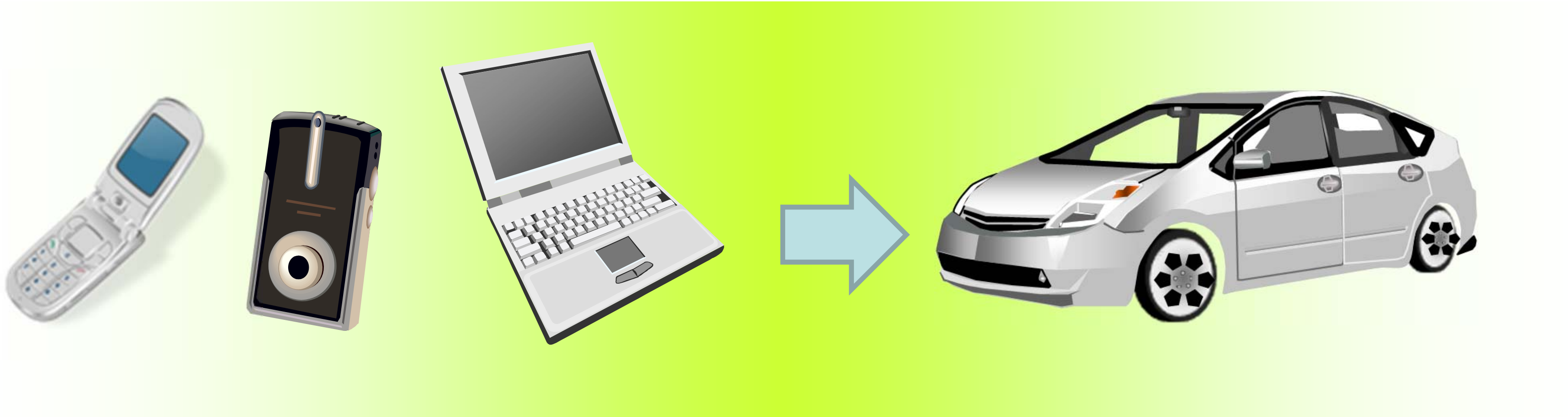
3. Cell performance

> All-solid-state rechargeable lithium battery using LLT

> All-solid-state rechargeable lithium battery using LLZ

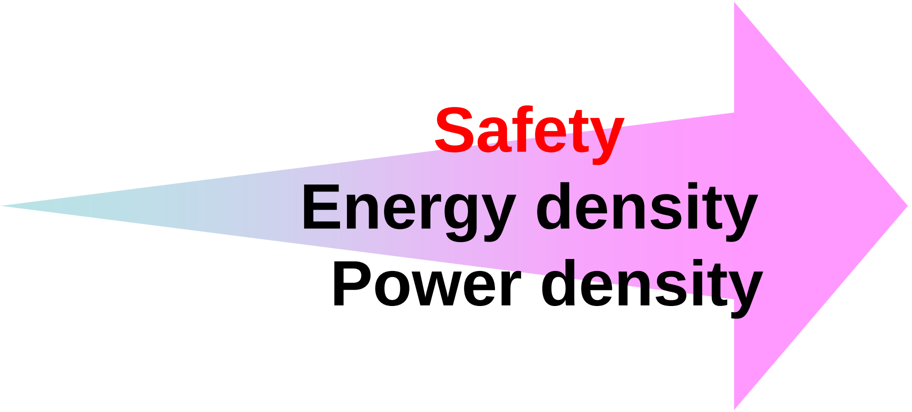
4. Conclusions

Extending applications of LIBs



Portable electronic devices

Electric vehicle



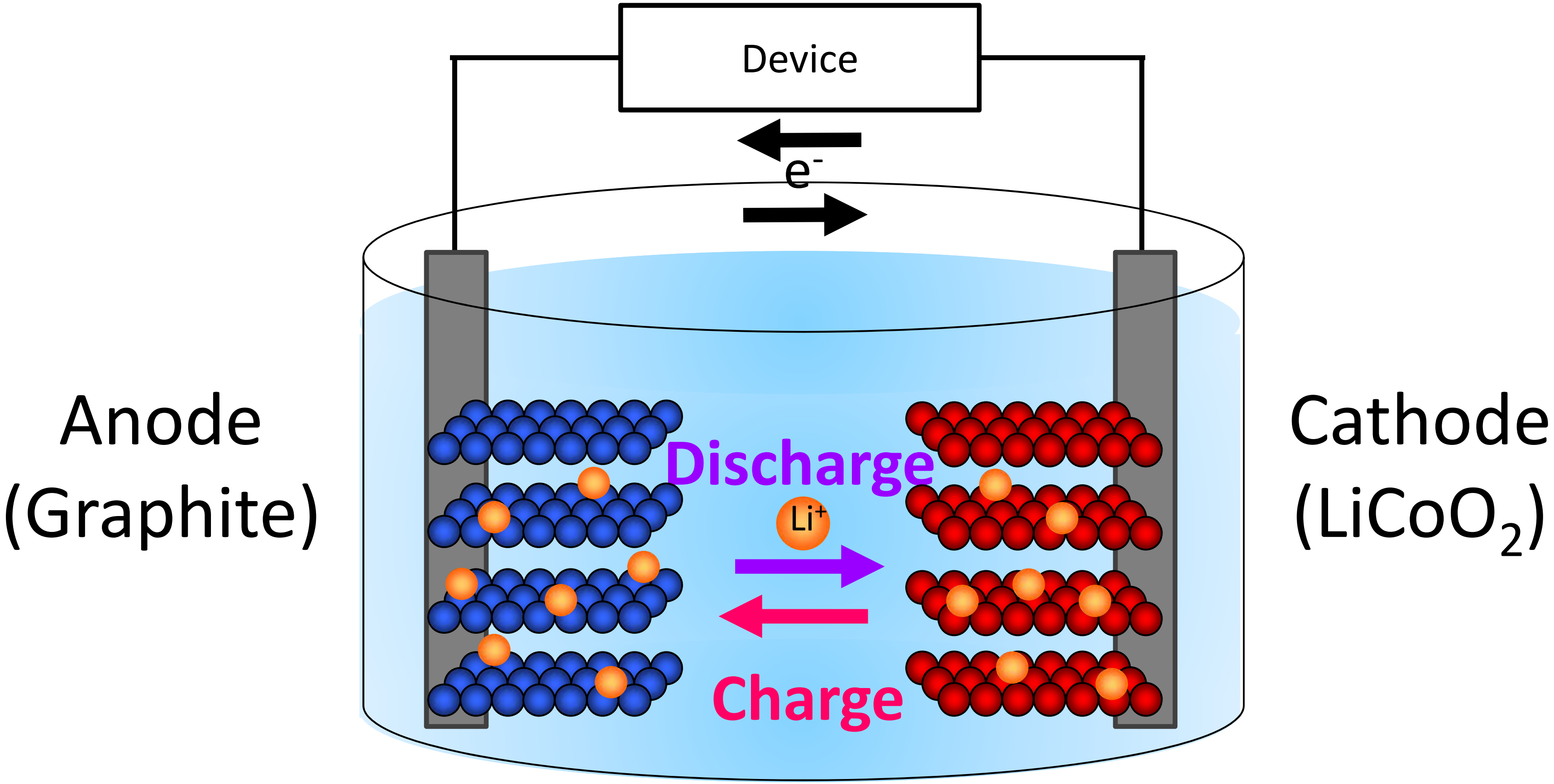
Safety

Energy density

Power density

The safety is more important in large-scale batteries.

Electrolyte in LIBs



Inorganic solid electrolyte
(non-flammable)

Merits of inorganic solid electrolytes

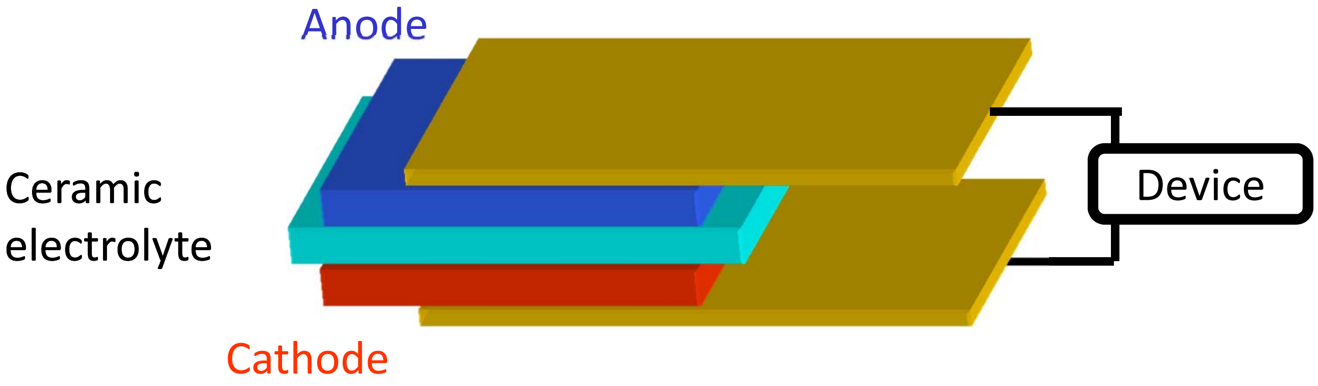
Inorganic solid electrolytes:

- Non-flammability
- Extending the upper limit of operating temperature
- Low self-discharge
- Simple package (bipolar batteries)
- 3D structured battery

-> New battery applications

Current all-solid state batteries

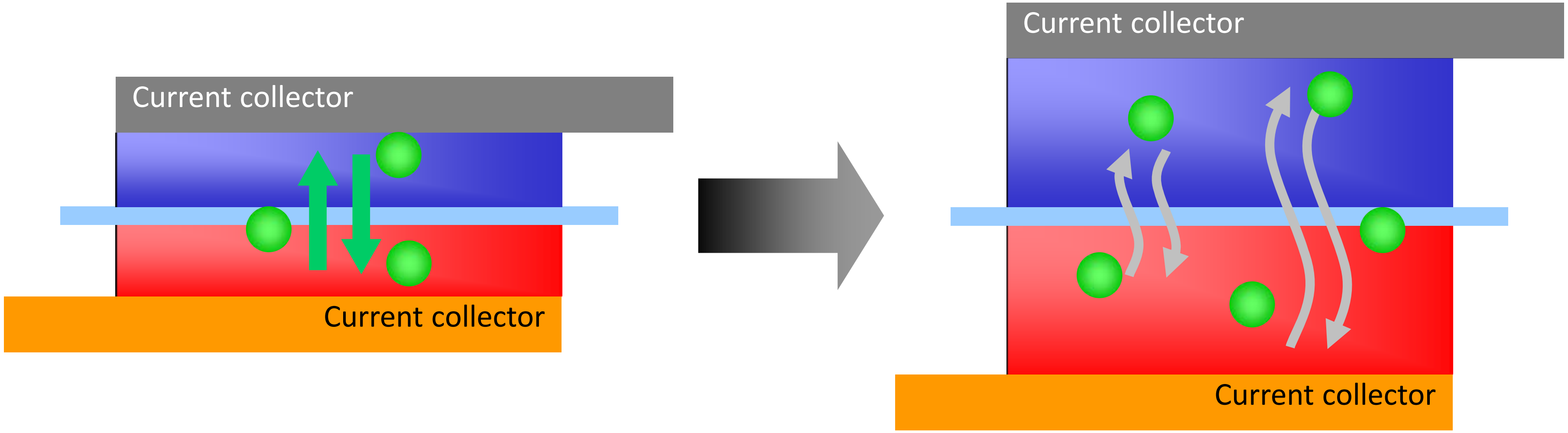
Thin film battery (2D)



2-dimensional (thin-layered) electrode configuration provides high rate performance due to fast lithium ion transport by short distance between cathode and anode, but…

Low capacity !

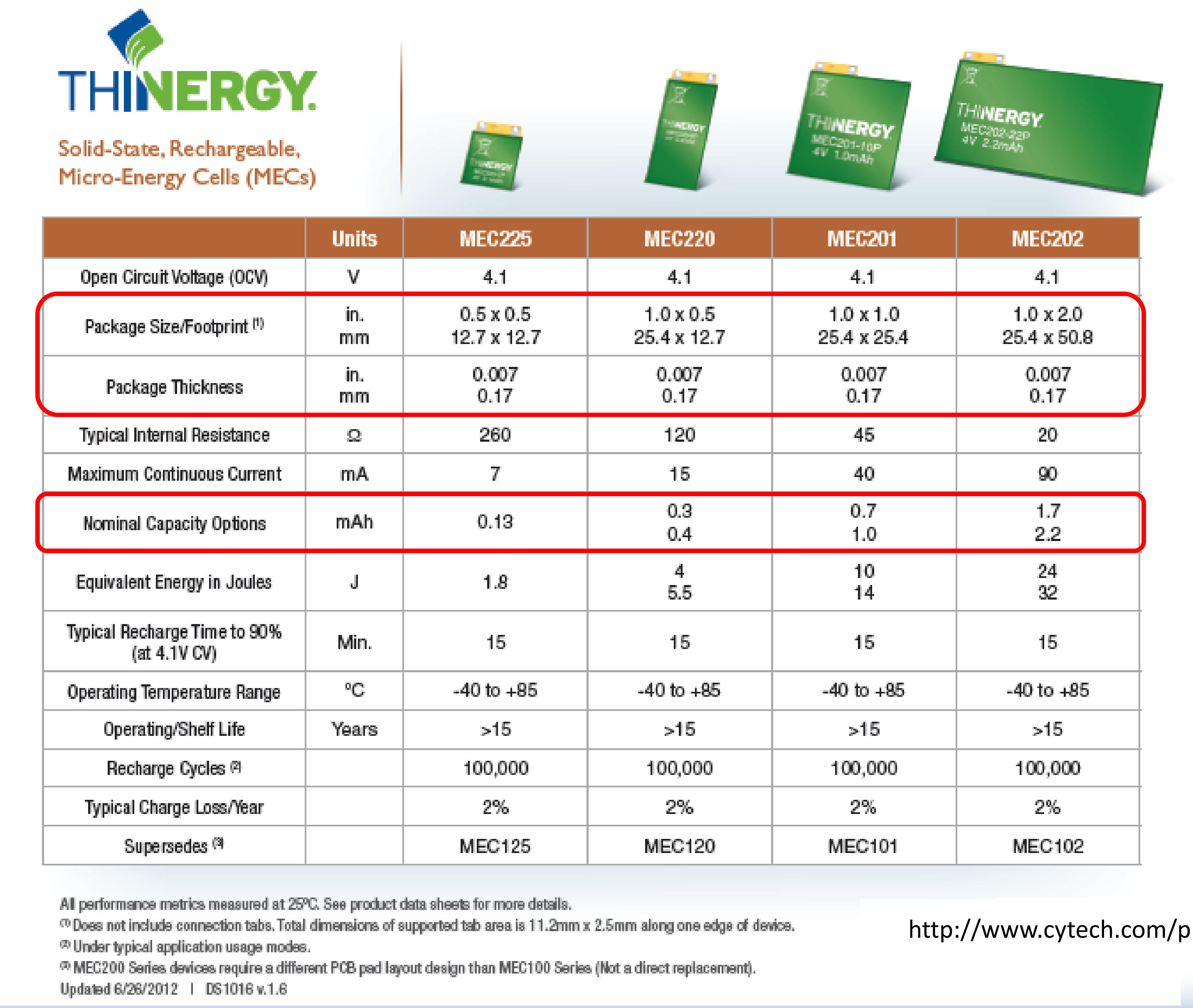
Capacity limitation by cell dimension



The electrode material situated away from an electrolyte layer does not work efficiently due to long diffusion length of lithium-ions.

It is difficult to obtain high cell capacity even though thick electrodes are prepared.

Commercially available thin film batteries



THINERGY

Solid-State, Rechargeable,
Micro-Energy Cells (MECs)

	Units	MEC225	MEC220	MEC201	MEC202
Open Circuit Voltage (OCV)	V	4.1	4.1	4.1	4.1
Package Size/Footprint (1)	in. mm	0.5 x 0.5 12.7 x 12.7	1.0 x 0.5 25.4 x 12.7	1.0 x 1.0 25.4 x 25.4	1.0 x 2.0 25.4 x 50.8
Package Thickness	in. mm	0.007 0.17	0.007 0.17	0.007 0.17	0.007 0.17
Typical Internal Resistance	Ω	260	120	45	20
Maximum Continuous Current	mA	7	15	40	90
Nominal Capacity Options	mAh	0.13	0.3 0.4	0.7 1.0	1.7 2.2
Equivalent Energy in Joules	J	1.8	4 5.5	10 14	24 32
Typical Recharge Time to 90% (at 4.1V CV)	Min.	15	15	15	15
Operating Temperature Range	°C	-40 to +85	-40 to +85	-40 to +85	-40 to +85
Operating/Shelf Life	Years	>15	>15	>15	>15
Recharge Cycles (2)		100,000	100,000	100,000	100,000
Typical Charge Loss/Year		2%	2%	2%	2%
Supersedes (3)		MEC125	MEC120	MEC101	MEC102

All performance metrics measured at 25ºC. See product data sheets for more details.

(1) Does not include connection tabs. Total dimensions of supported tab area is 11.2mm x 2.5mm along one edge of device.

(2) Under typical application usage modes.

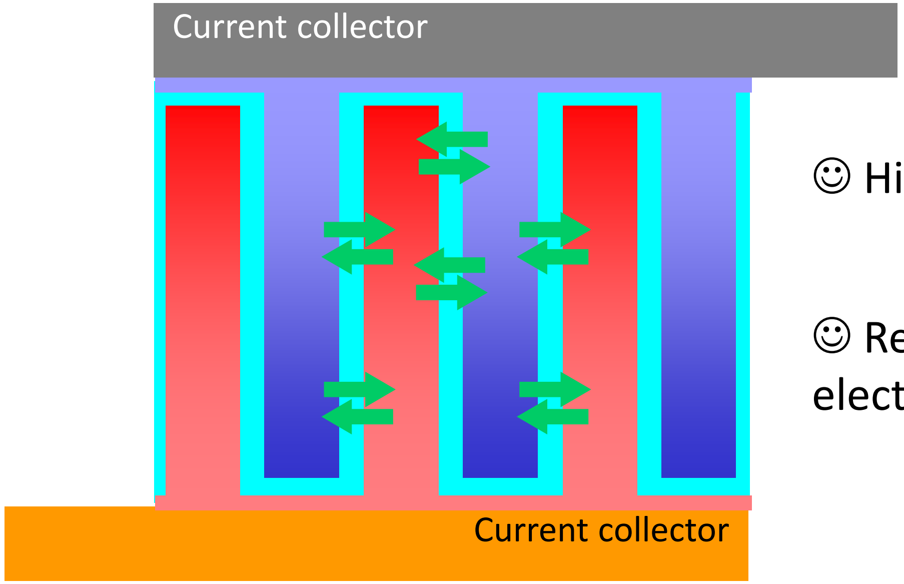
(3) MEC200 Series devices require a different PCB pad layout design than MEC100 Series (Not a direct replacement).

Updated 6/26/2012 | DS1016 v.1.6

http://www.cytech.com/products-ips

3D electrode configuration

Interdigitated electrode (3D) configuration

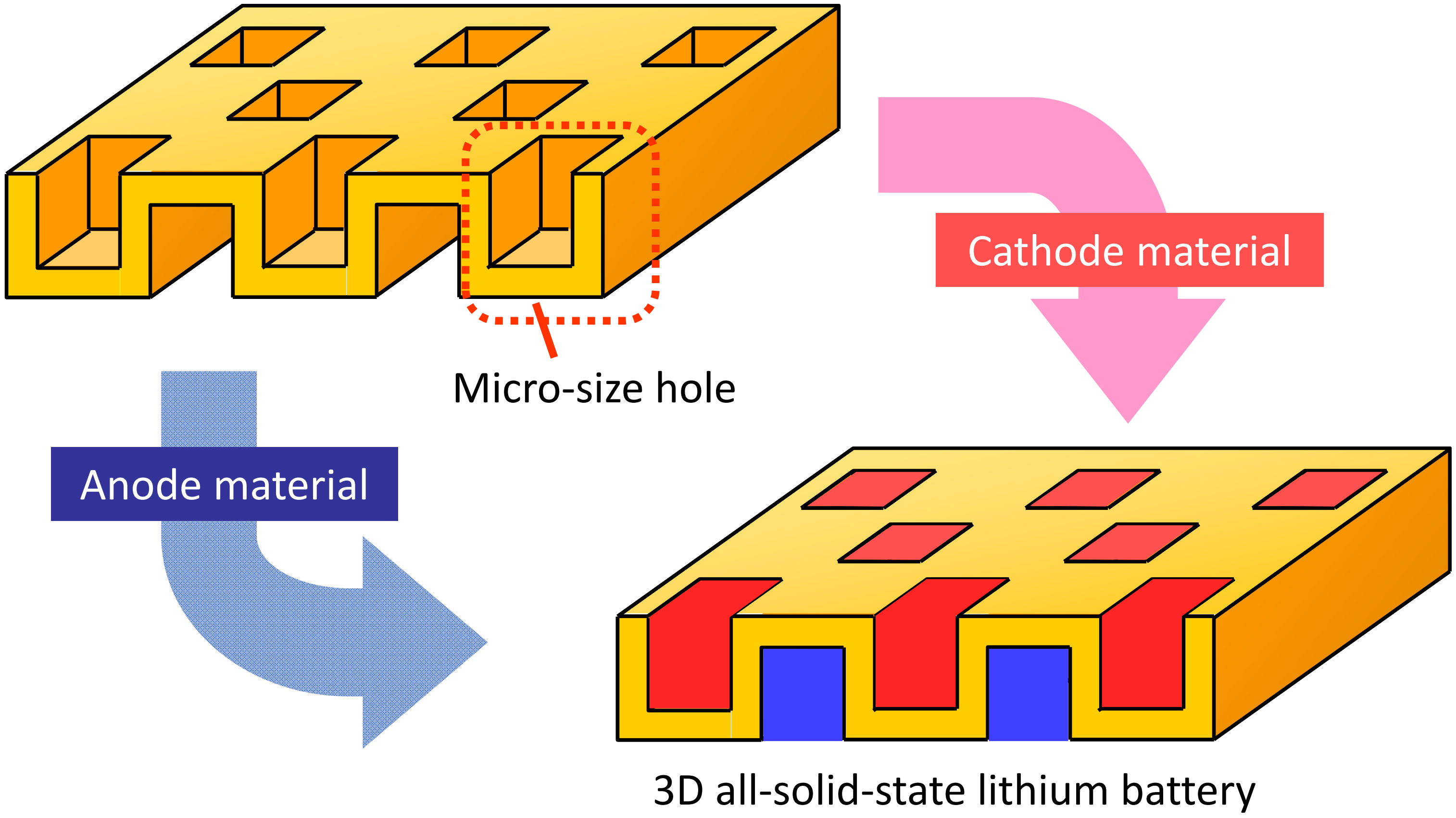


☺ High cell capacity and high current density

☺ Reduction of internal resistance by large electrochemical interface per unit volume

This kind of 3D electrode configurations have been suggested by many research groups as a next generation battery structure not only for all-solid-state batteries but also for conventional liquid electrolyte batteries.

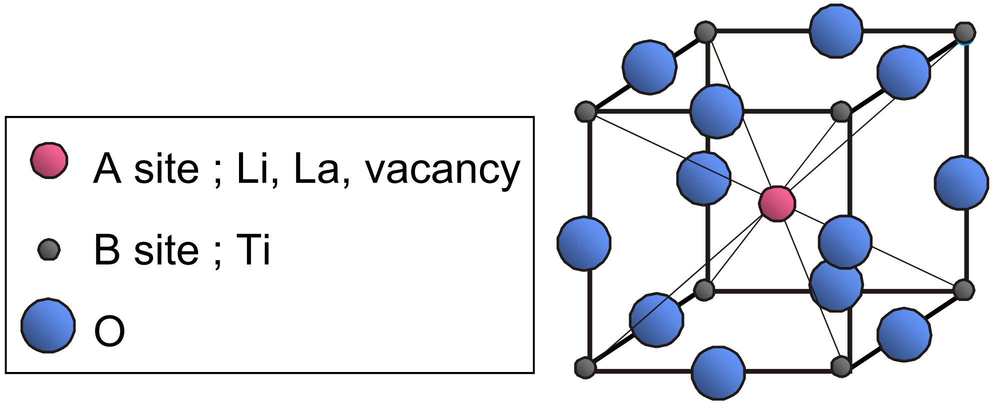
3D patterned solid electrolyte



3D all-solid-state battery can be prepared by impregnation of cathode and anode materials into the holes on the top and bottom faces of a patterned ceramic electrolyte membrane.

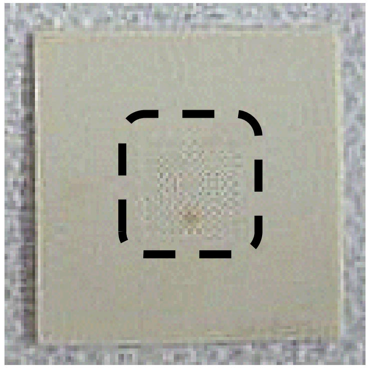
Li^+-conducting solid electrolytes

solid electrolyte	conductivity (S cm^{-1})	tempreture (°C)	reference
$Li_{4.2}Al_{0.2}Si_{0.8}O_4$	1.58×10^{-3}	300	Y. Saito et al. *Solid State Ionics*. **40/41**, 34 (1990)
$Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$	7×10^{-4}	25	C. Masquelier et al. *Solid State Ionics*. **79**, 98 (1995)
$Li_{3.6}Ge_{0.6}V_{0.4}O_4$	4×10^{-5}	18	J. Kuwano et al. *Mat. Res. Bull*., **15**, 1661 (1980)
Li_3N	6×10^{-3}	25	T. Lapp et al., *Solid State Ionics*, **11**, 97 (1983)
$Li_{0.35}La_{0.55}TiO_3$	1.4×10^{-3}	27	Y. Inaguma et al, *Solid State Ionics*. **86-88**, 257 (1996)



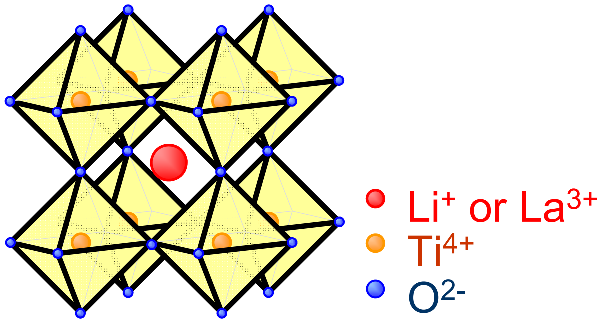
Lithium lanthanum titanium oxide (LLT) was used to prepare a hole-array structured membrane due to high lithium-ion conductivity and mechanical strength.

Hole array $Li_{0.35}La_{0.55}TiO_3$

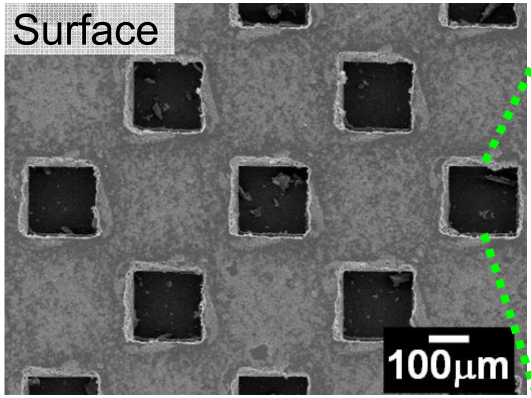


NGK INSULATORS Co., LTD.

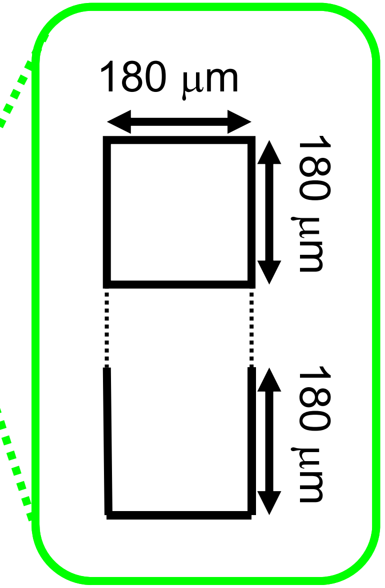
Perovskite structure

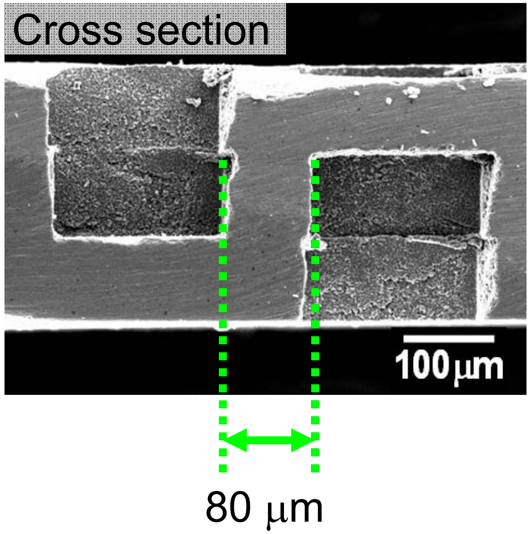


LLT ($Li_{0.35}La_{0.55}TiO_3$)
$\sigma = 1.2 \times 10^{-3}$ S cm^{-1} at R.T.

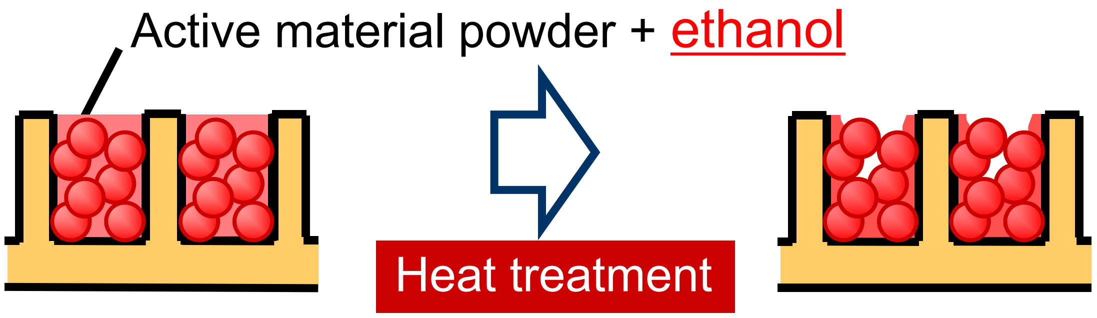


200 holes on each side

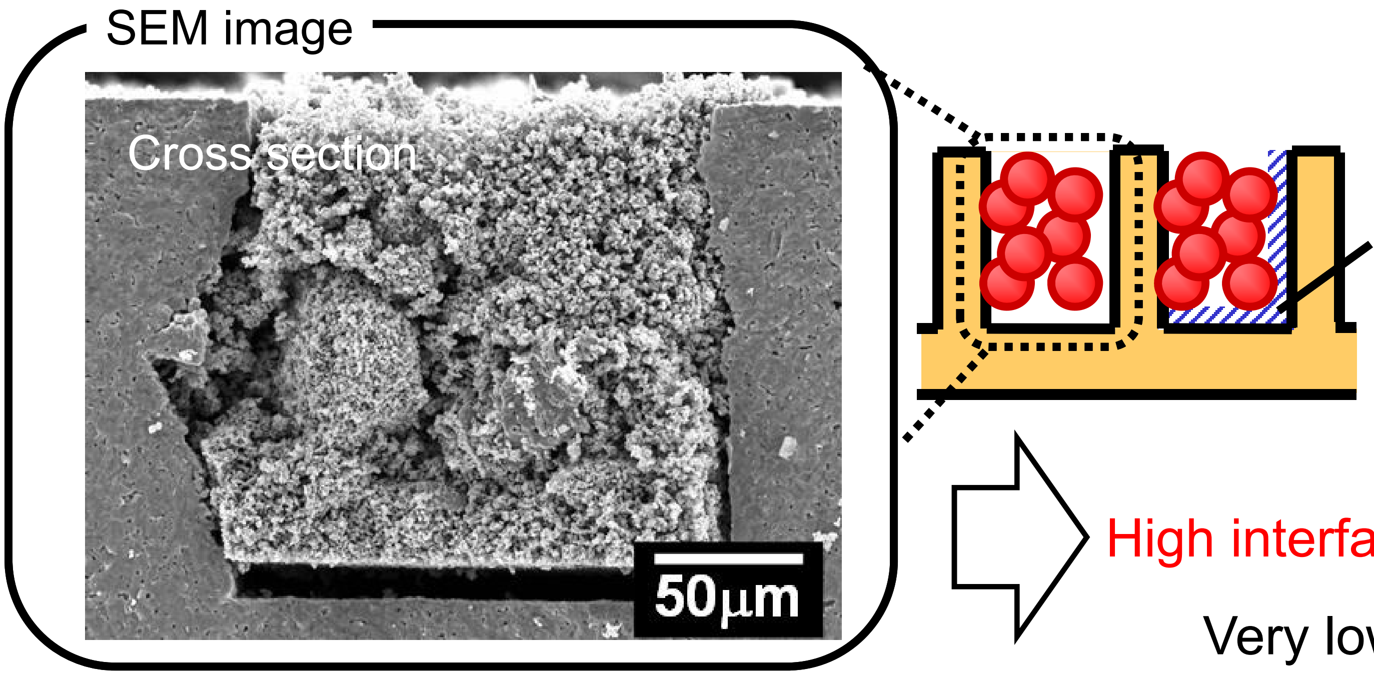




Powder impregnation



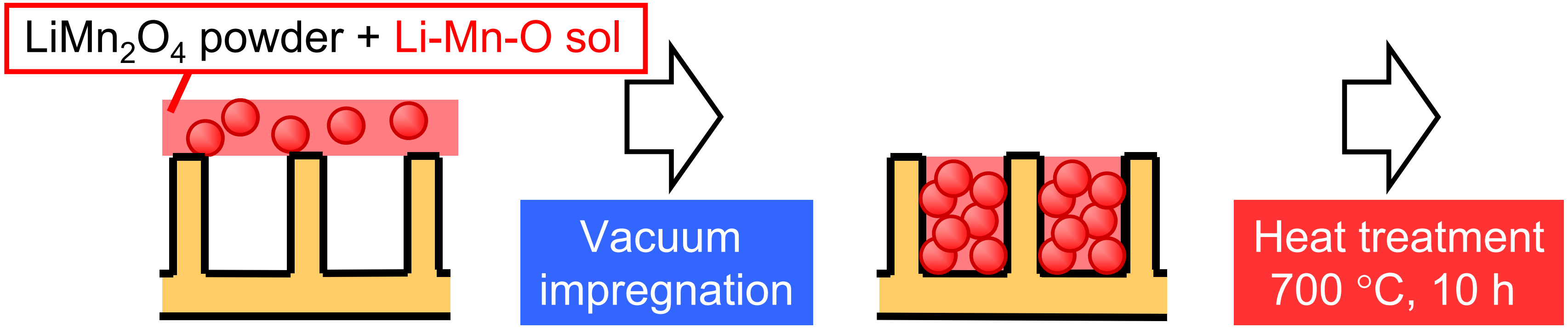
LLT / electrode composite



High interfacial resistance !!

Very low capacity
0.025 mA h g^{-1}

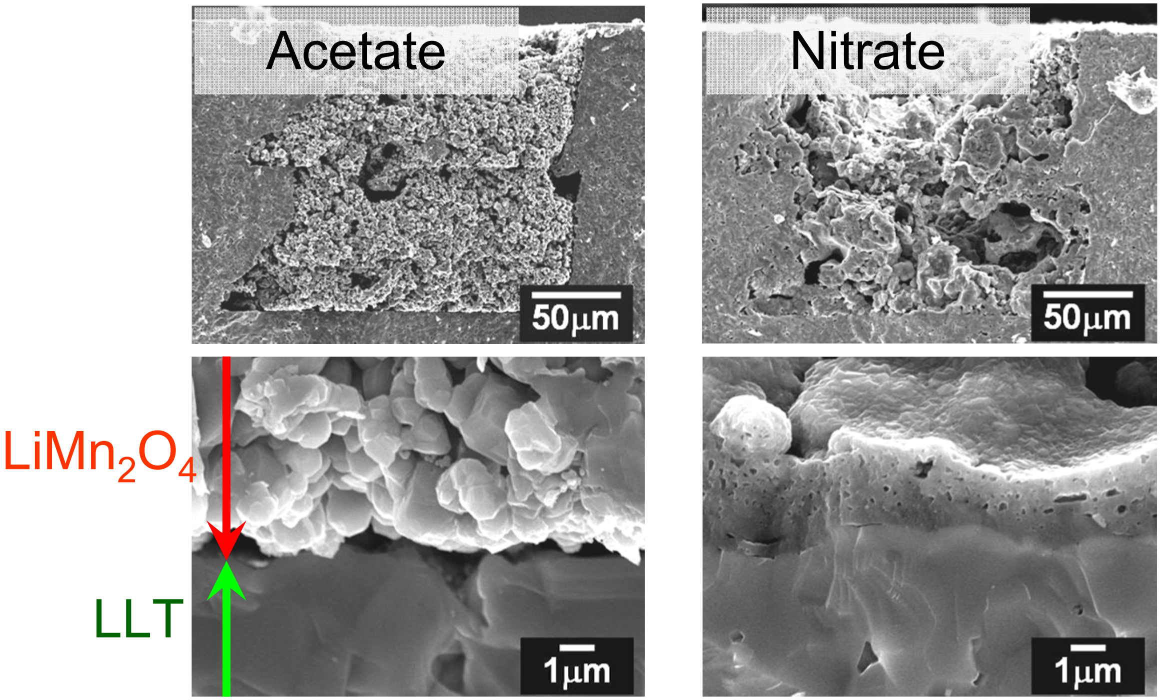
Application of precursor sol



$LiMn_2O_4$ powder + Li-Mn-O sol

Vacuum impregnation

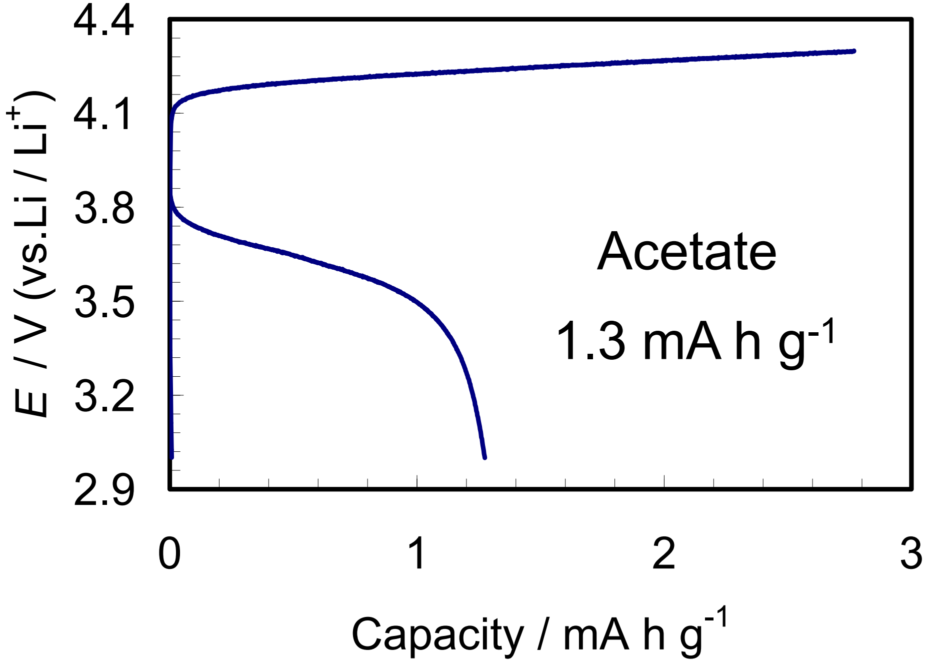
Heat treatment 700 °C, 10 h

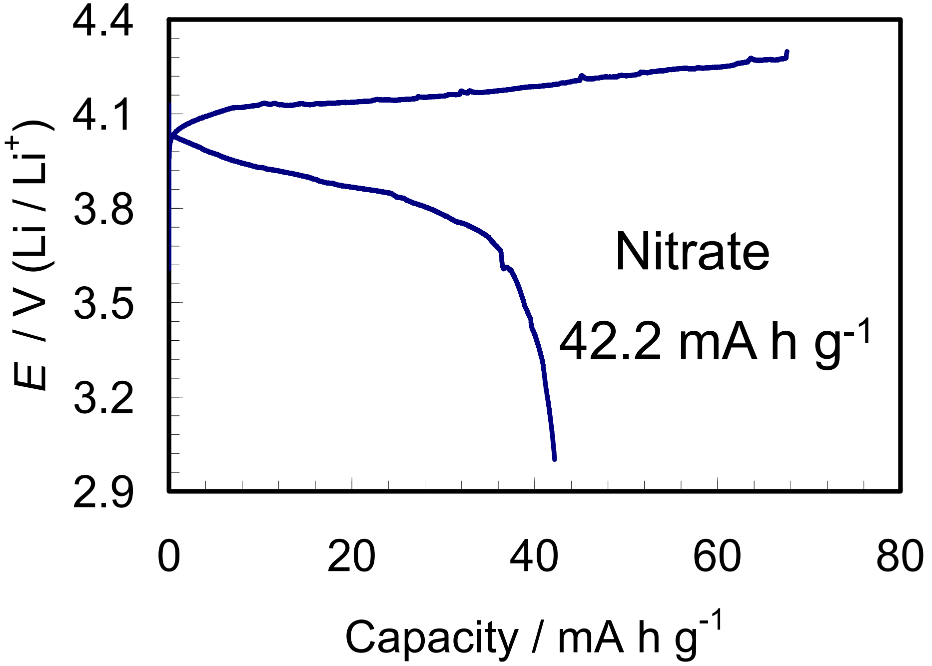


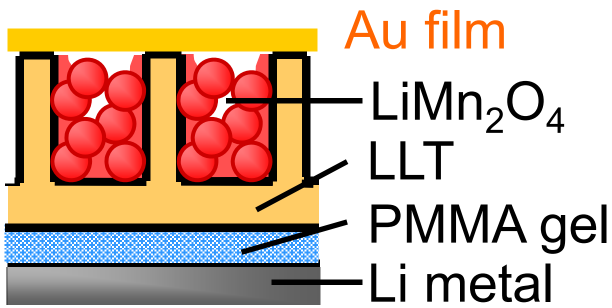
Precursor sol works as a binder to provide good contact.

Charge/discharge test

Without sol: 0.025 mA h g^{-1}



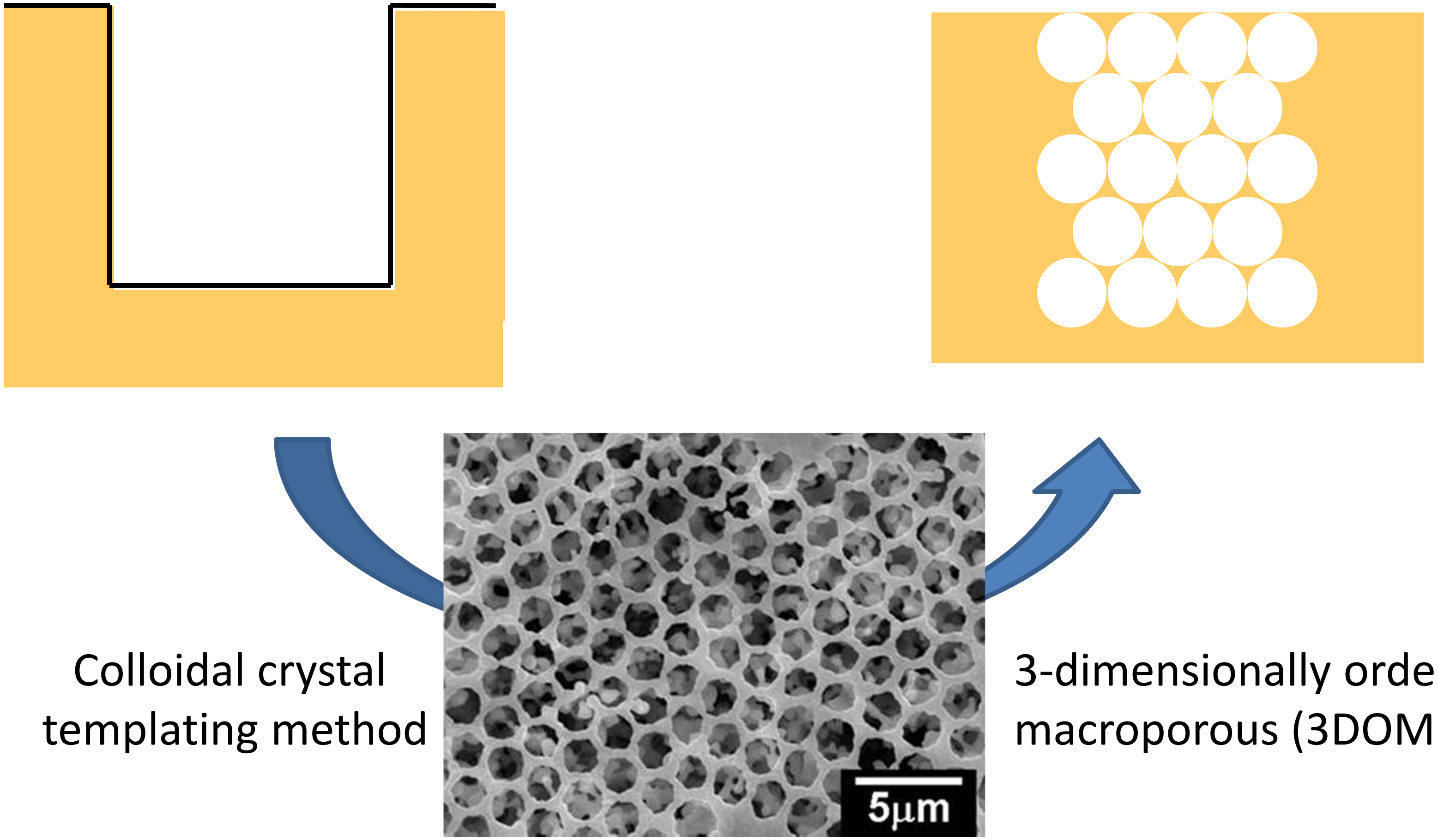




Cathode: $LiMn_2O_4$
Anode: Li metal
Electrolyte: Honeycomb LLT/PMMA
Current: 12.5 μA cm^{-2}
Cuf off: 3.0 – 4.3V

Theoretical capacity 148 mA h g^{-1}

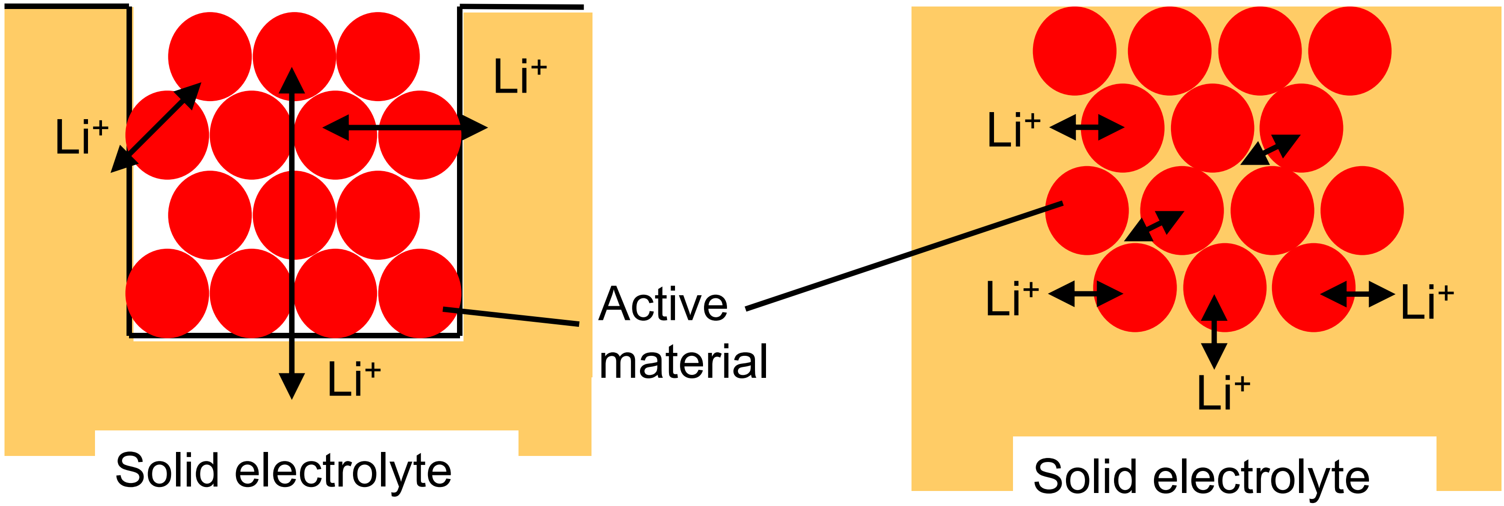
Formation of 3DOM LLT



Colloidal crystal
templating method

3-dimensionally ordered
macroporous (3DOM) LLT

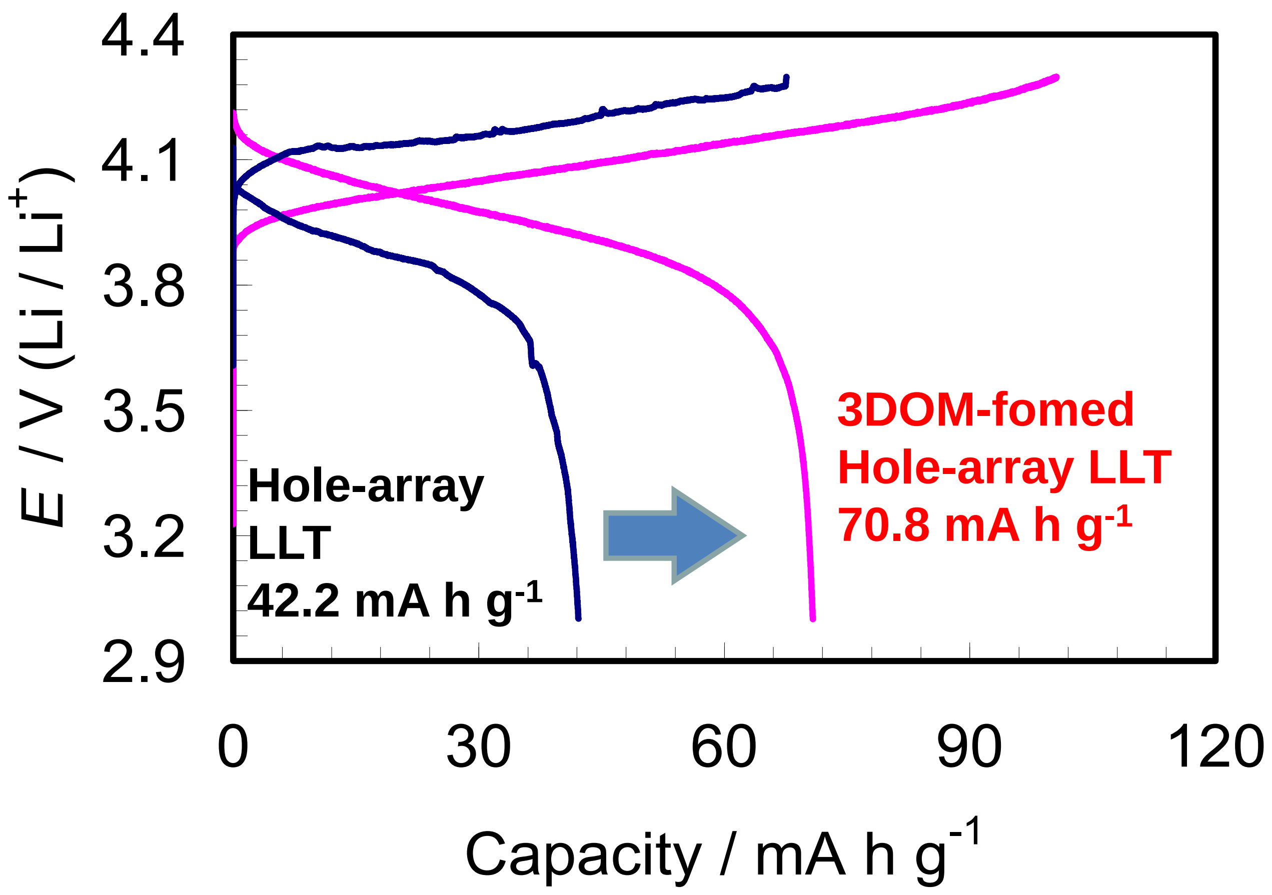
3DOM-hybrid hole-array


Simple hole-array

3DOM-hybrid hole-array

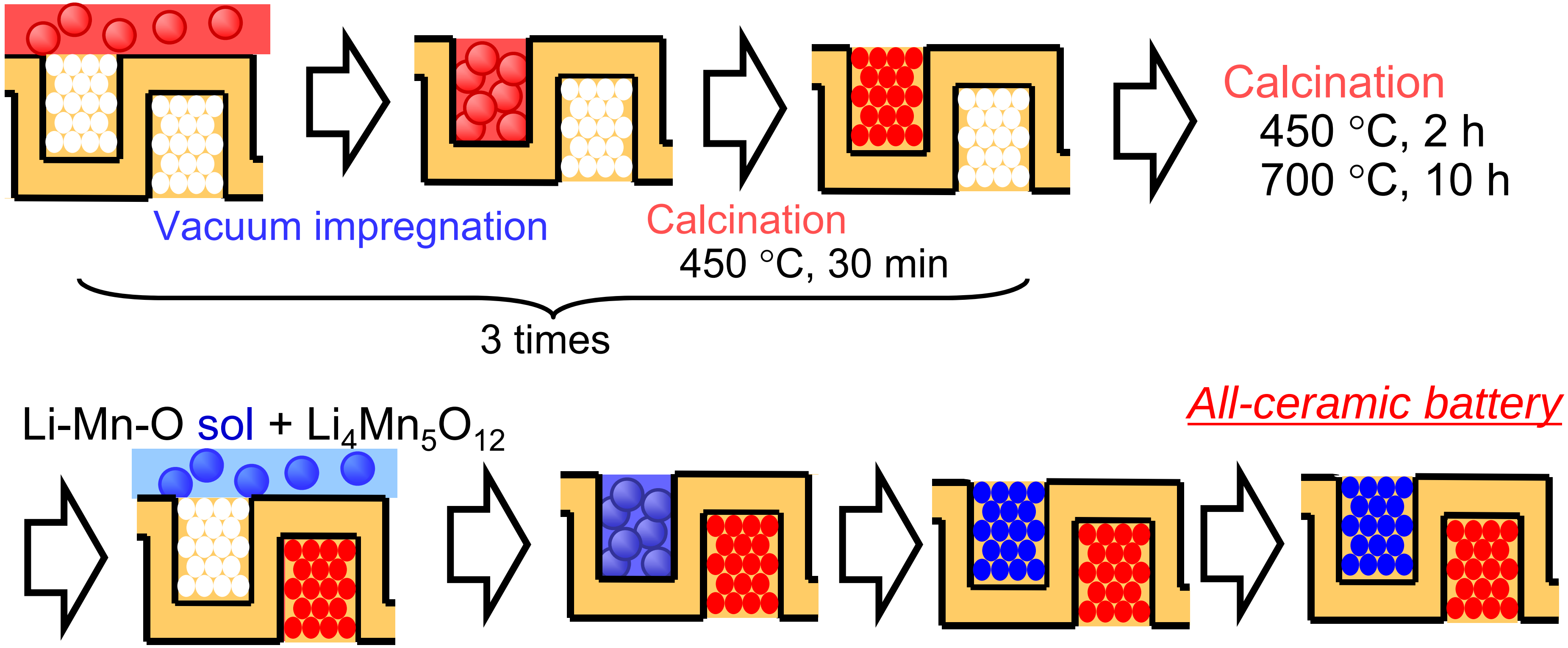
- ➢Short diffusion length of Li^+
- ➢Large contact area (Low internal resistance)

Charge/discharge test



Cathode: $LiMn_2O_4$
Anode: Li metal
Electrolyte: porous-layered honeycomb LLT / PMMA
Current: 12.5 mA cm^{-2}
Cuf off: 3.0 – 4.3V

Full cell preparation procedure



Li-Mn-O sol + $LiMn_2O_4$

Vacuum impregnation

Calcination
450 °C, 30 min

3 times

Calcination
450 °C, 2 h
700 °C, 10 h

Li-Mn-O sol + $Li_4Mn_5O_{12}$

All-ceramic battery

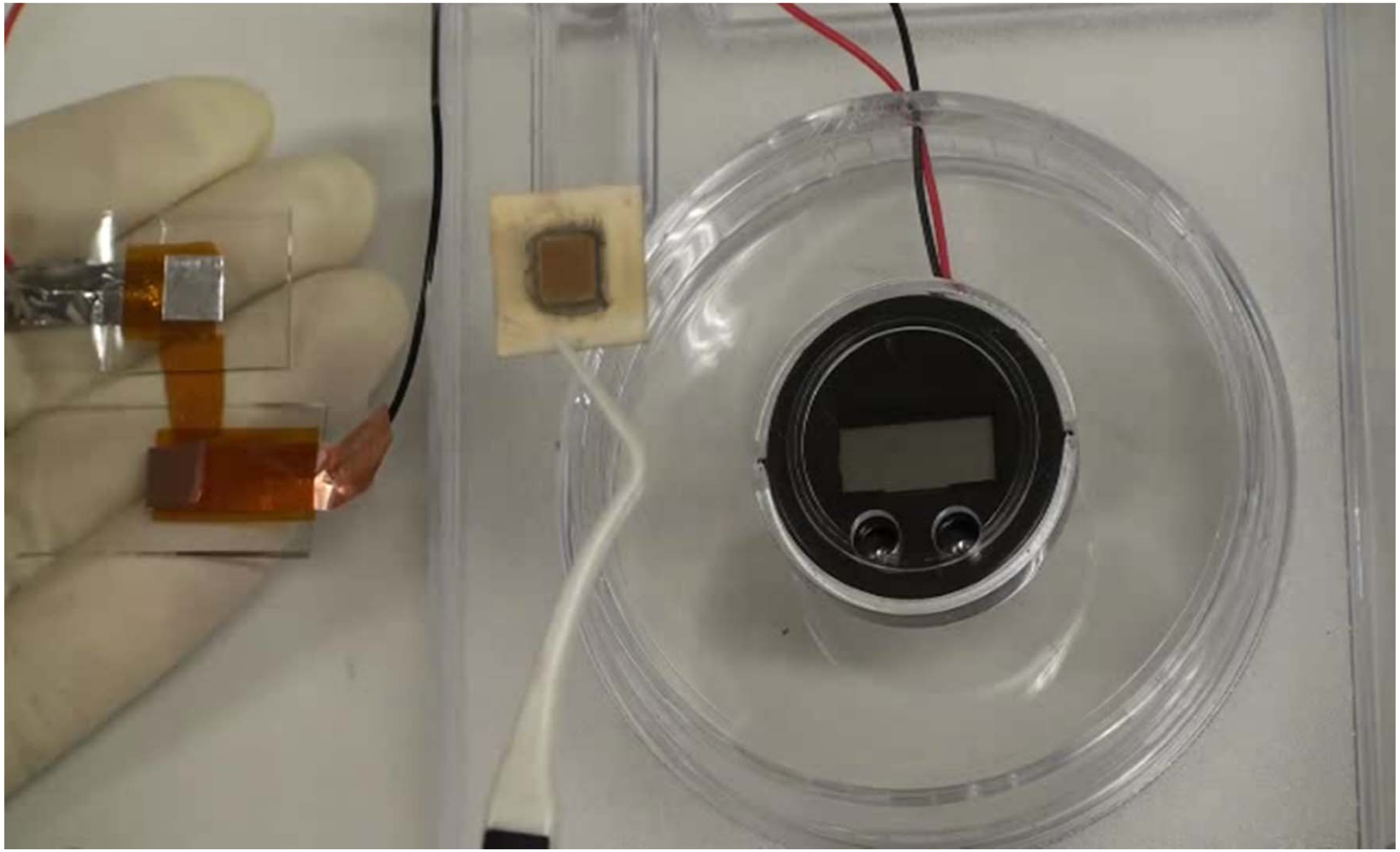
Vacuum impregnation

Calcination
450 °C, 30min

3 times

Calcination
450 °C, 2 h
600 °C, 10 h

Operation at room temperature



Operation of all-solid-state rechargeable lithium-ion battery at room temperature

$Li_7La_3Zr_2O_{12}$

New solid electrolyte

$Li_7La_3Zr_2O_{12}$ (LLZ)

Advantages

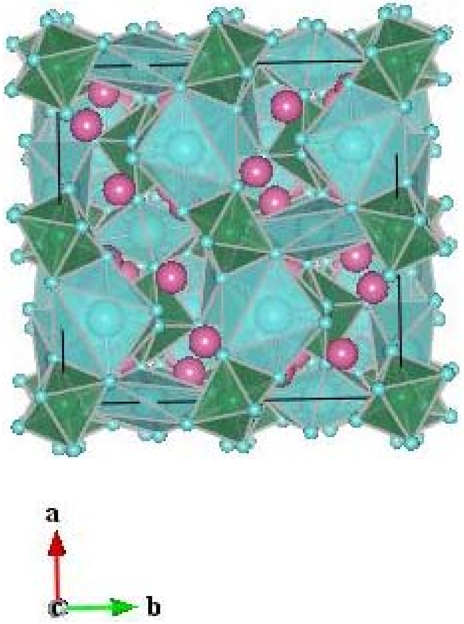
High lithium-ion conductivity (10^{-4} S cm^{-1} at R.T.)

High stability against lithium-metal

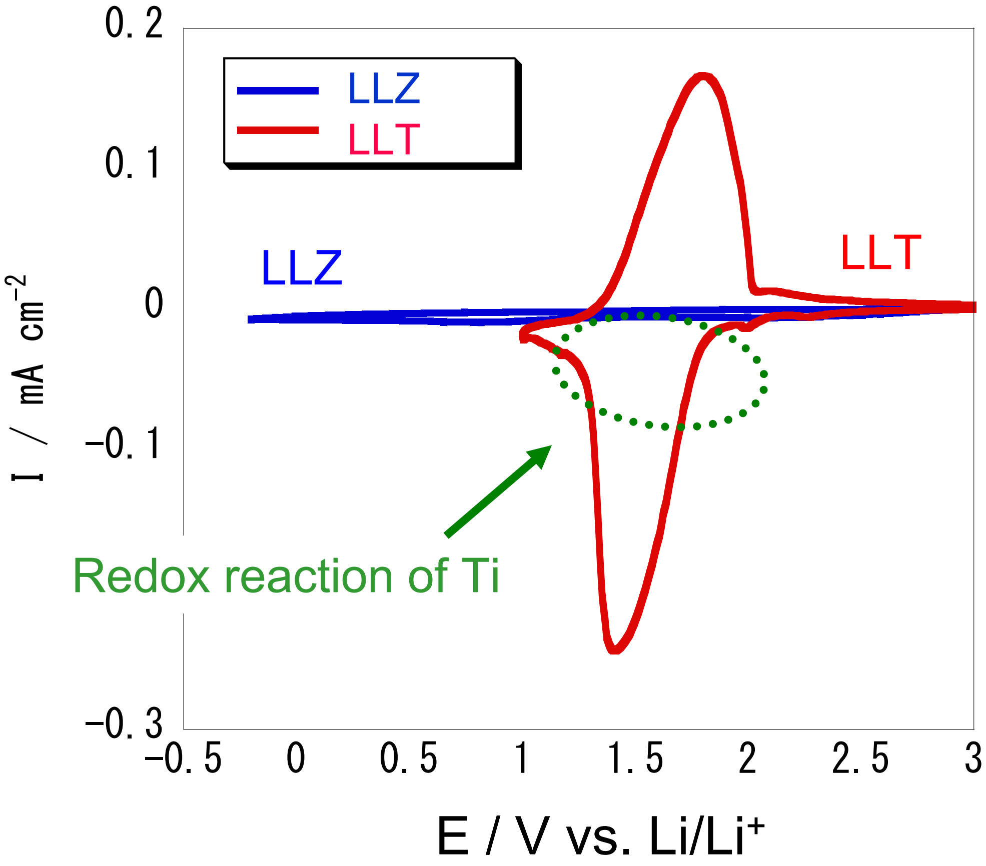
Can lithium-metal (3861 mA h g^{-1}) be used as anode?

W. Weppner et al., *Angew. Chem. Int. Ed.*, 46 ,1,(2007).

(garnet-like structure)



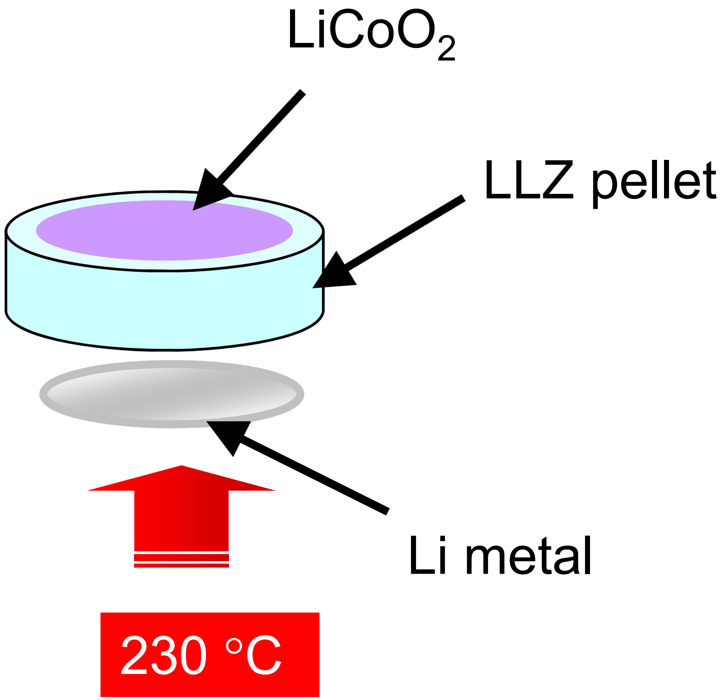
Electrochemical window

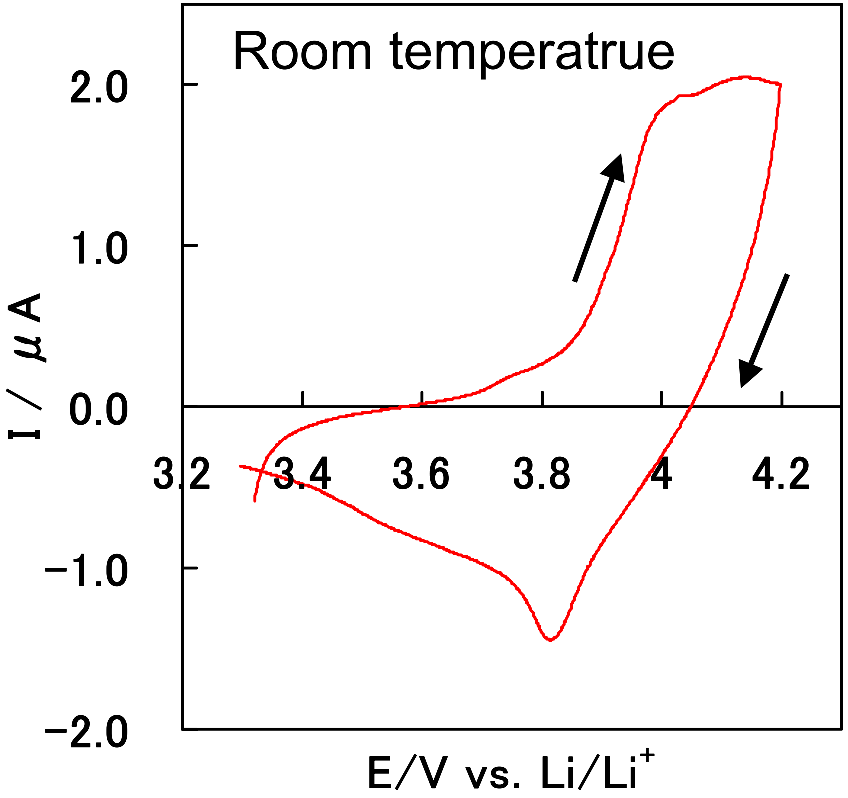


LLT shows the redox reaction of titanium at 1.8 V while LLZ is stable even at 0 V.

=> Lithium-metal can be used as anode in the LLZ system.

Li metal / LLZ / $LiCoO_2$ cell



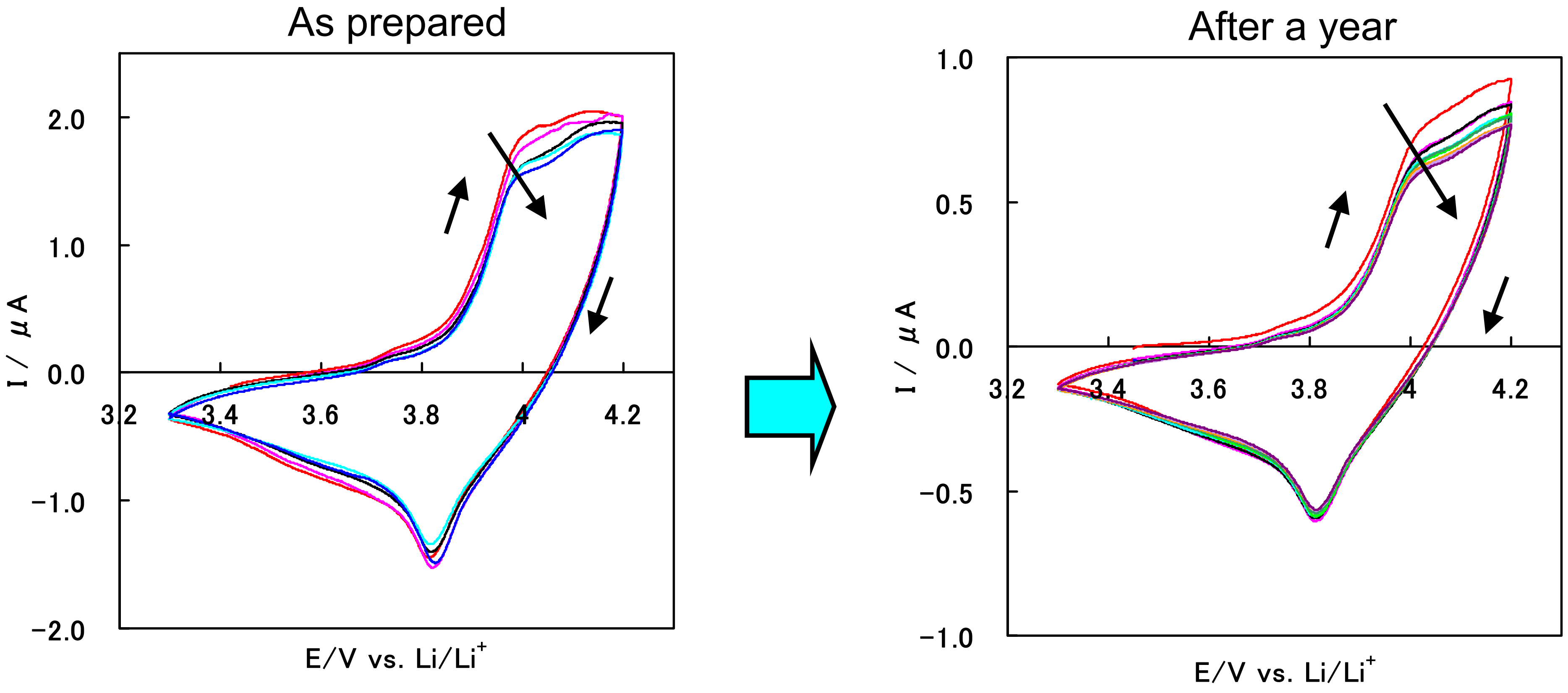


Scan rate : 1 mV min^{-1}

Cut off : 3.3 – 4.2 V vs. Li / Li^+

Redox peaks of $LiCoO_2$ were observed around at 3.9 V vs. Li/ Li^+.

Durability test


As prepared

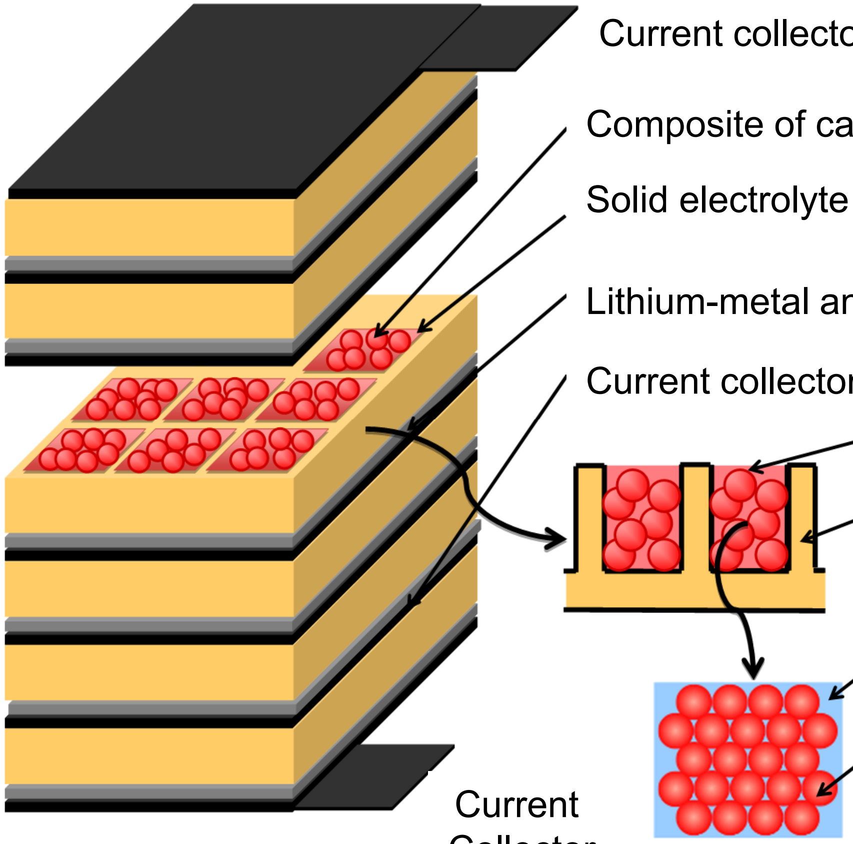
After a year

Scan rate : 1 mV min^{-1}

Cut off : 3.3 – 4.2 V vs. Li / Li^{+}

The prepared cell stably worked after a year.

Bipolar-type battery



Current collector tab

Composite of cathode material and solid electrolyte

Solid electrolyte membrane with hole array structure

Lithium-metal anode

Current collector for anode (carbon/nickel composite)

Honeycomb hole

Solid-electrolyte substrate

3DOM structured solid-electrolyte

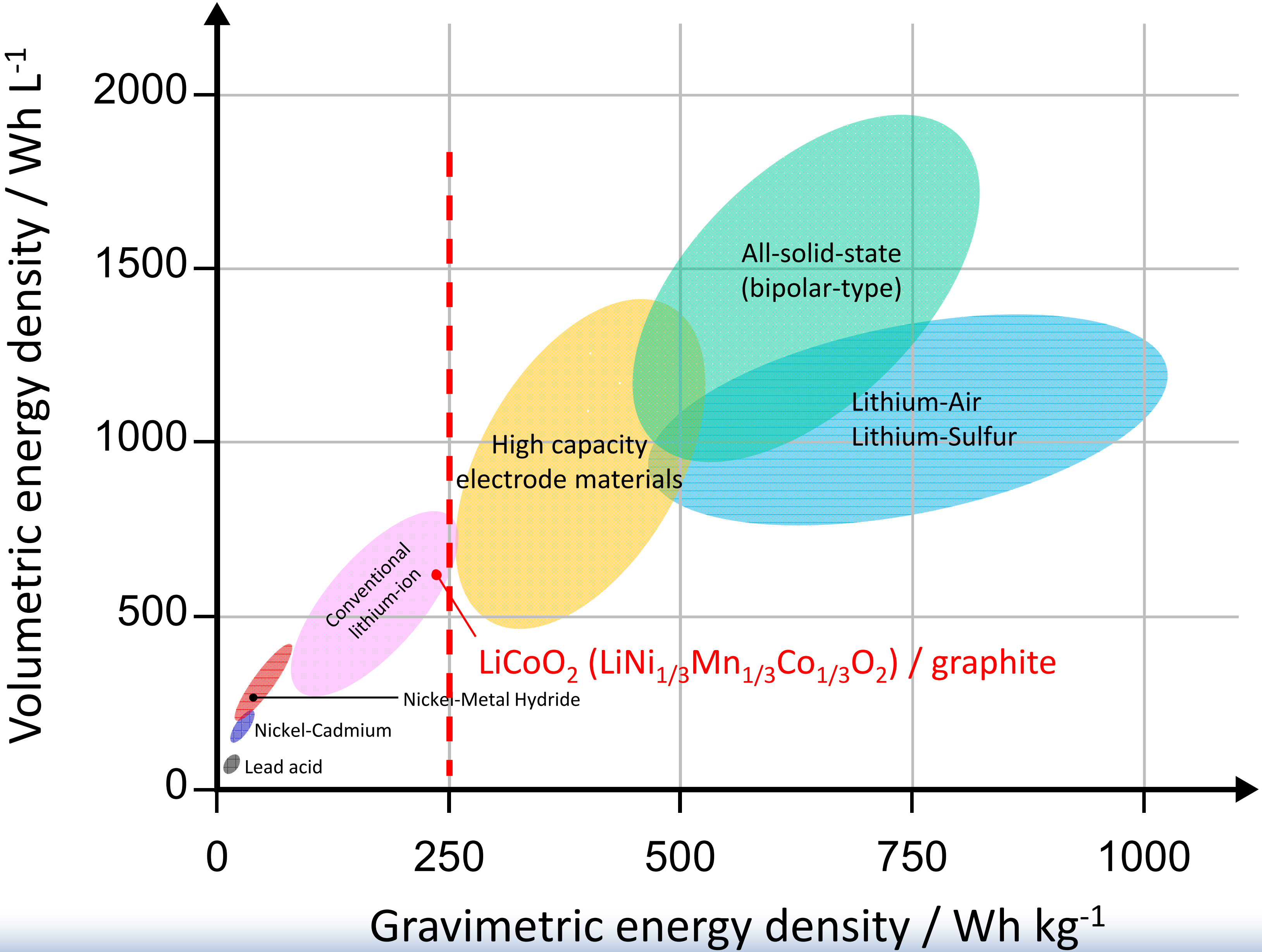
Cathode material

Current Collector Tab

Bipolar-type battery

Cell voltage: 200 V
Energy density: > 500 Wh kg^{-1}
Fast charge/discharge: > 10 min
High safety
Long life

Energy density



Conclusions

3D electrode configuration is one of prospective ways to improve the performance of all-solid-state rechargeable lithium batteries.

For further improvement of cell performance, the following developments are needed:

- Higher aspect ratio in 3D electrode configuration
- Optimization of electrolyte/electrode interface
- Cell stacking for bipolar-type all-solid-state battery