Lecture #13: All Solid-state Thin-film Batteries (micro-battery)

- Thin-film batteries offers advantage where small footprint, low power and thin profile are required (example – on-board micro-chip power for micro-sensors, medical implantable devices, radio frequency identification (RFID) cards, etc.)
- Outstanding cycle-life, calendar life, low self-discharge, and safety
- Fabricated by wide range of deposition (sputtering, pulsed laser deposition (PLD), e-beam, laser ablation, atomic layer deposition (ALD), chemical vapor deposition (CVD), thermal evaporation, etc.) and patterning technologies (mechanical masks, microfabrication technologies compatible with integrated circuit (IC) technology), photolithography, reactive etching, etc.).
- Thin-film / Micro battery: 100 µm x 100 µm
- Negligible SEI formation allows use of high energy anode such as Li metal anode
- Capacity limited by the mass of electrodes
- Slow and costly manufacturing process are current commercial limitations.

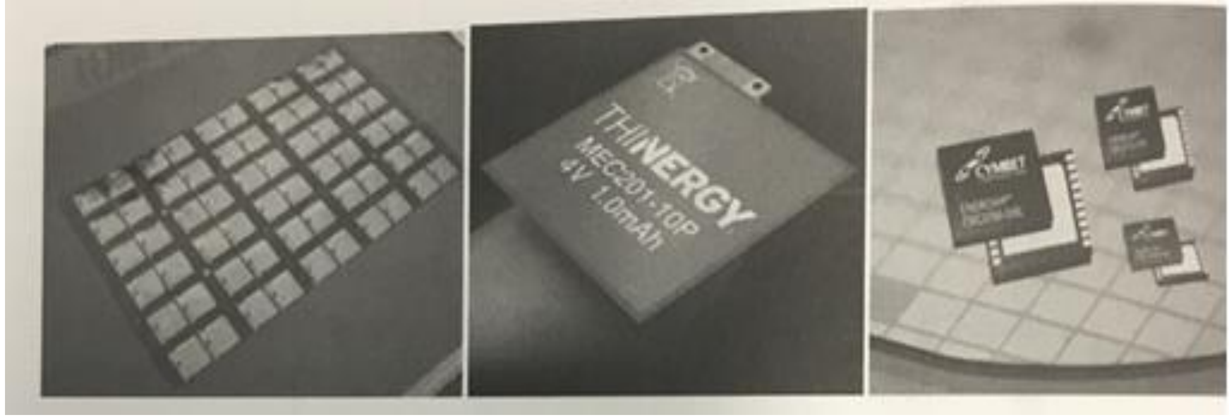


Fig. 1. thin-film batteries by Excellatron, Infinite Power Solutions and Cymbet Corporation

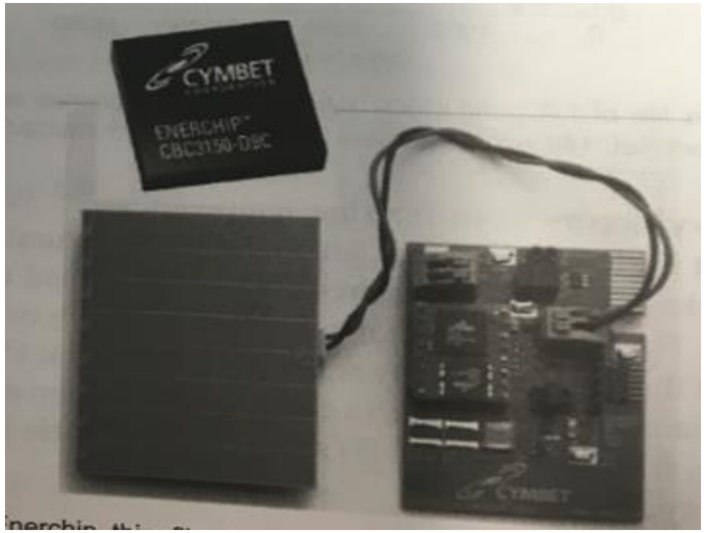


Fig. 2. Enerchip thin-film battery and the energy harvesting evaluation kit manufactured by Cymbet Corporation

Fabrication methods

Fabrication techniques:

- Pulsed laser deposition (PLD) – high power pulsed laser (KrF excimer laser (ca. 1 J/pulse) ablate material from target under vacuum.
- Magnetron Sputtering – (gases like Ar, O_2, N_2 ionized to Ar+, O2+, N2+ plasma that then accelerated by a high electric field toward target. DC sputtering is used for conducting material like metals and for non-conducting RF (AC 13.56 MHz) and magnetron sputtering are used).
- e-beam / Laser ablation physical vapor deposition (materials having high melting point ~1500°C are melted by electron beam).
- Atomic layer deposition (ALD) - These precursors react with the surface of a material one at a time in a sequential, self-limiting, manner.
- Chemical vapor deposition (CVD) – precursor gas or gases flow into chamber containing one or more heated substrates (chemical reaction sites) to be coated.
- Sol-gel deposition viscous solution of precursors are applied using spray, dip, spin coating conditioned (thermal treatment).
- Electrochemical deposition – conducting materials like cathode, Li etc. can be electrochemically deposited on desired substrate.
- Thermal evaporation – materials (<1500°C) are melted and vaporized under vacuum and deposited on substrate.

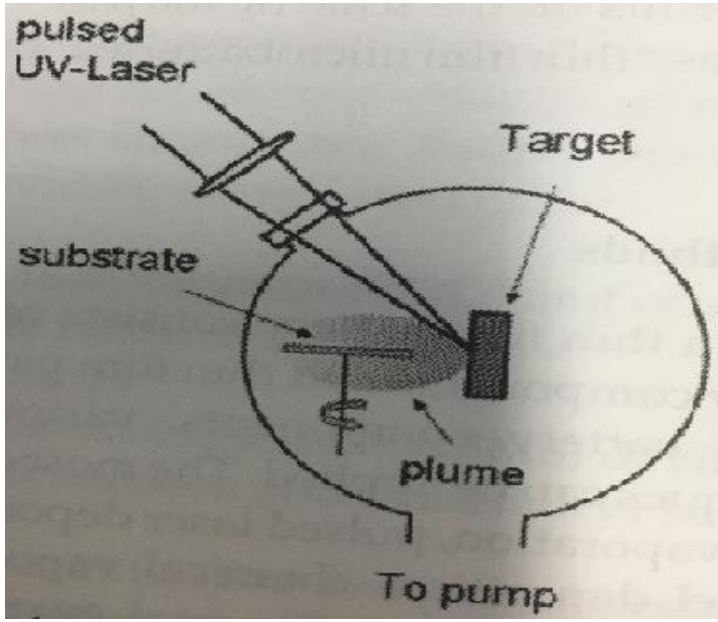


Fig. 3. PLD system. The ablated material is collected on substrate in the form of thin-film.

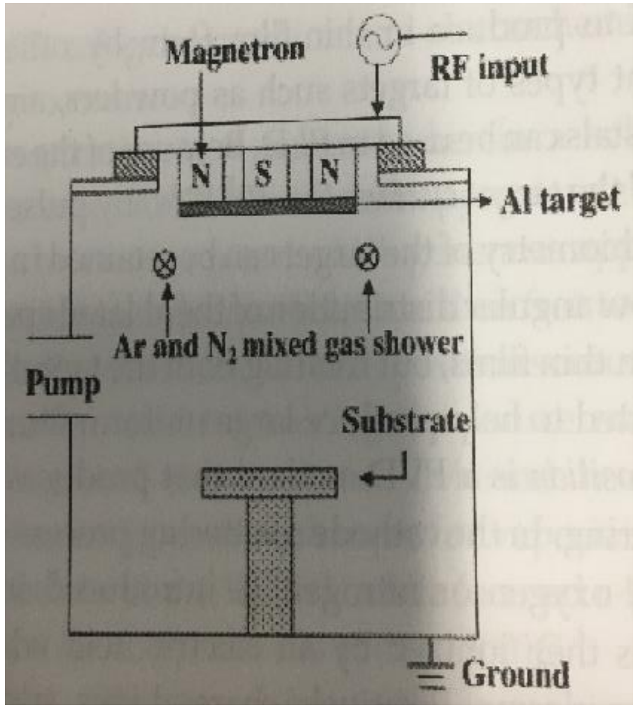


Fig. 4. reactive RF magnetron sputtering system.

Fabrication methods: patterning, CCs, and device fabrication

- Mechanical mask: stainless-steel (limited to > several mm2 area
- Photolithography: transfers a pattern using light or electrons onto a substrate, usually a wafer.

  - Multilayers are prepared on substrates which could be silicon wafers, alumina plates, metal foils and plastics.
  - Cell components: cc, cathode film, solid-electrolyte film, anode film and protective coating.

- CCs: good adhesion to substrate, high temperature stability (200-1200°C) in oxidizing atmospheres
- Example: Titanium (Ti), gold (Au), platinum (Pt), Cu, TiN

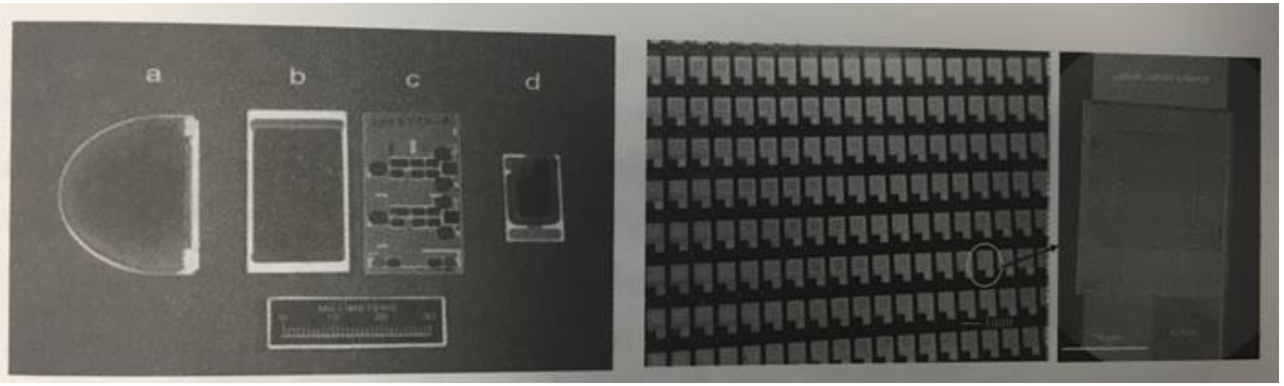


Fig. 5. thin-film batteries patterned by mechanical masks (left) and microfabrication procedures (right)

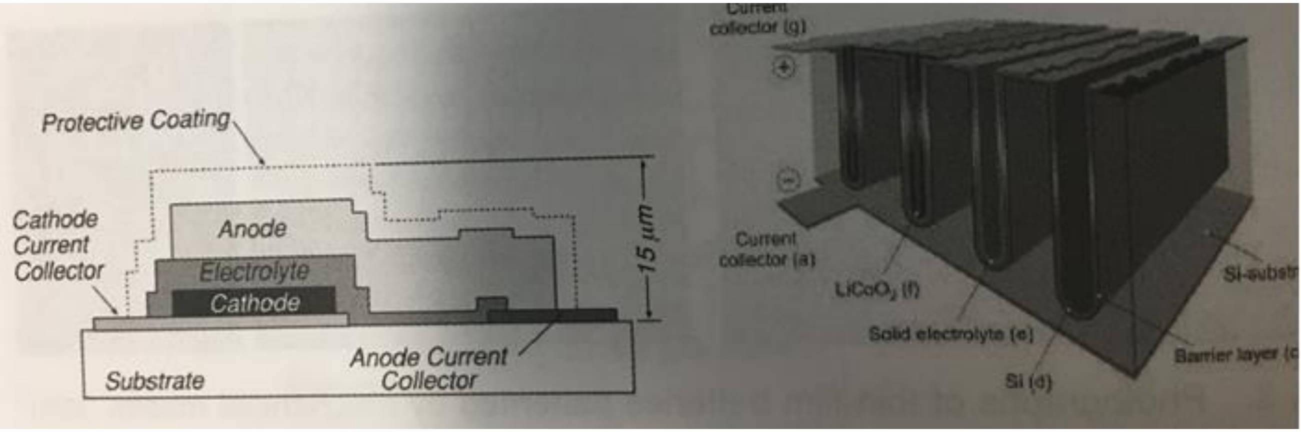


Fig. 6. thin-film batteries 2D (left) and 3D (right).

- Protective coating: eliminate exposure of battery components to air/moisture
- Example: Metals, ceramics, ceramic/metal combination, polymer (Parylene)-metal combination, polymer/ceramic combination or a polymer/metal/ceramic combination.

Cell components: Cathode LiCoO2

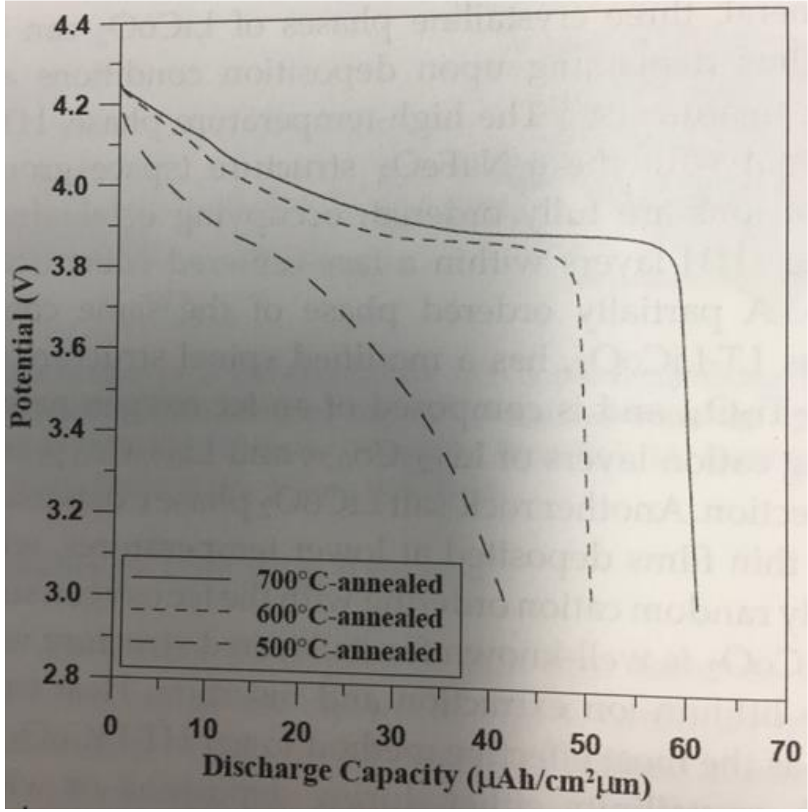


Fig. 7. discharge Li/LiCoO$_2$ cell with LiCoO$_2$ films annealed in O2 at 500, 600, and 700°C for 2 h.

- Post fabrication thermal conditioning changes crystal structure (Li+ ion occupancy and transport) and hence cell performance.
- High temperature may cause film crack or voids.

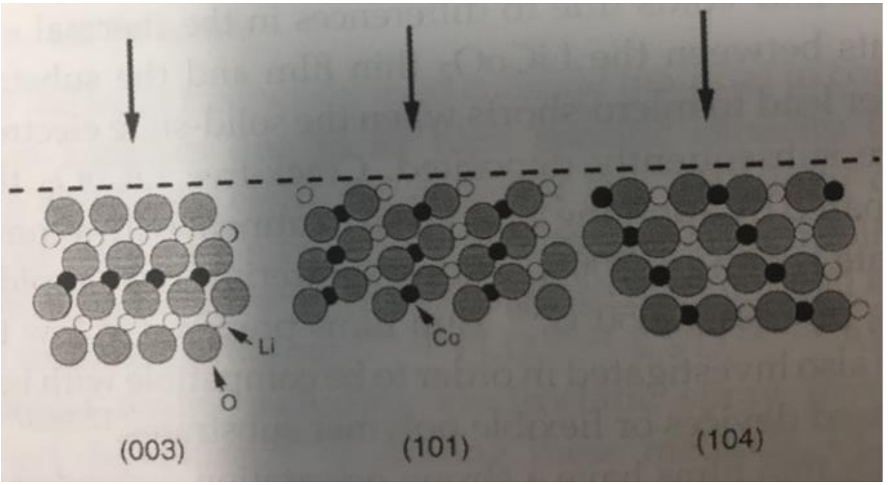


Fig. 8. Lithium-ion diffusion and intercalation pathways in LiCoO$_2$ thin-film layers oriented to various lattice planes.

- 003 orientation – Li+ intercalation pathways is horizontal to the substrate surface
- 101 orientation - Li+ intercalation pathways is vertical to the substrate surface
- 104 orientation exhibits a larger Li+ chemical diffusion coefficient value than the 003 oriented film.
- The crystalline lattice growth of LiCoO2 thin-film is determined by the competition between the surface energy and volume strain energy.
- Orientation is controlled by film thickness, deposition method, and substrate temperatures during deposition.

Cell components: Cathode LiMn2O4, LiFePO4

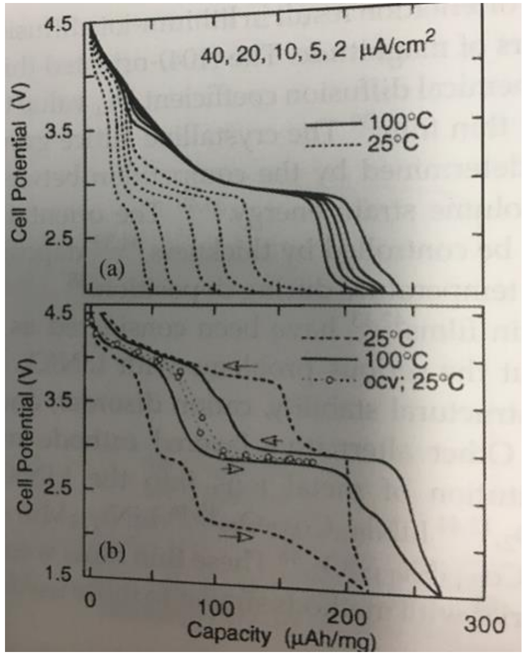


Fig. 9. Li/LiMn2O4 discharge at 25 and 100°C with increasing discharge current densities.

- Performance at higher temperature is better (top)
- Polarization at lower temperature is more (bottom).

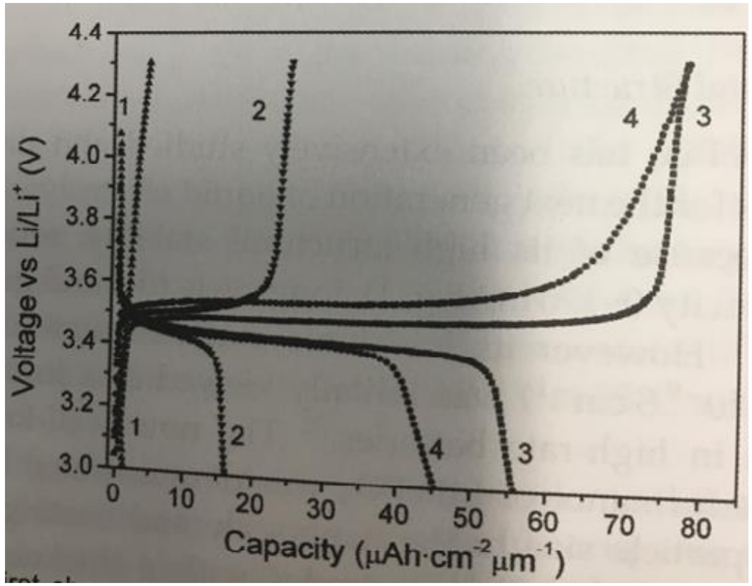


Fig. 10. Li/LiFePO4 discharges with variable substrate temperatures (1- 25, 2- 300, 3- 400, 4 – 500°C.

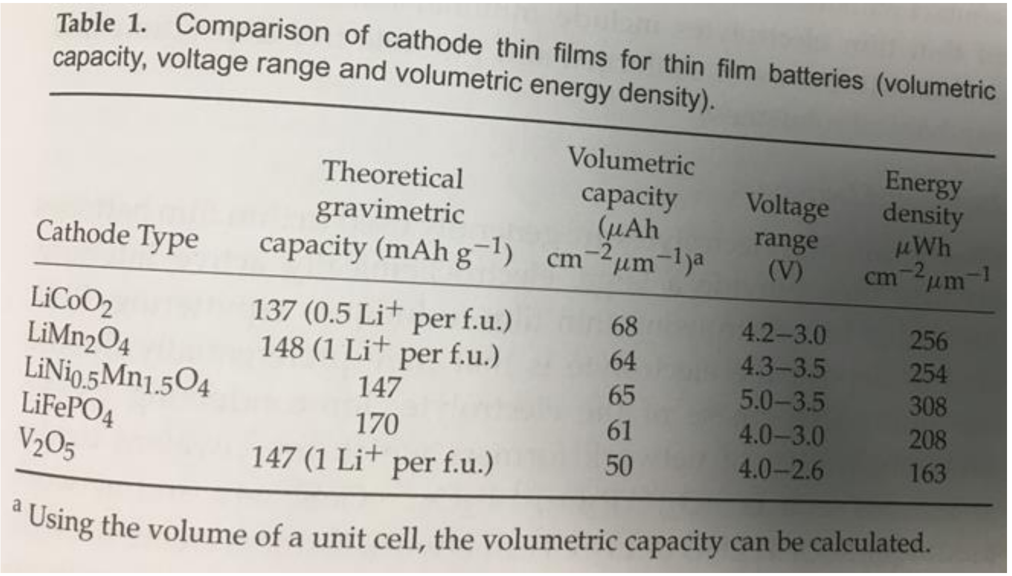


Table 1. Comparison of cathode thin films for thin film batteries (volumetric capacity, voltage range and volumetric energy density).

Cathode Type	Theoretical gravimetric capacity (mAh g^{-1})	Volumetric capacity (μAh $cm^{-2}\mu m^{-1}$)[a]	Voltage range (V)	Energy density μWh $cm^{-2}\mu m^{-1}$
$LiCoO_2$	137 (0.5 Li^+ per f.u.)	68	4.2–3.0	256
$LiMn_2O_4$	148 (1 Li^+ per f.u.)	64	4.3–3.5	254
$LiNi_{0.5}Mn_{1.5}O_4$	147	65	5.0–3.5	308
$LiFePO_4$	170	61	4.0–3.0	208
V_2O_5	147 (1 Li^+ per f.u.)	50	4.0–2.6	163

[a] Using the volume of a unit cell, the volumetric capacity can be calculated.

Cell components: Electrolyte

Glassy, inorganic electrolytes: LiPON – commercially used electrolyte:

- High stability with Li anode
- Low Li^+ ion conductivity; $\sigma = 10^{-6}$ S/cm

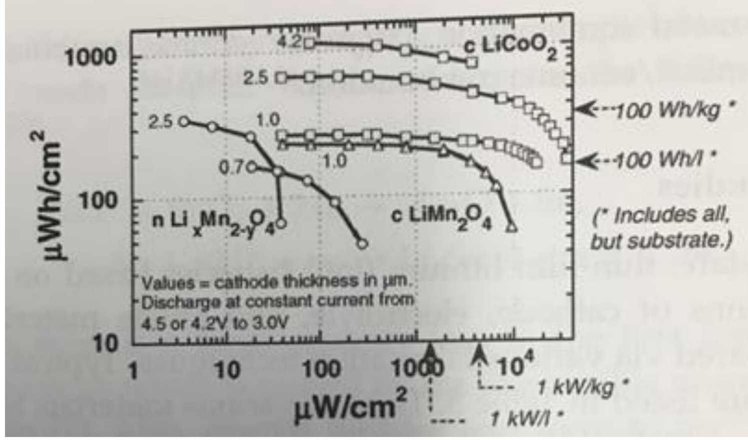


Fig. 11. Power and energy per active battery area for Li/LiPON/$LiCoO_2$ ($LiMn_2O_4$ and $Li_xMn_{2-y}O_4$). Cathode thickness is given in µm.

Ceramic, inorganic electrolytes:

- Perovskite – $Li_{0.35}La_{0.55}TiO_3$; $\sigma = 10^{-4}$ S/cm
- NASICON – $LiTi_2(PO_4)_3$; $\sigma = 10^{-3}$ S/cm
- Garnet – $Li_7La_2Zr_2O_{12}$; $\sigma = 10^{-4}$ S/cm
- Sulfides – Li_2S-GeS_2; $\sigma = 10^{-2}$ S/cm
- low stability with Li anode
- High Li+ ion conductivity

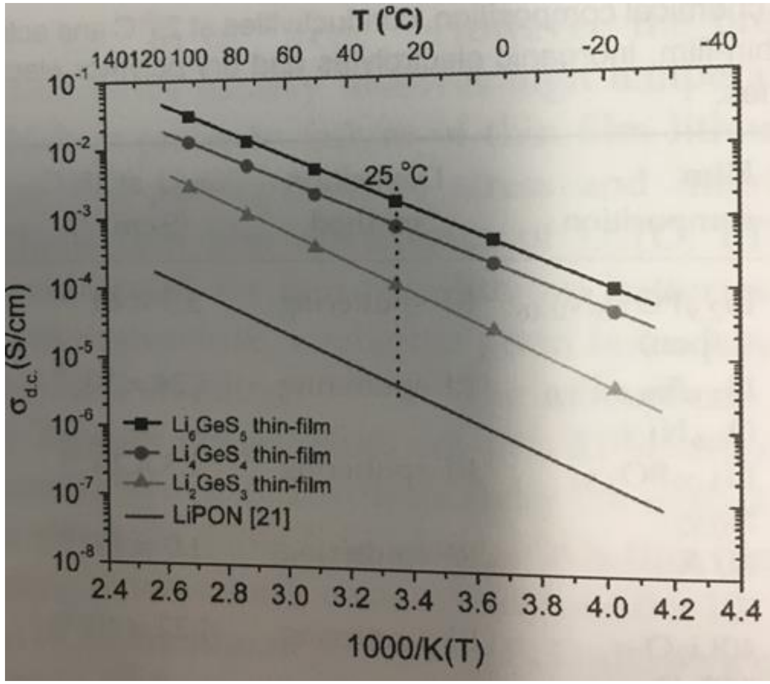


Fig. 12. ion conductivity comparison between sulfides and LiPON.

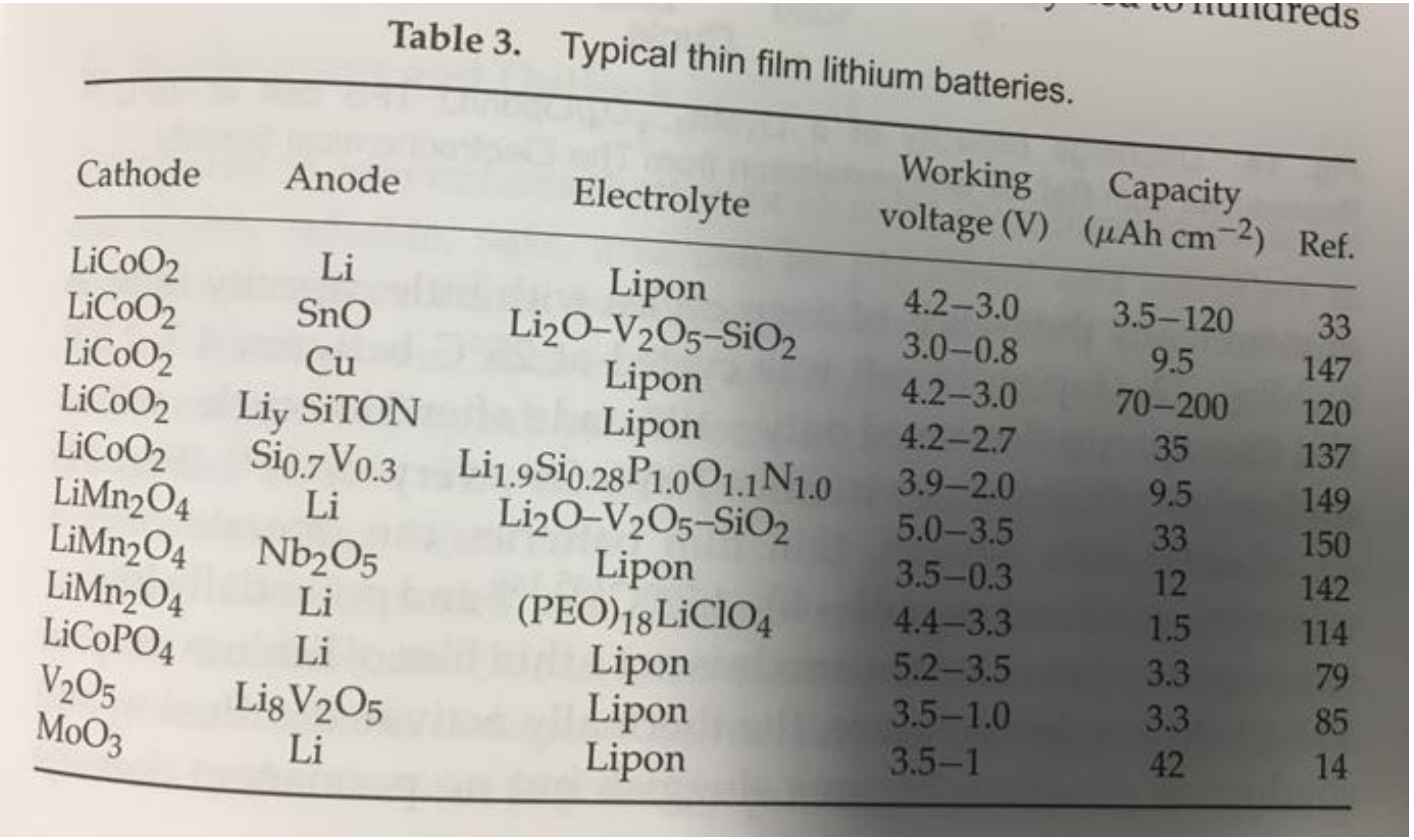
Polymer electrolytes: example PEO based:

- High manufacturability
- Low Li^+ ion conductivity; $\sigma = 10^{-6}$ S/cm

Cell components: Anodes and typical thin-film batteries and cycling performances at high temperature

Potential Anodes:

- Lithium
- Graphitized carbon
- Lithium titanate Li4Ti5O12
- Metal oxide TiO2, etc.



to hundreds

Table 3. Typical thin film lithium batteries.

Cathode	Anode	Electrolyte	Working voltage (V)	Capacity (μAh cm^{-2})	Ref.
$LiCoO_2$	Li	Lipon	4.2–3.0	3.5–120	33
$LiCoO_2$	SnO	$Li_2O–V_2O_5–SiO_2$	3.0–0.8	9.5	147
$LiCoO_2$	Cu	Lipon	4.2–3.0	70–200	120
$LiCoO_2$	Li_y SiTON	Lipon	4.2–2.7	35	137
$LiCoO_2$	$Si_{0.7}V_{0.3}$	$Li_{1.9}Si_{0.28}P_{1.0}O_{1.1}N_{1.0}$	3.9–2.0	9.5	149
$LiMn_2O_4$	Li	$Li_2O–V_2O_5–SiO_2$	5.0–3.5	33	150
$LiMn_2O_4$	Nb_2O_5	Lipon	3.5–0.3	12	142
$LiMn_2O_4$	Li	$(PEO)_{18}LiClO_4$	4.4–3.3	1.5	114
$LiCoPO_4$	Li	Lipon	5.2–3.5	3.3	79
V_2O_5	$Li_8V_2O_5$	Lipon	3.5–1.0	3.3	85
MoO_3	Li	Lipon	3.5–1	42	14

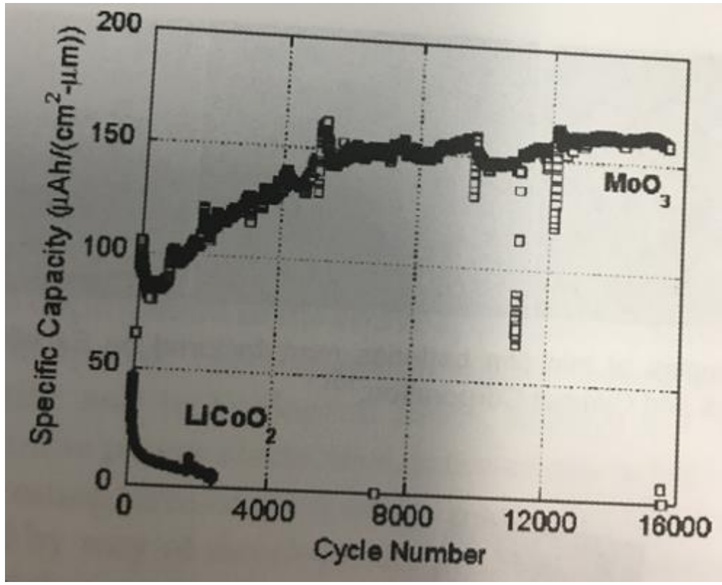


Fig. 13. cycle life of Li/LiPON/$LiCoO_2$ (MnO3) thin-film batteries at 150°C.

Future outlook:

Future expansion of thin-film batteries will depend on progress in three fields:

- new ultra-low power electronics,
- higher efficiency energy harvesters (solar, thermoelectric, RF, etc.),
- Advancements in the solid-state battery field (high energy electrodes, high conductivity-high electrode stability electrolytes, better and faster fabrication techniques, robust cell packaging.