Development of New Electrolyte and Electrode Materials for All-Solid-State Thin Film Lithium Batteries through Solution Process

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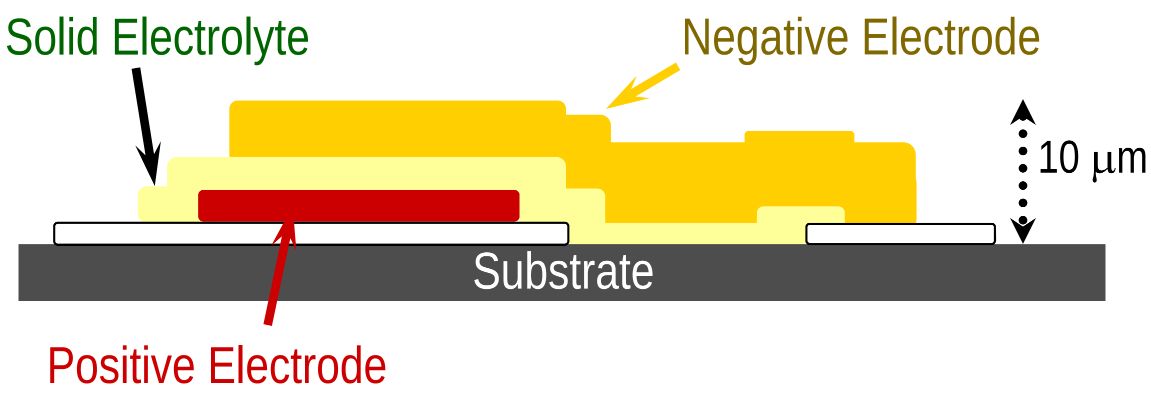
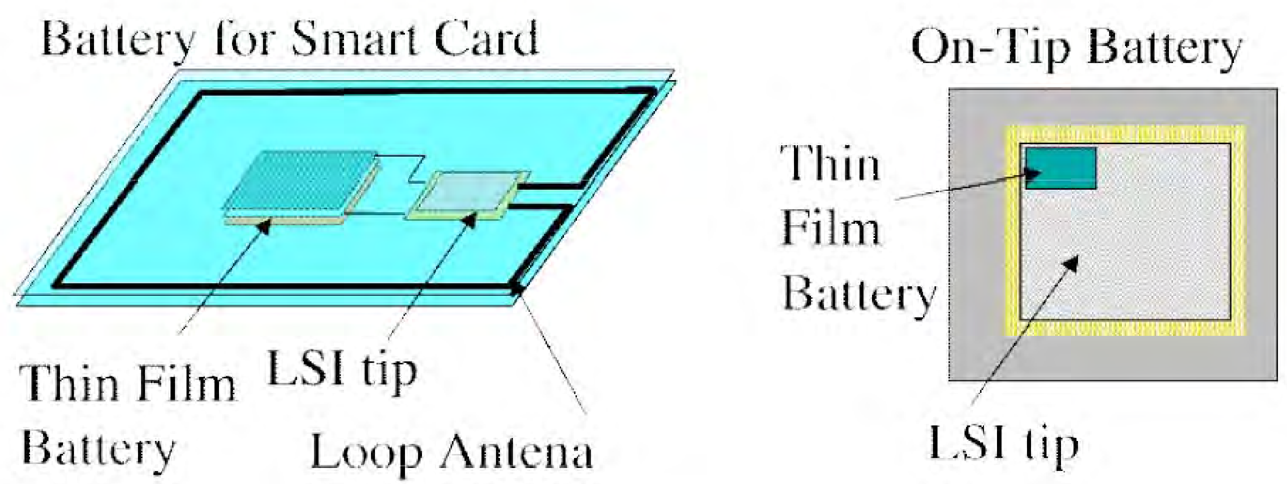
Thin-film battery



Thin film lithium batteries will be used in things like smart cards, RFID tags, and other low power portable devices.



Possible application of thin film lithium batteries

Thin film battery is an important element in **realizing next-generation sheet devices**, as it needs to be formed as a small, thin-film device.

Examples of preparation of thin film batteries by physical processes

Sputtering・・・$LiCoO_2$, $LiMnO_2$, LiPON（lithium phosphate oxynitride）…
Pulse Laser Deposition・・・ $LiCoO_2$, $LiMnO_2$, Li-V-Si-O amorphous thin film

Advantages of solution processes

- **Large area and good quality, or nano-structured thin films can be prepared**
- **Chemical compositions of thin films can be controlled.**
- **Rather thick films are easily obtained.**

Solution processes are very attractive for the development of thin film batteries.

Purpose of our project

Our project attempts **to develop electrolyte and electrode materials for all-solid-state thin film lithium batteries using solution processes**, as a clean and efficient energy production and storage device.

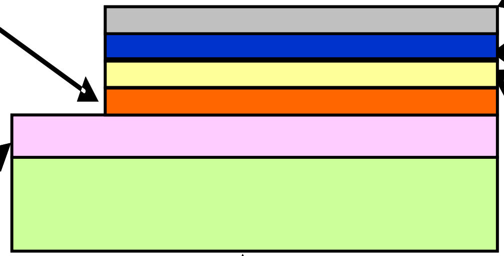
Safe, thin-film lithium secondary cells which are free from such hazards as liquid leakage and/or fires will be developed by employing electrolytes prepared from inorganic or inorganic-organic hybrid solid-state materials by using solution processes.

Conceptual schematic of this project

Current collector: Au

Positive electrodes
OPU: $LiMn_2O_4$

Negative electrodes
OPU: $Li_4Ti_5O_{12}$
CSIC: $Li_4Ti_5O_{12}$

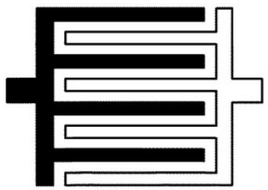


Current collector: Au

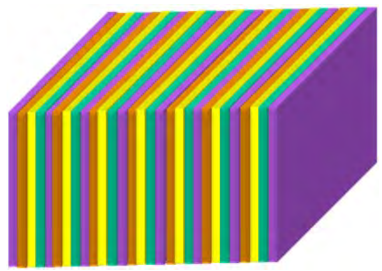
Substrate
Pt, Au, Ti, Pt/Si,
SiO_2 glass, , etc.

Solid electrolyte
OPU: $Li_7La_3Zr_2O_{12}$
$Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$
CSIC: organic-inorganic hybrid

Further development



Micro patterning



Multi layered battery

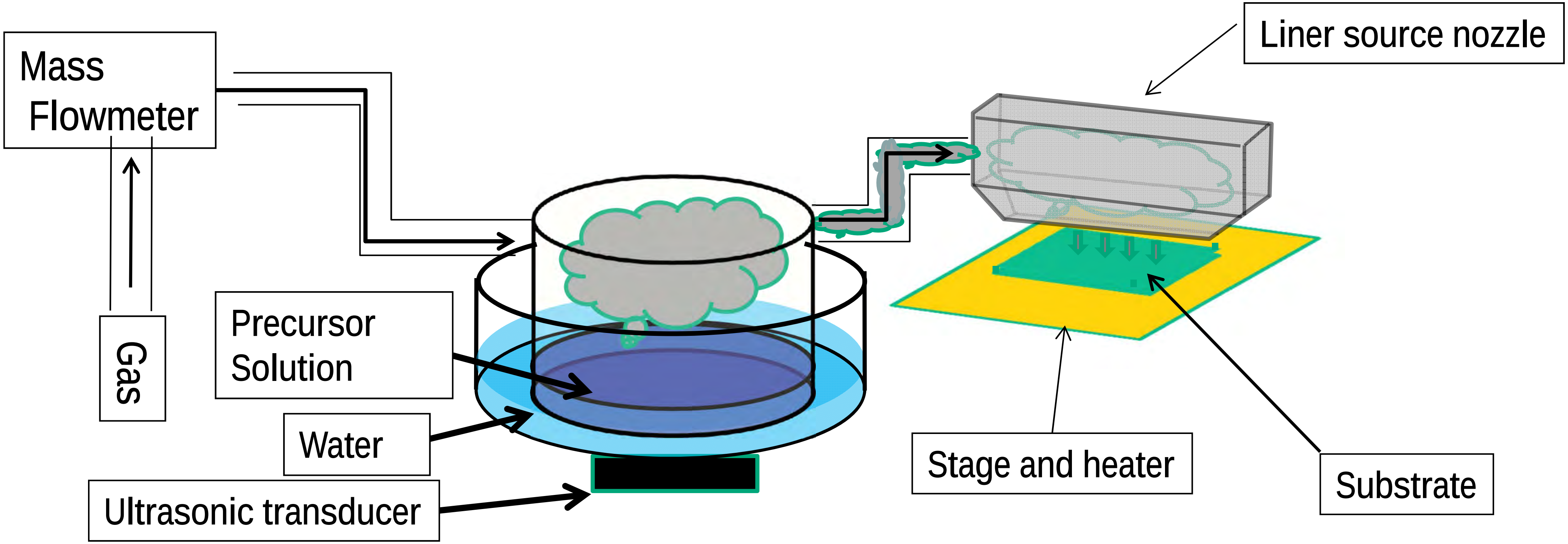
Solution-based processes

Solution-based processes used in OPU, for the preparation of electrode and electrolyte thin films

- Sol-gel process
- Mist-CVD process
- Electrophoretic deposition of particles prepared by sol-gel
- Aerosol deposition of particles prepared by sol-gel

Mist CVD process

In the mist CVD process, aqueous solution of starting material is ultrasonically atomized to form mist particles with a size of about 3 μm, and mists are transferred by a carrier gas to the substrate to form thin films.



Features

1. This process does not need vacuum systems because it is operated at atmospheric conditions.
2. Various precursor solutions can be used for the source, including innocuous and nonpoisonous ones.
3. This process possesses various advantages such as: safety, cost-effectiveness, environmentally friendly, and the ability to apply to various types of materials.

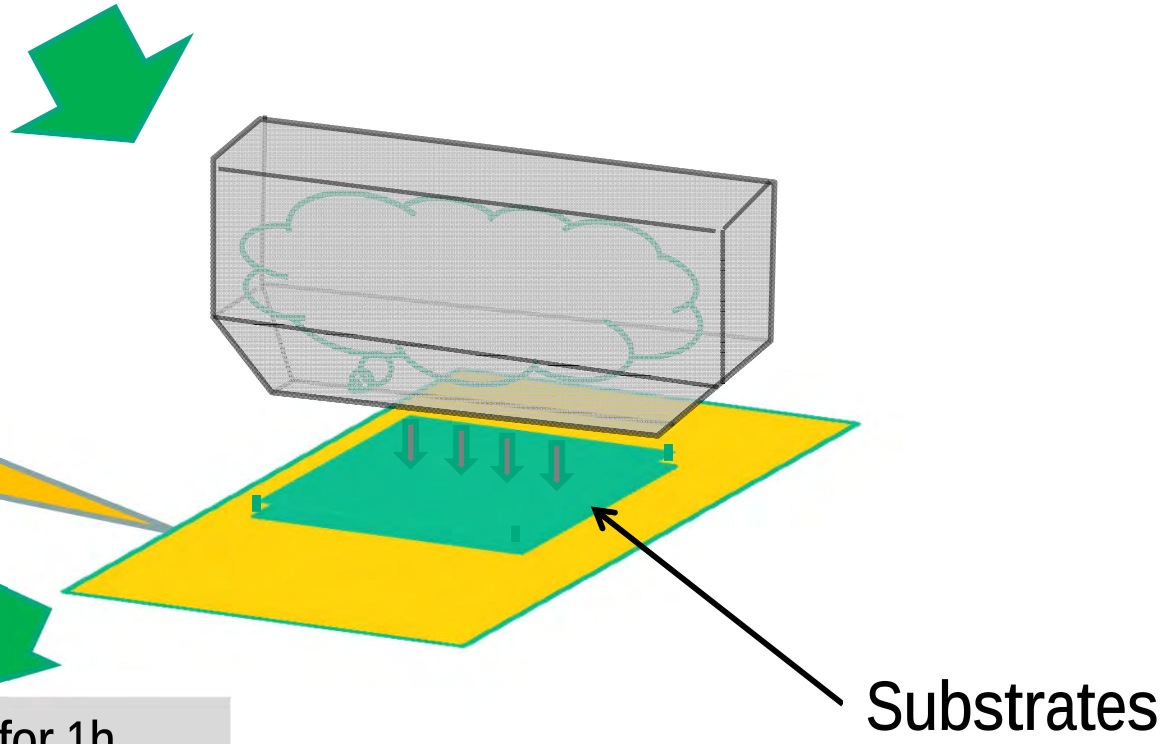
Preparation of $LiMn_2O_4$ thin films by mist-CVD process

0.06M $Mn(OCOCH_3)_2 \cdot 4H_2O$

+ 0.033M $Li(OCOCH_3)$

Molar ratio (Li : Mn=1.1:2)

Flow rates 8 L/min
Substrate temperature 200-400^{o}C

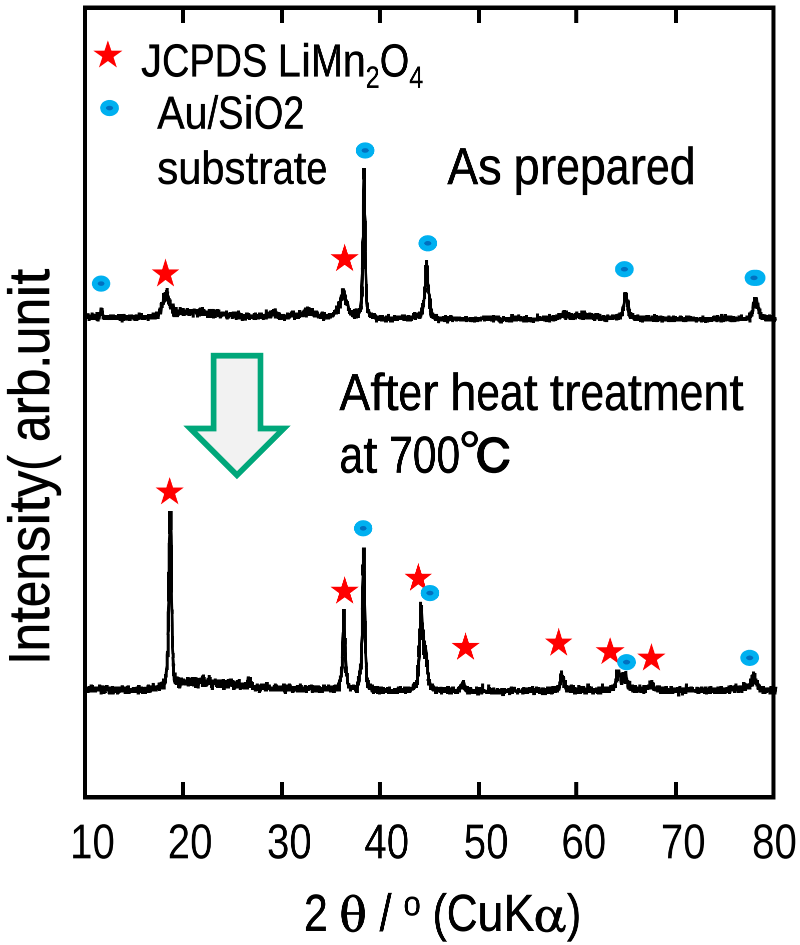


Heat-treated at 500-800^{o}C for 1h

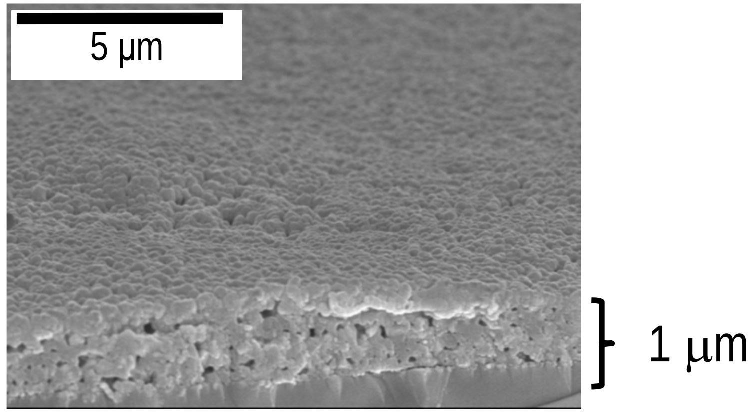
$LiMn_2O_4$ thin films

$LiMn_2O_4$ has advantages of low-cost, environmental friendliness, and high abundance.

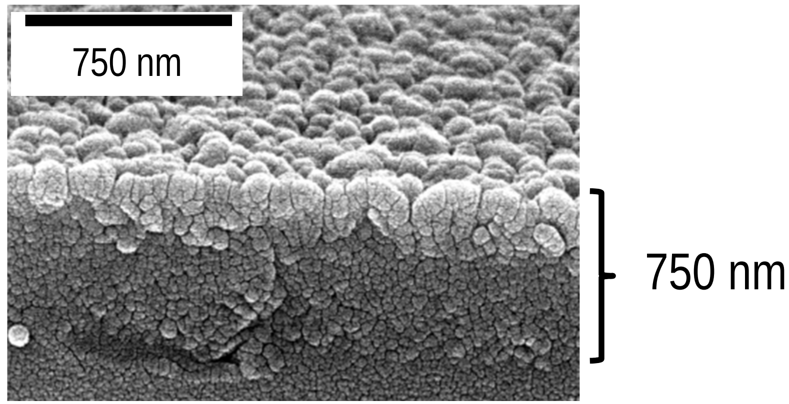
$LiMn_2O_4$ thin films (substrate temperature: 200°C)



As prepared by mist-CVD process

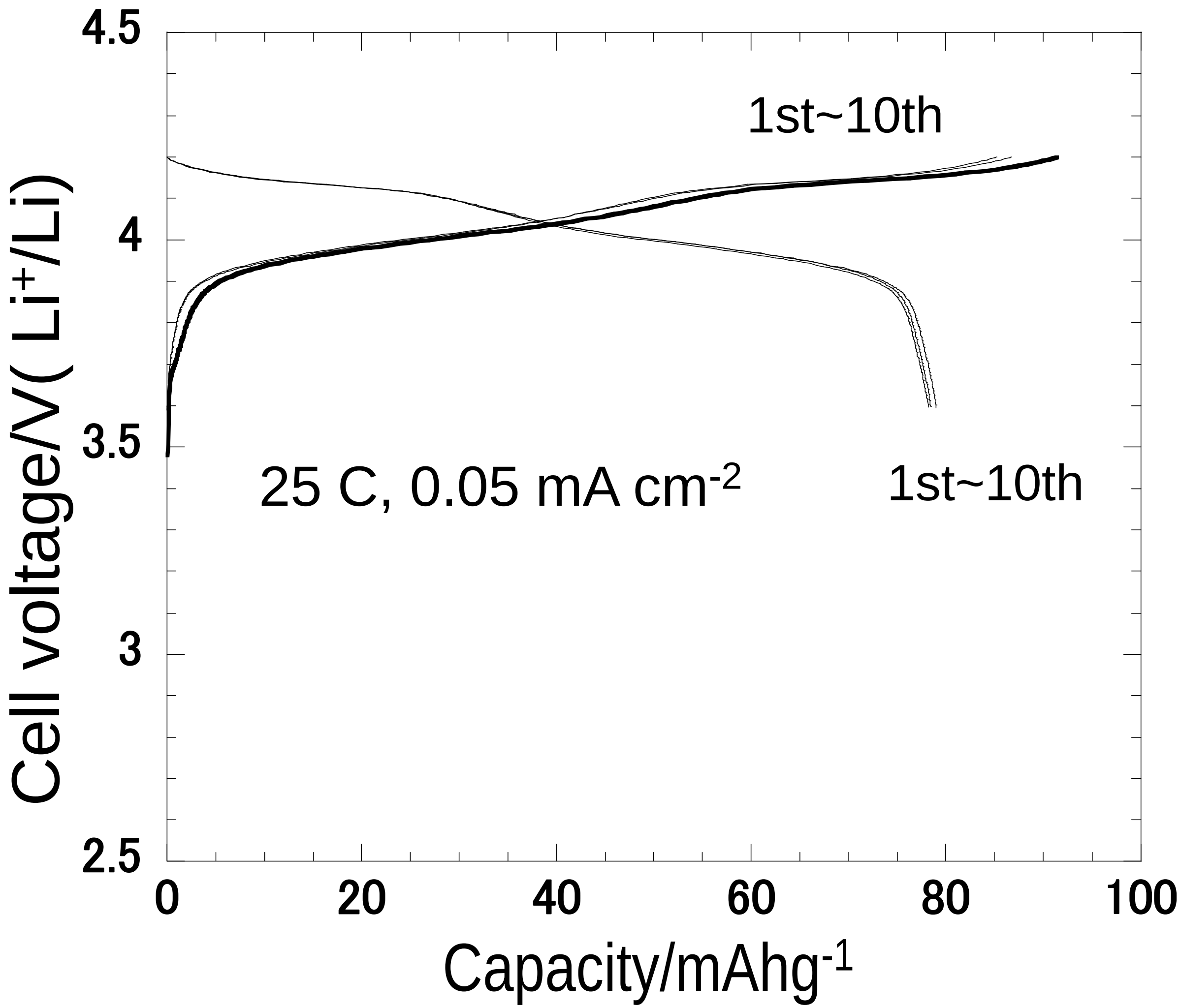


After the heat treatment at 700°C

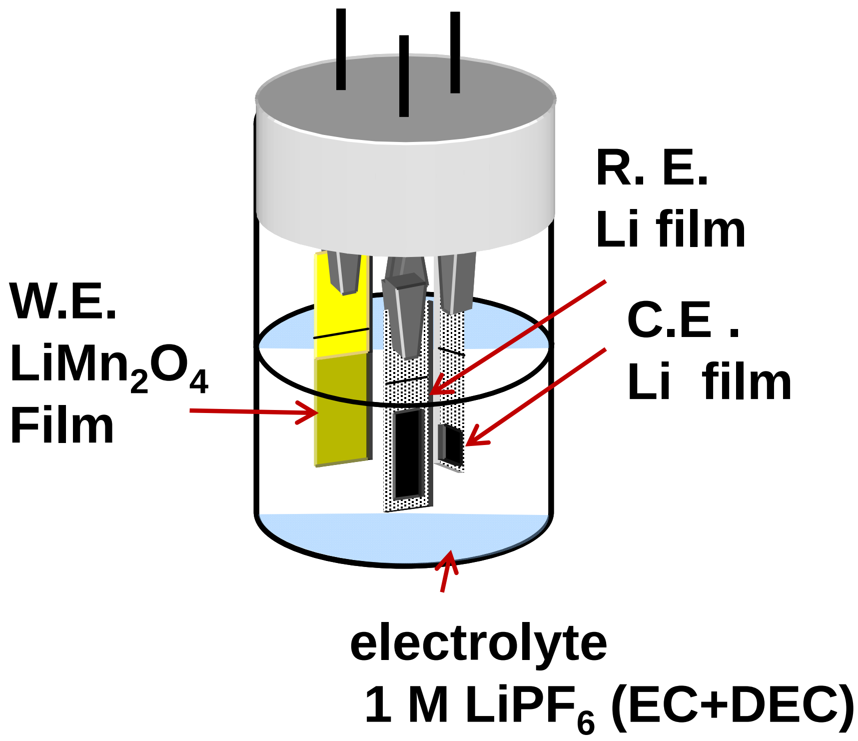


Spinel type $LiMn_2O_4$ single-phase thin film was obtained.

Electrochemical behavior of heat-treated $LiMn_2O_4$ thin film



beaker cell with three electrodes



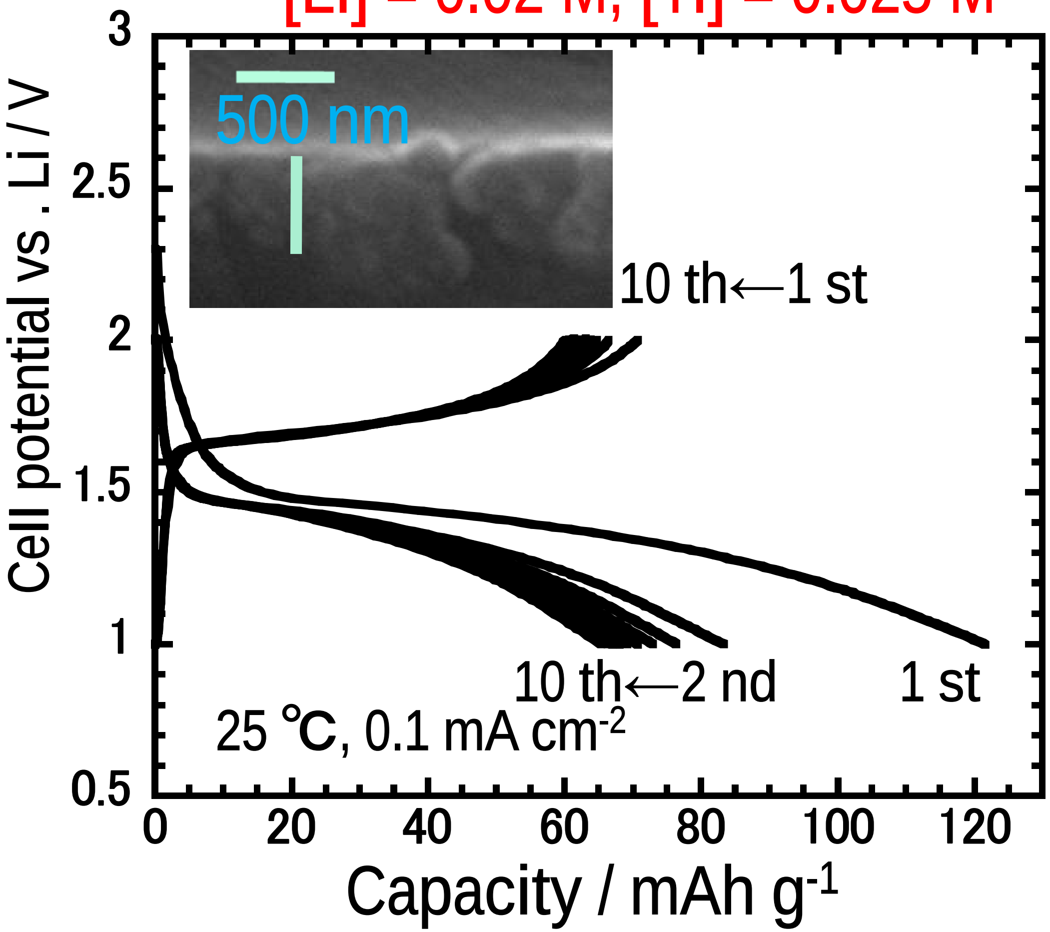
The $LiMn_2O_4$ thin-film electrode produced with the mist CVD method

- Capacity is 80 $mAhg^{-1}$
- Good cycle performance

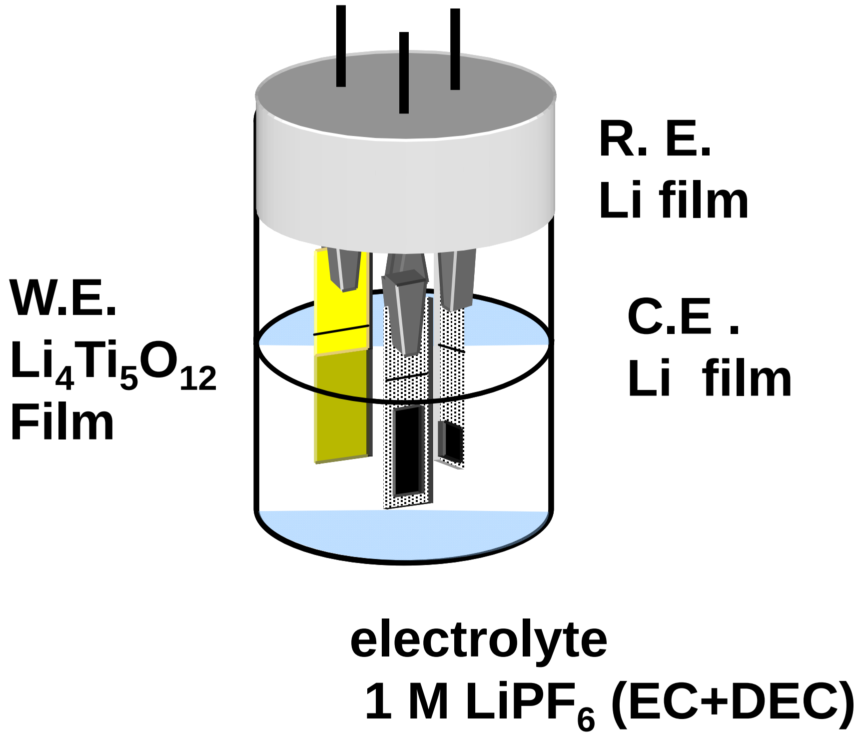
Charge-discharge behavior of $Li_4Ti_5O_{12}$ thin films prepared by the mist-CVD

Substrate temperature :400 ºC + Heat-treatment at 700 ºC for 1 h

[Li] = 0.02 M, [Ti] = 0.025 M



beaker cell with three electrodes



Thick film with cracks showed good cycle performance.

Preparation of $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ thin films by mist-CVD process

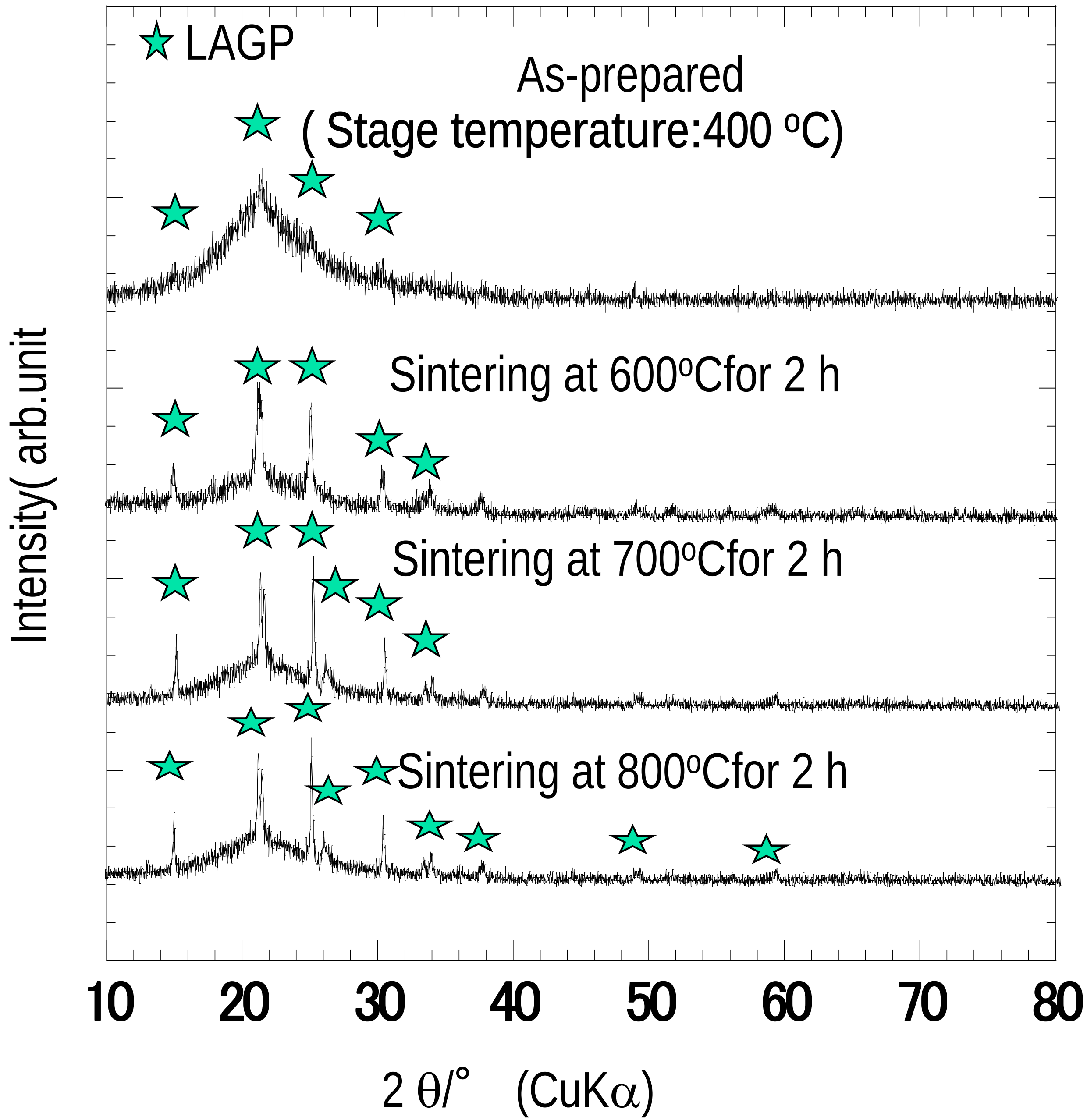
Solid electrolyte for thin film battery

Electrolyte thin films are formed on electrode thin films
=> low temperature synthesis is expected.

⇩

$Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ (LAGP) electrolyte can be prepared with a rather low sintering temperature.

XRD pattern of the LAGP thin films

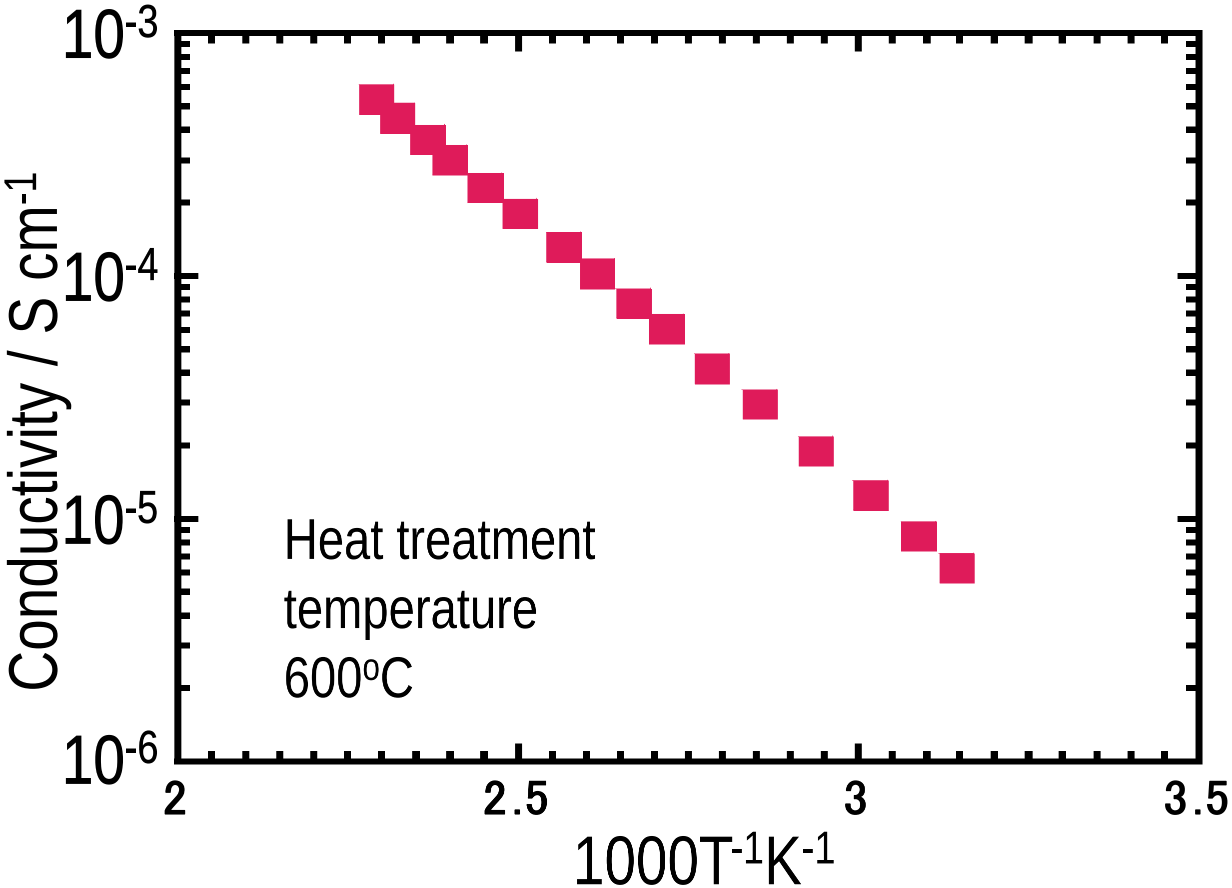


- Peaks due to LAGP were observed in the as-prepared thin film.

- LAGP phase was obtained as single-phase.

- crystallinity increases with an increase in heat treatment temperature.

Ionic conductivity of the LAGP thin film



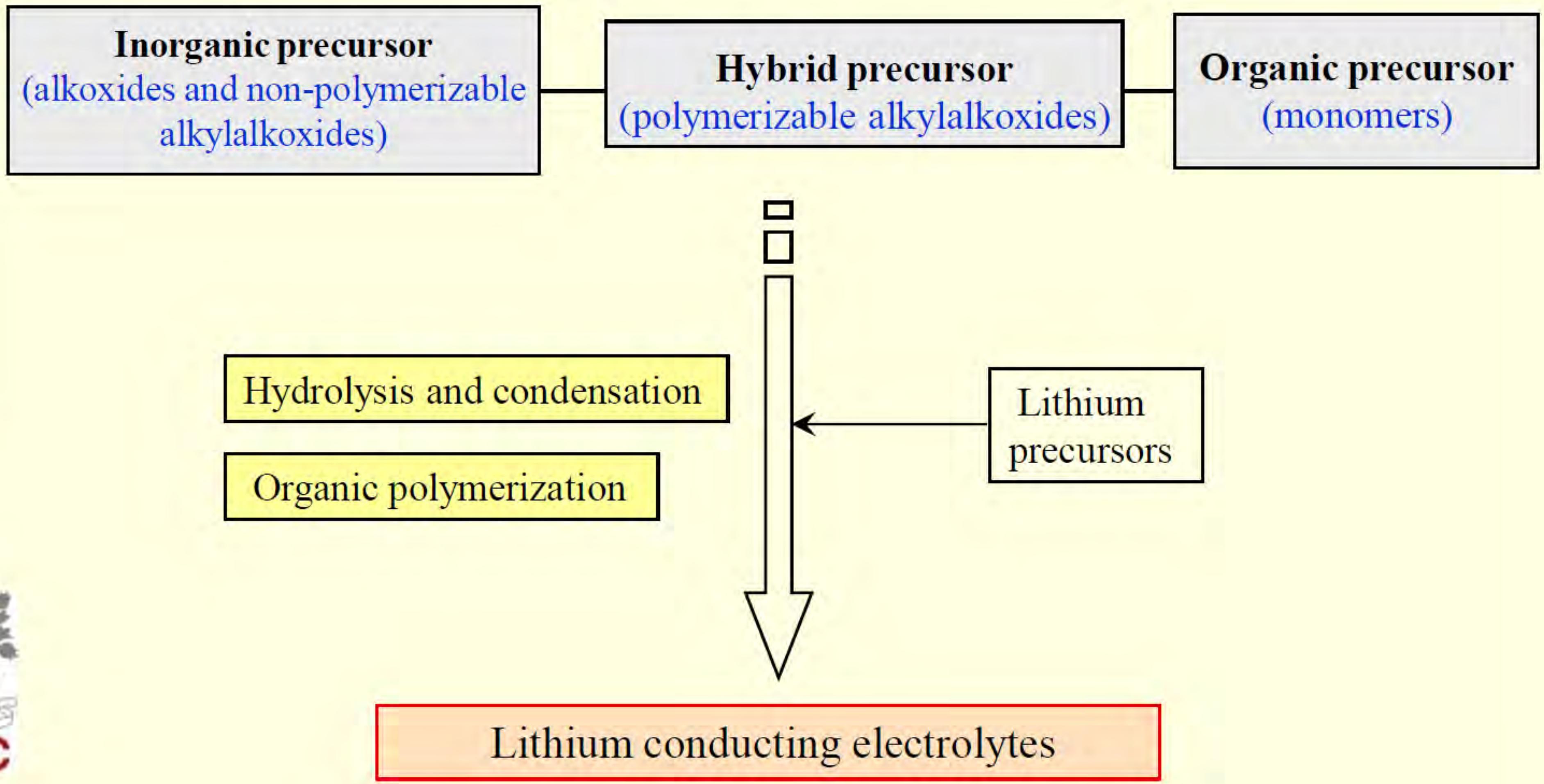
Conductivity in room temperature
: about 2×10^{-6} S cm^{-1}

Activation energy of conduction
: About 40 kJ mol^{-1}

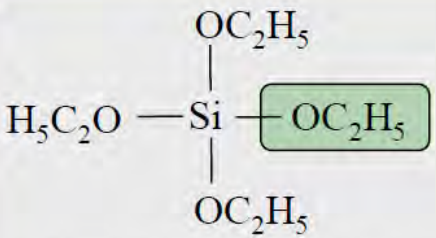
Solid electrolyte

Hybrid organic-inorganic electrolytes

New systems: towards more polymeric materials

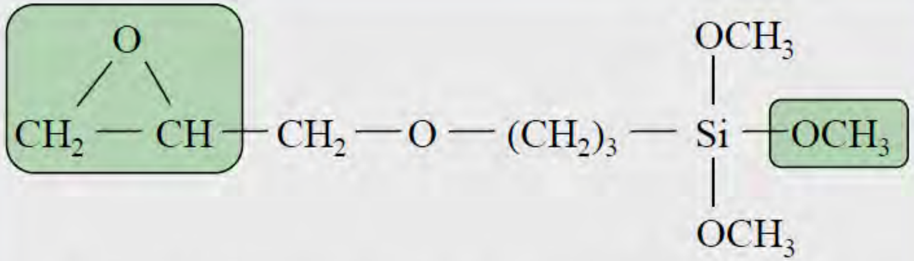


Silica - epoxy electrolytes

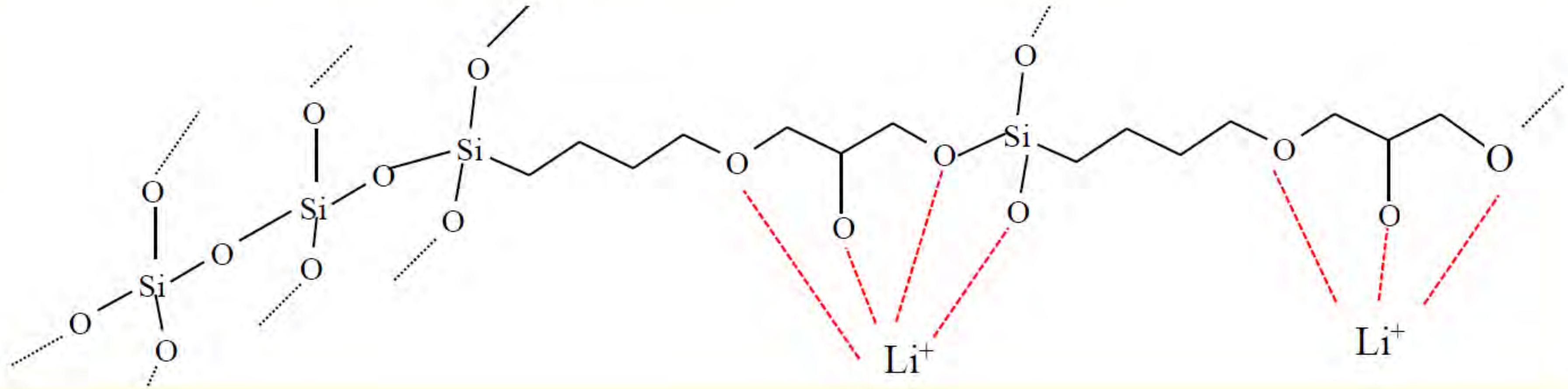


Tetraethyl orthosilicate (TEOS)

Lithium acetate



3-glycidoxypropyl trimethoxysilane (GPTMS)



Conclusions

- $LiMn_2O_4$ cathode thin films, $Li_4Ti_5O_{12}$ anode thin films, and $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ (LAGP) solid electrolyte thin films were prepared by the mist CVD process.

- $Li_4Ti_5O_{12}$ anode thin films were prepared by a sol-gel process.

- New lithium ion conductive inorganic-organic hybrid was developed.