Battery (related) research at SDU

Per Morgen

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in collaboration with

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and

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Activities at Odense, 1973-2013

Surface physics

- Physics (electronics and optics) of clean surfaces
- Reactions and chemistry at surfaces
- Thin film systems: Oxides, nitrides, carbides and metals
- Tribology and rheology
- Analytical techniques

Materials science

- Nanostructured materials: 1D-, 2D-, and 3D SiC; porous alumina
- Plasmonic structures: Au, Ag, and Cu on inverted nanodomes (anod. alumina)
- Electrode- and electrolyte materials and deposition for microbatteries (Bangalore)

Energy and environment

Vacuum based processing

- Thin film composite systems (SONOS) for flash disks; microbatteries (plasma))
- New dielectrics for MOS
- Ultrathin SiC films on Si
- In-situ growth of oxides, carbides and nitrides (films)

Furnace or wet processes

- Conversion of C into SiC (hydrogen storage; diesel particle filters and catalyst supports; fuel cell catalyst support)
- Anodization of Al forming self-organized porous alumina
- Li-air batteries
- Corrosion studies

Energy R/D in Odense

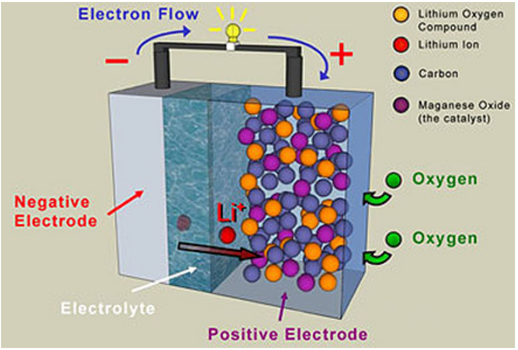
History at SDU (Odense)

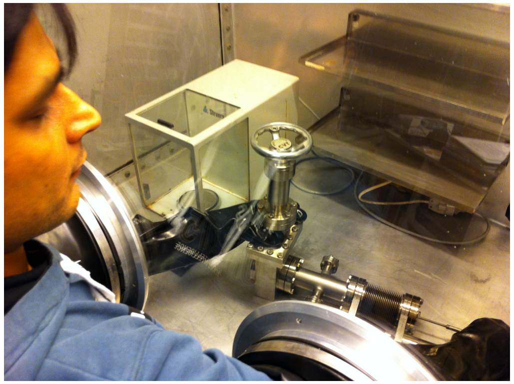
- Energilaboratoriet (Johs Jensen et al.): Li-batteries
- Development of electrolyte with Harwell (Li-ion)
- Spin-out companies: Hope Batteries, IRD, Danionics, and one-man companies
- Technical Faculty (2012): An education in Energy Systems

Present developments

- Fuel cell research with IRD
- Functional nanomaterials with Kiel (Fachhochschule)
- Hydrogen storage materials
- Photovoltaic nanostructures
- ReLiable: Li-air batteries
- Supercapacitors with Kiel

ReLiable Odense





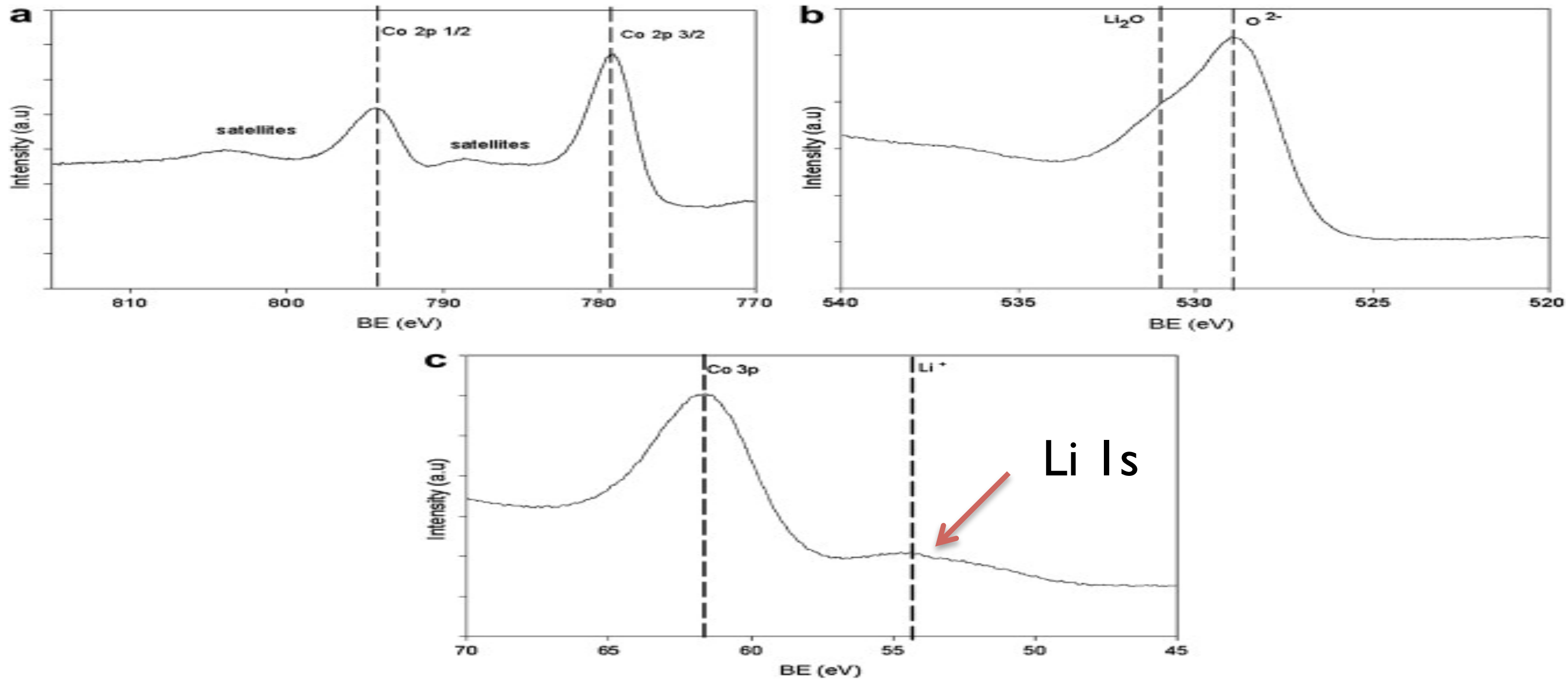
Post. doc. Rajnish Dhiman, PhD

Work packages:
(1) Electrolyte selection (DME for now)
(2) Studies of interfaces with relevant techniques (from prototypes)

Facilities:

- Glove box and transfer system
- Surface analytical instrumentation
- AFM and STM
- Vacuum based deposition and plasma
- Raman microscopes
- X-ray diffraction
- Electrochemical workstations (Tech.)
- Electron microscopes with EDS / AES
- Gas evolution monitoring

Examples of XPS ($LiCoO_2$)



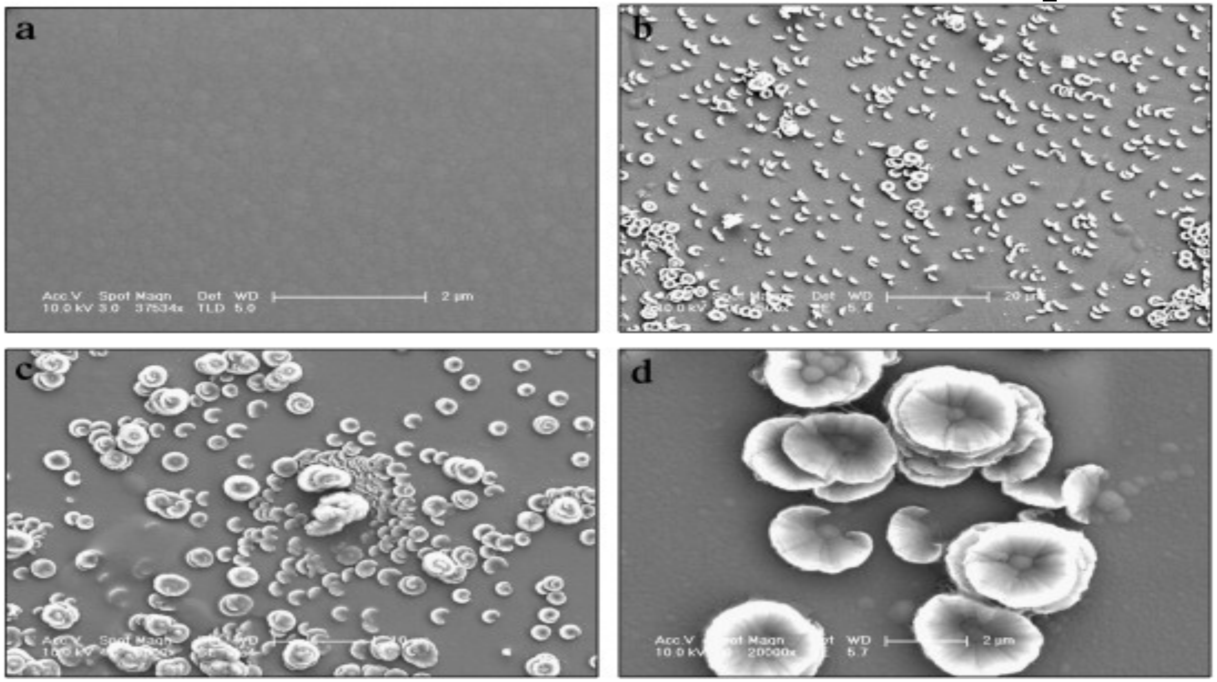
Co 2p, O 1s and Li 1s XPS spectra of LiCoO 2 thin film.

C.S. Nimisha , M. Ganapathi , N. Munichandraiah , G. Mohan Rao
Studies on the target conditioning for deposition of LiCoO2 films

Vacuum Volume 83, Issue 6 2009 1001 - 1006

http://dx.doi.org/10.1016/j.vacuum.2008.12.002

Other techniques



SEM

LiPON
sputtered film

SEM micrographs from LiPON films, (a) fresh sample after fabrication, (b), (c), (d) exposed samples

C.S. Nimisha , G. Mohan Rao , N. Munichandraiah , Gomathi Natarajan , David C. Cameron

Chemical and microstructural modifications in LiPON thin films exposed to atmospheric humidity

Solid State Ionics Volume 185, Issue 1 2011 47 - 51

http://dx.doi.org/10.1016/j.ssi.2011.01.001

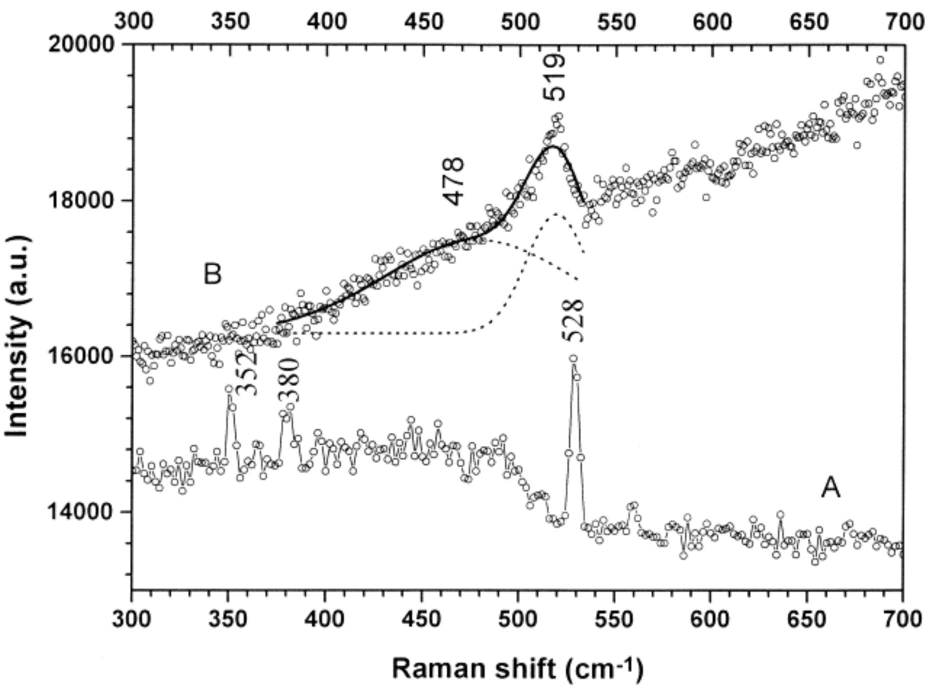
Materials issues for Li-batteries

- Electrode materials (ex. non-Li anode materials)
- Electrolyte materials (aprotic for Li-air)
- Packaging (sealing, temperature control)
- Connections (stable, non-corrosive)
- Charging and discharging process reversibility
- Role of material crystallinity and crystallography (perovskites)
- New nanostructures to overcome lacking functionalities of conventional material classes (high porosity)
- Tailoring of material conductivity and stability vs. cycling
- New combinations of materials (ionic and electronic cond.)

Working with Li on Si (SiC)

The crystal structure and morphology of nanosized Si particles and wires after Li-insertion/extraction electrochemically have been studied by ex-situ XRD, Raman spectroscopy and electronic microscopy.

Raman spectra of the Li-inserted SiNWs electrode after annealing treatment.
(A) Li insertion;
(B) after step (A), then vacuum-annealing at 400°C for 5 h.



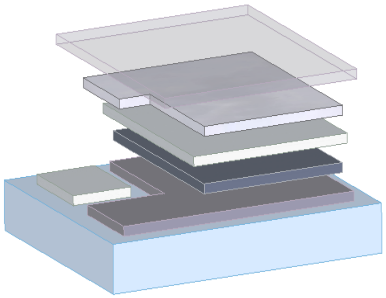
The crystal structural evolution of nano-Si anode caused by lithium insertion and extraction at room temperature (Solid State Ionics)
Hong Li[a], Xuejie Huang[a], Liquan Chen[a, ,], Guangwen Zhou[b], Ze Zhang[b], Dapeng Yu[c], Yu Jun Mo[d], Ning Pei[d]

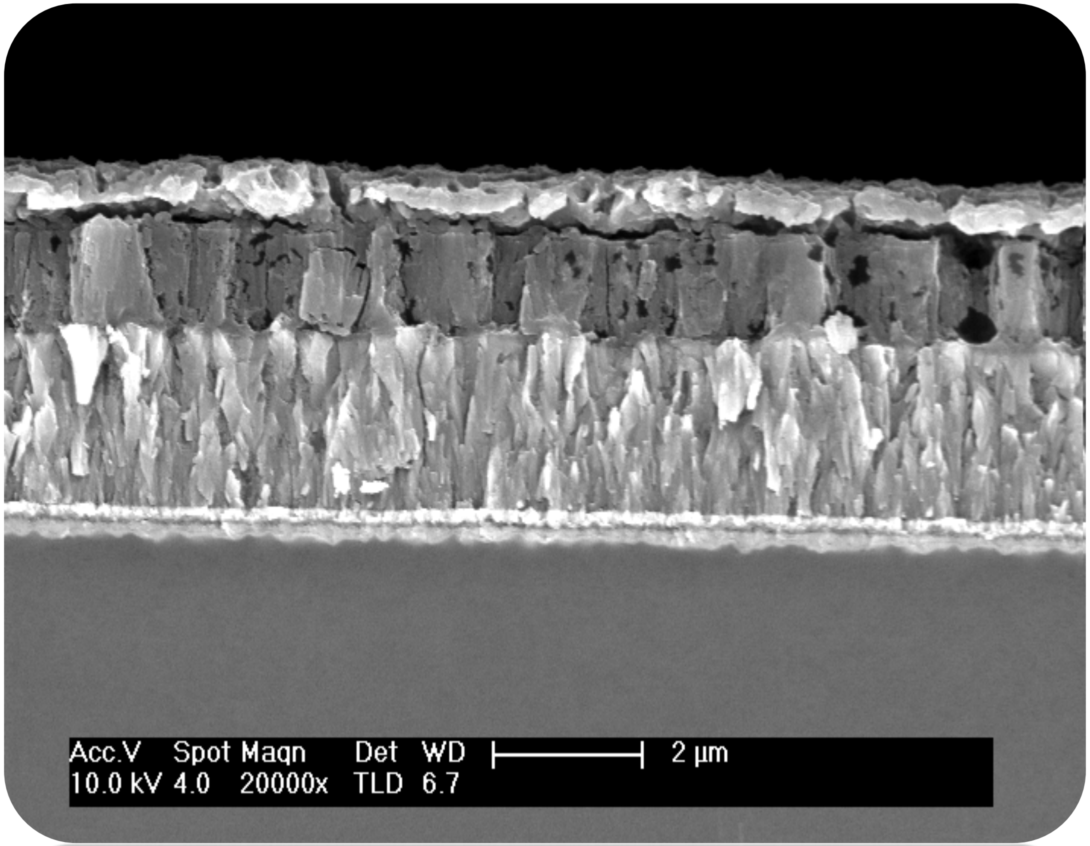
Li “studies” in Odense for Li-air

- Li adsorbed on Si surfaces (with SAES getter sources):
  - Thermal treatment, diffusion, desorption, structural changes of surface or subsurface regions
  - Bonding and reactivity for oxygen, nitrogen and methane (C)
- Li adsorbed on SiC/Si or SiC; SiO_2/Si and Si_3N_4/Si
  - Thermal treatment, same as for Si
  - Bonding and reactivity for oxygen and nitrogen

- Could be important information for choice of anode material

Li-ion thin-film microbatteries





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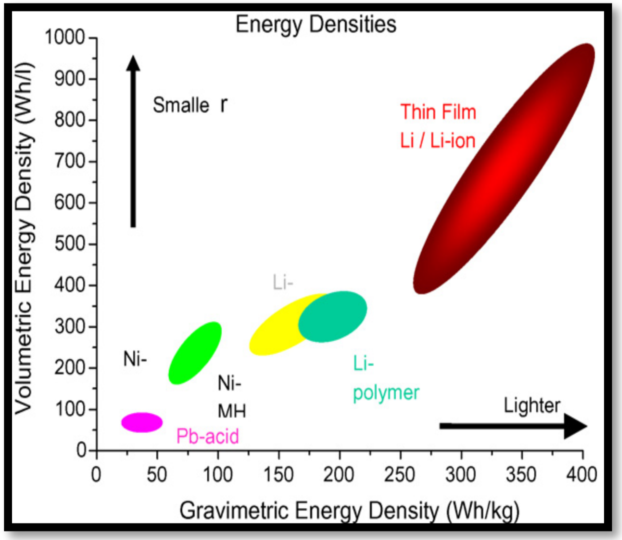
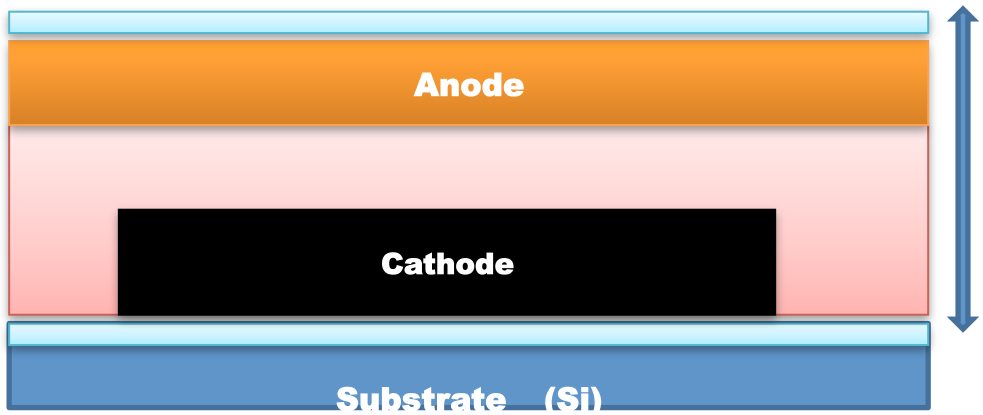
Thin film batteries (Why?)

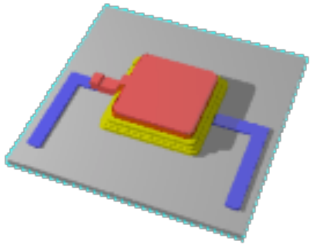


$LiCoO_2$ | LiPON solid electrolyte | Li / Sn(O) / V_2O_5

Battery Type	Voltage	Energy Density		Discharge time (hrs)		(min)
	(V)	(Wh/kg)	(Wh/l)	5mm	1mm	1mm
Ni-Cd	1.2	40	100	11.25	0.090	5.4
Ni-MH	1.2	90	245	27.60	0.221	13.2
Ag-Zn	1.5	110	220	24.75	0.198	11.9
Li-ion	3.6	155	400	45.00	0.360	21.6
Li-polymer	3.6	180	380	42.75	0.342	20.4
Thin Film Li-ion	3.6	250	1000	112.5	0.900	54

Example of a thin film battery





Less than 10 μm

All solid state components

Thin film fabrication of all battery components

Substrates
Si, Al_2O_3, quartz

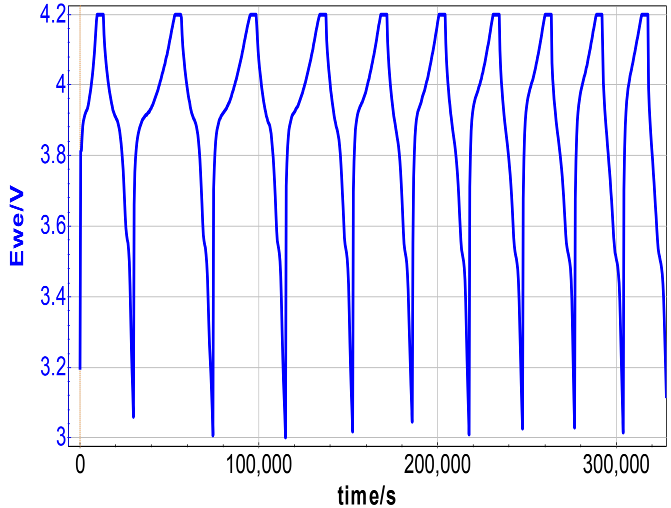
Flexible substrate: Kapton

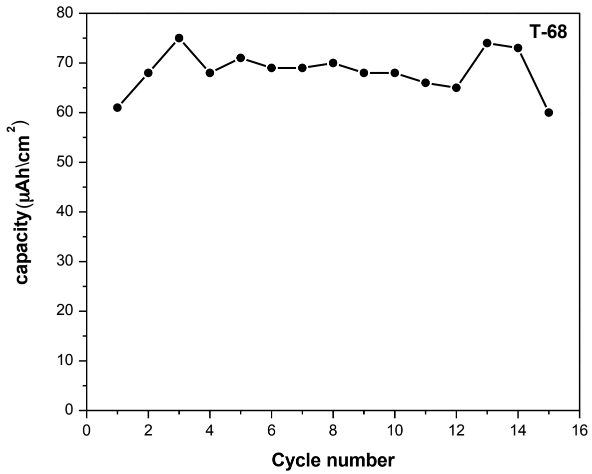
Realization of TFB - *Materials and processing*

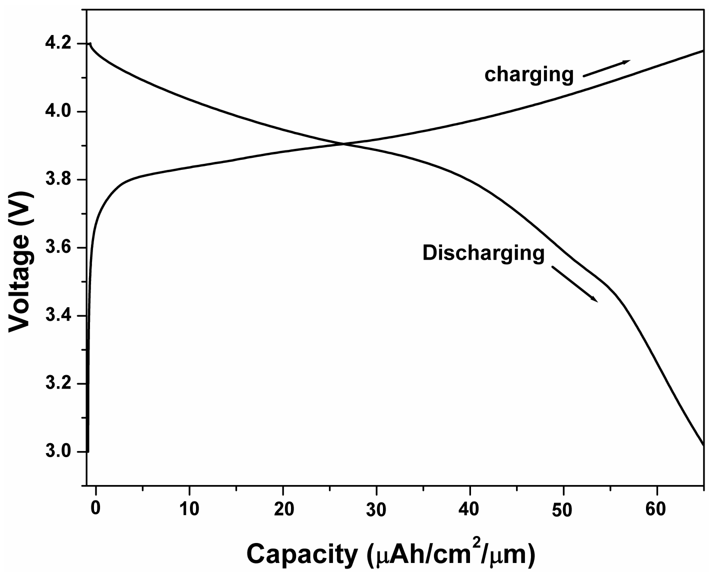
Layer	Material	Deposition Tech:
Cathode	**$LiCoO_2$**	**RF sputtering** **in Ar and O_2 ambient.** **Post annealing at 700°C for 2 hour.**
Electrolyte	LiPON ($Li_{2.9}PO_{3.3}N_{0.36}$)	RF sputtering in N_2 ambient. Room temperature deposition Amorphous thin film is formed.
Anode	**Metals (Cu,Sn,Al)**	**Sputtering / Evaporation** **TFB in discharged state** **Elemental Li can be avoided**

Substrate materials: Pt/Si, Stainless steel, Pt/Al_2O_3

Electrochemical Performance of $LiCoO_2$ thin film

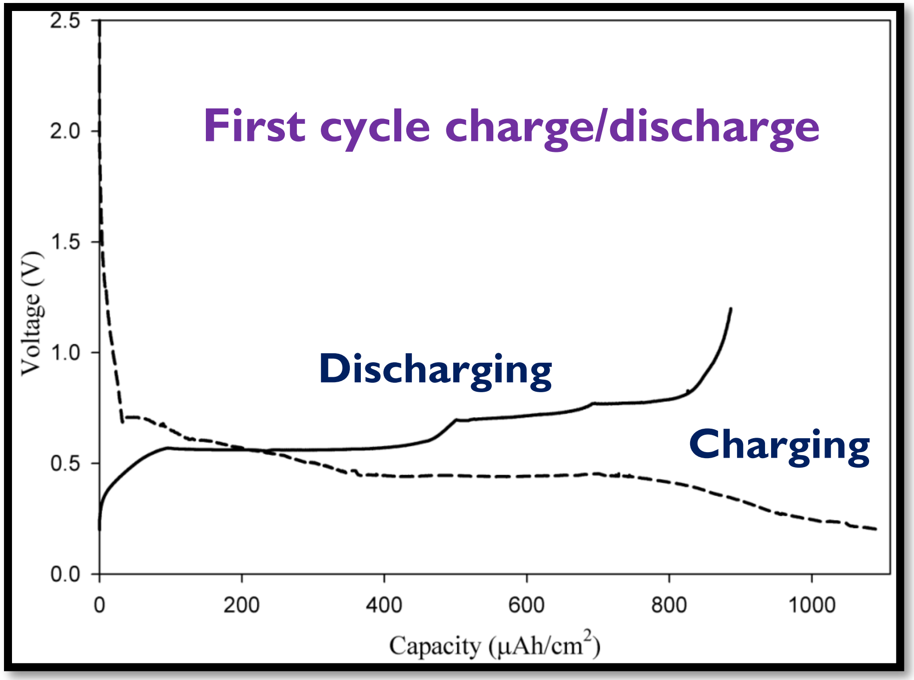


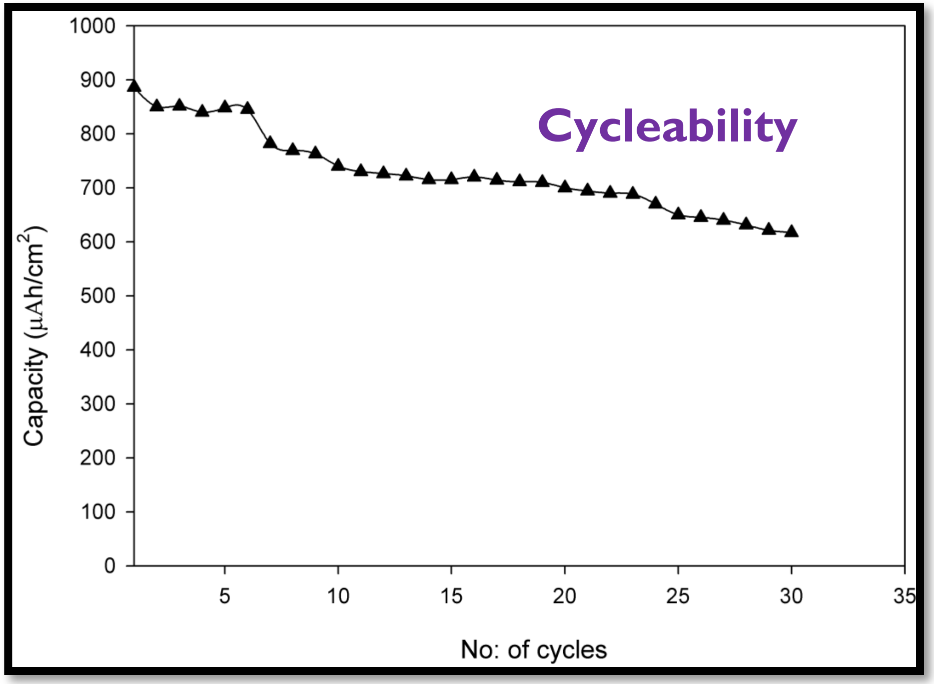




UNIVERSITY OF SOUTHERN DENMARK.DK

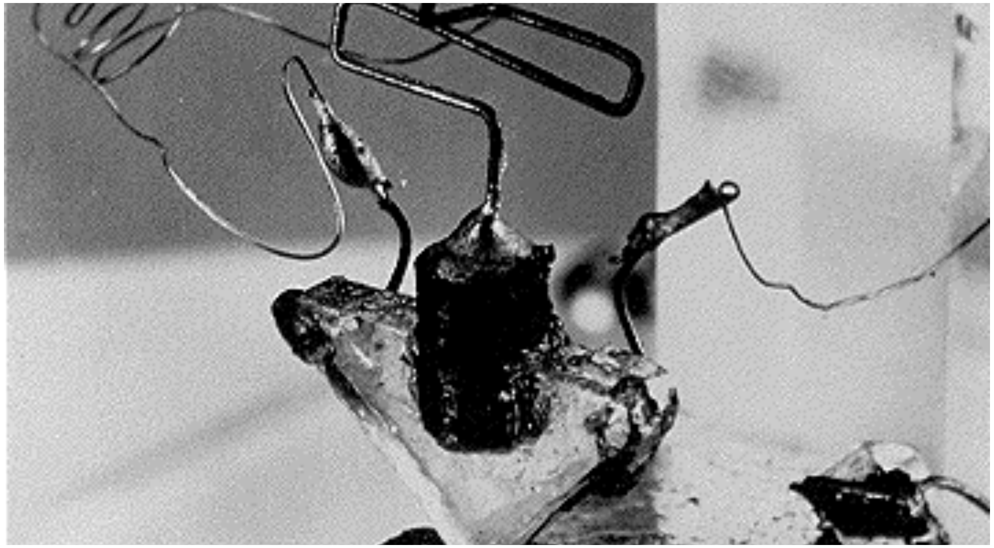
Prototype TFB





- ‘Nanobeads’ of ≈ 40nm size increases surface roughness
- volume change associated is taken care of due to porous nature
- capacity reduction up to 30 % after 30 cycles (compares well)

From here…



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Thank you