Powering Specknets : Advanced Rechargeable Lithium Batteries

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Requirements

"Autonomous speck with renewable power source"

- Require Specks to be small → limit to energy storage
- Long periods between recharge → high energy density Wh/l
- Powerful supply for comms. → sustain high currents

Lithium Ion Batteries

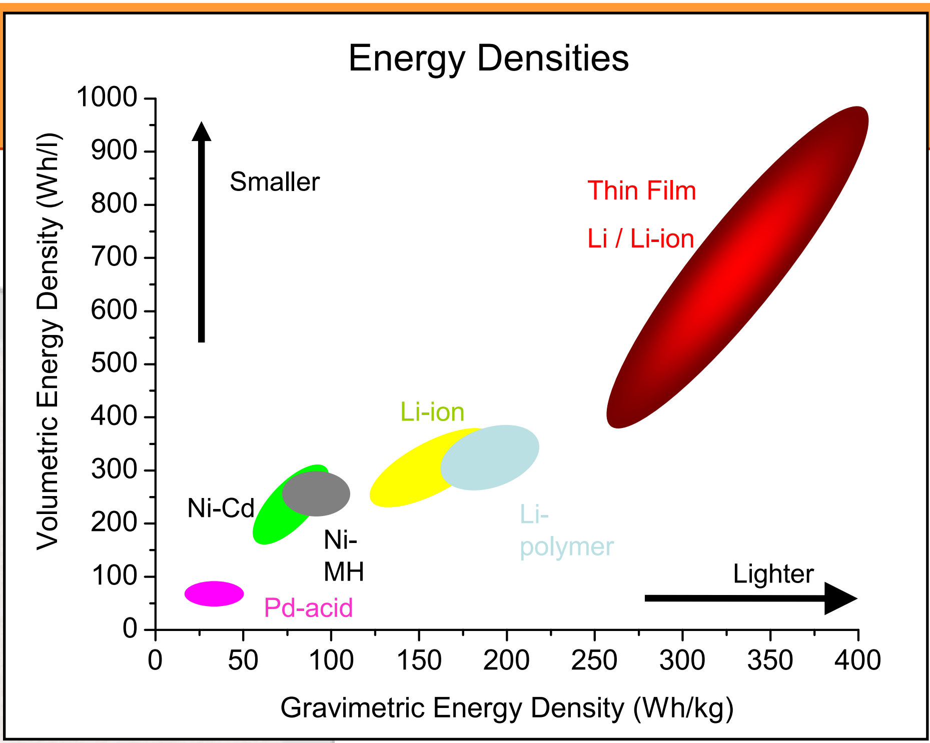
Alternatives :

- Radioactive Primary Batteries
  - Efficiency too low. lots of energy stored, can't get at it.
- Capacitors and Thermoelectric Generators
  - Relatively large devices.
- Solar Cells
  - Still require energy storage when dark / cloudy
  - Low power

Other Issues :

- Recharge - by solar cell or external
- Packaging

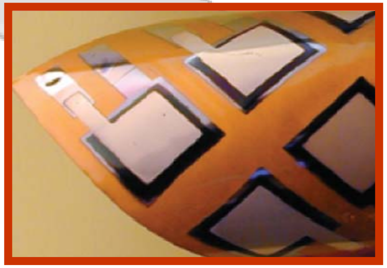
Secondary Batteries



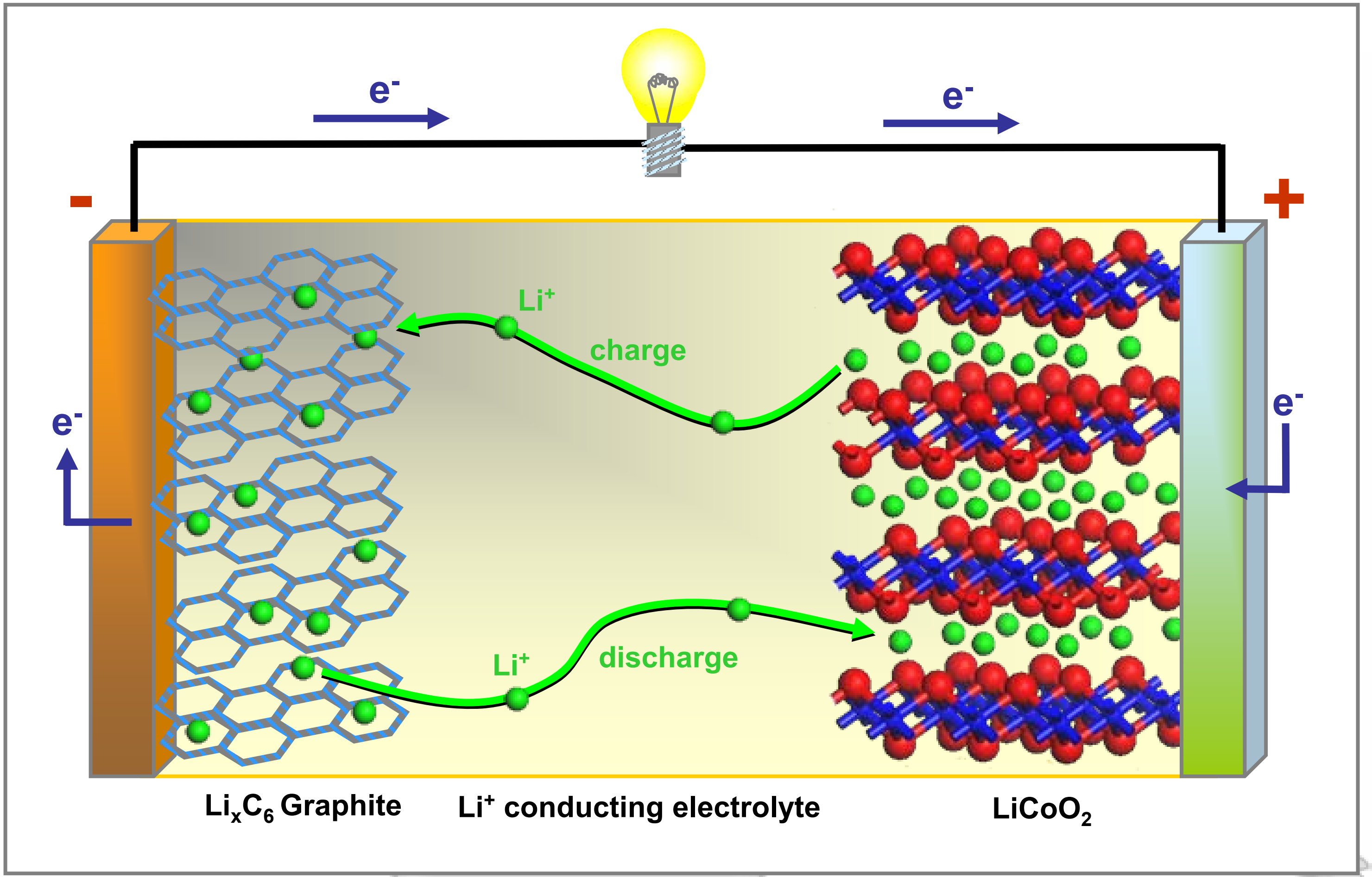
Lithium Ion : 3.5V, 2000+ Cycles

- Higher energy density
- No memory/self discharge effect
- Lower toxicity
- More complex charging
- Sustain high currents

- A - Coin / Button Cells (Li-ion)
  - $LiMnO_2$ | $LiPF_6$ in EC/DEC organic electrolyte | Graphite
  - Rigid Aluminium packaging
  - For clock / memory backup PDA type devices
- B - All Solid State (Thin Film Li-ion)
  - $LiCoO_2$ | **LiPON solid electrolyte** | Li / Sn(O) / V_2O_5
  - All solid state device – Can be made very small
  - Very thin battery (0.4mm)
  - Safer - No solvents/gasses/liquids to degrade or leak
  - Sustain very high continuous currents



“Rocking chair” Li-ion Battery



- Electrode redox reactions on charge:

Cathode oxidation : $LiCoO_2 \rightarrow Li_{1-x}CoO_2 + xLi^+ + xe^-$

Anode reduction : $xLi^+ + xe^- + C_6 \rightarrow LiC_6$

discharge is the opposite

Sanyo Micro-batteries

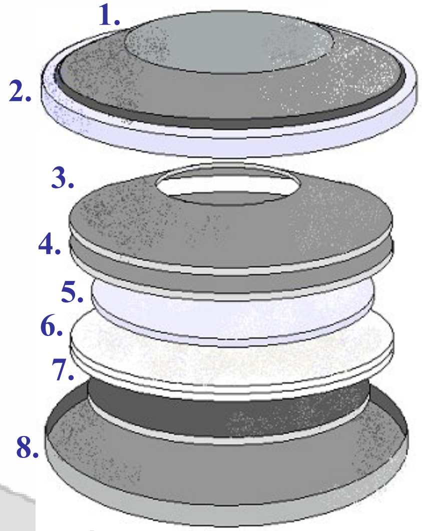
λ-MnO_2 | Liquid electrolyte | Li-Al Alloy

Model No :	ML414	ML421
Voltage :	3V	3V
Dimensions :	4.8 × 1.4 mm	4.8 × 2.1mm
5×5×5mm Speck :	3 cells	2 cells (parallel)

Total Rated Nominal Capacity for 5Cube: ~ 4mAh

Max rated Discharge Current : ~ 0.5mA

Standard Discharge Current : ~ 0.005mA

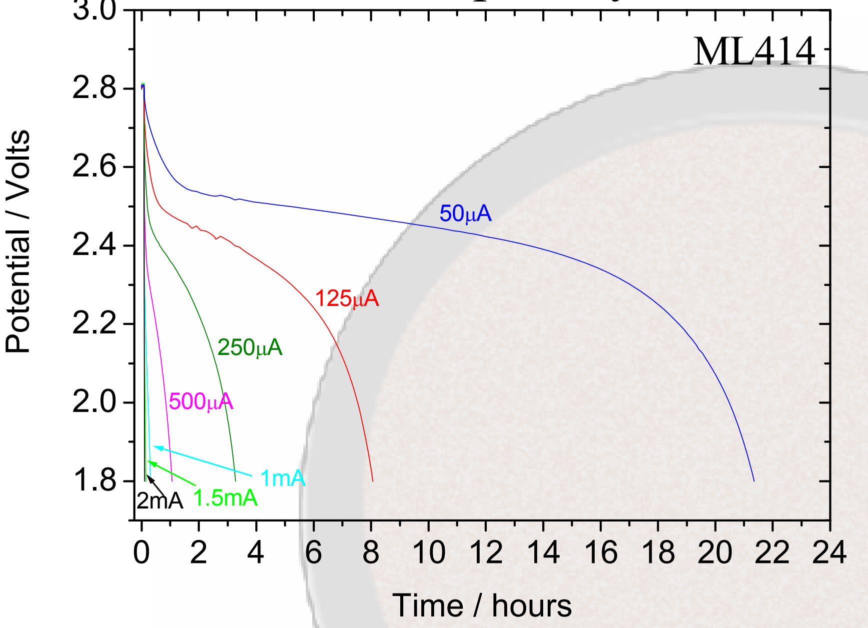


1. **Lid –*ve* terminal**
2. **Cell sealing grommet.**
3. **Spring.**
4. **Spacer.**
5. **Composite anode / Lithium metal.**
6. **Glass fiber separators / electrolyte.**
7. **Composite cathode disc on Al foil.**
8. **Base, +*ve* teminal**

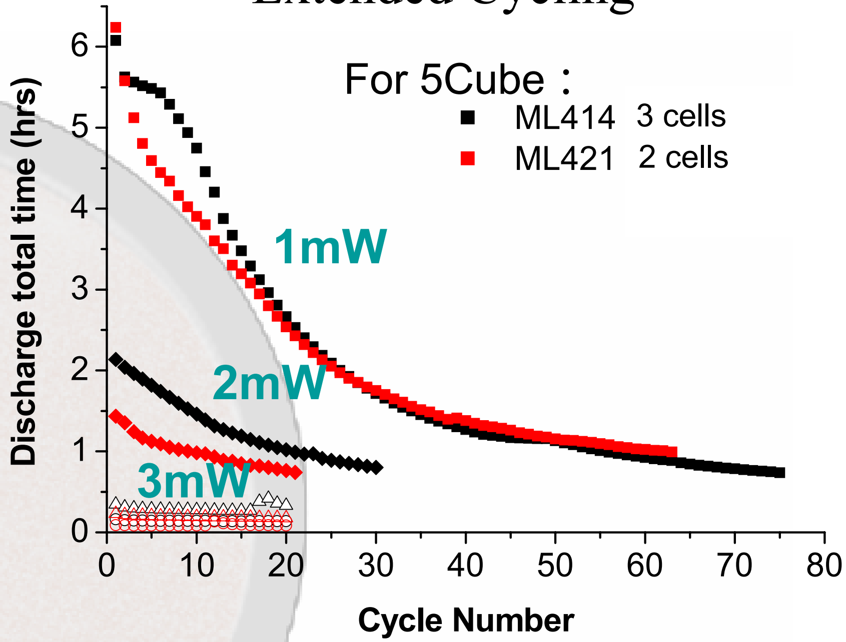
- Electrochemical testing to establish:
  - Sustainable high currents?
  - Batteries actual capacity and resulting run time?
  - Cyclability?
  - Rate capability?
  - Ease of recharge?

Initial Results

Rate Capability



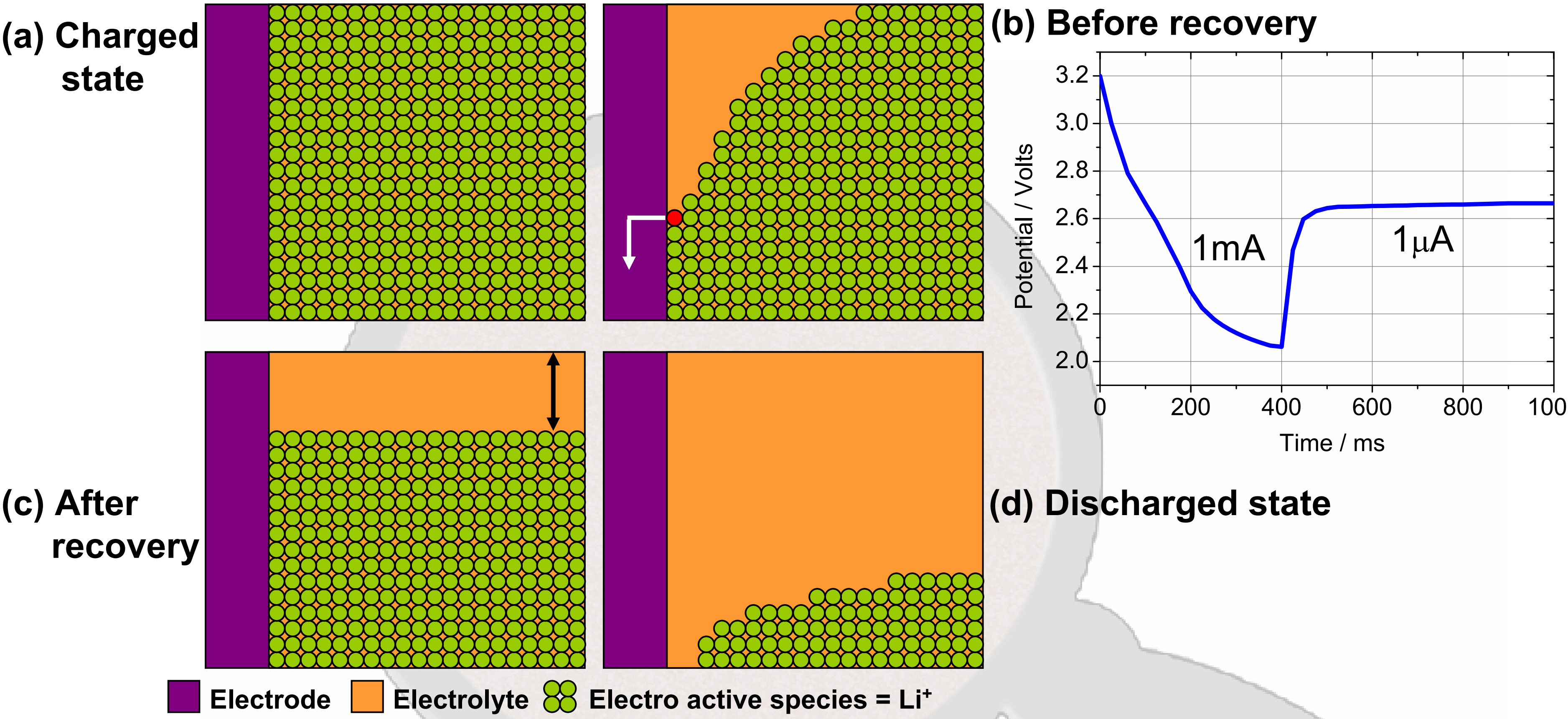
Extended Cycling



- High power dramatically reduces nominal capacity and run time.
- Limit of 2.8mA per cell
  - Voltage profile very steep
  - Complete polarisation

- Cycle life reduced by:
  - High depth of discharge
  - High currents, charge / discharge
- Pushing limits of size and max current for this system.

Battery Operation Schematic – half cell


(a) Charged state

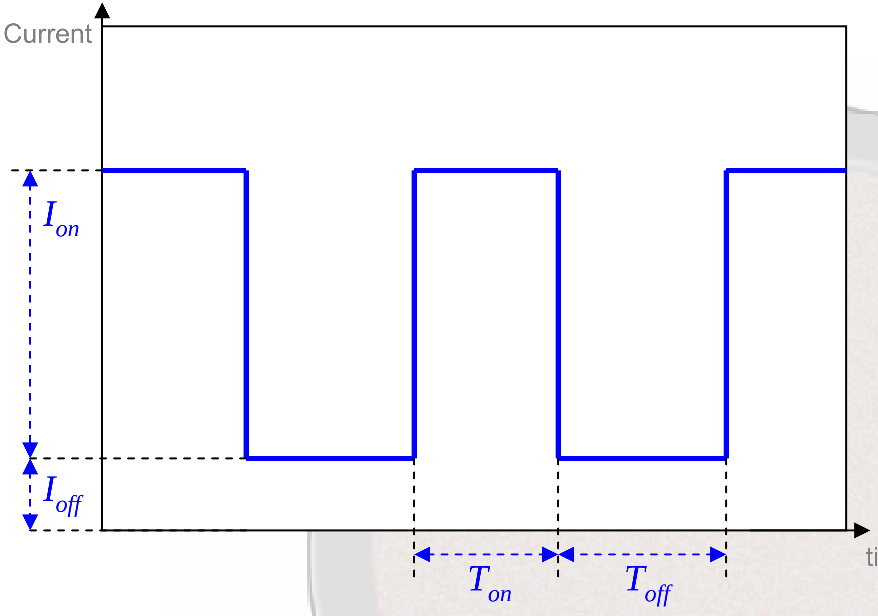
(b) Before recovery

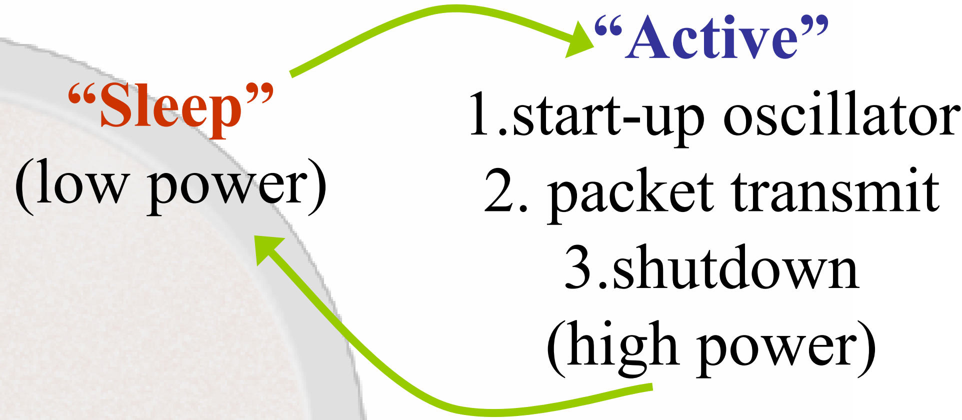
(c) After recovery

(d) Discharged state

- Max power determined by the rate at which you can move ions across the solid-electrolyte interface
- Polarisation occurs at high currents due to starvation
- Recovery - Cell rests for period of time or at low currents.

Pulse Discharging





“Sleep”

(low power)

“Active”

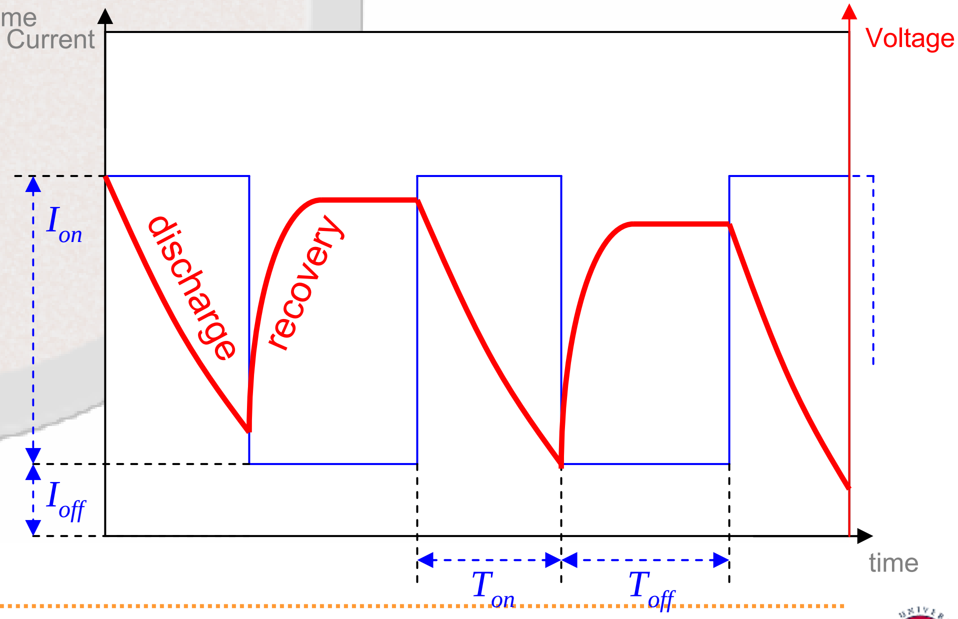
1.start-up oscillator

2. packet transmit

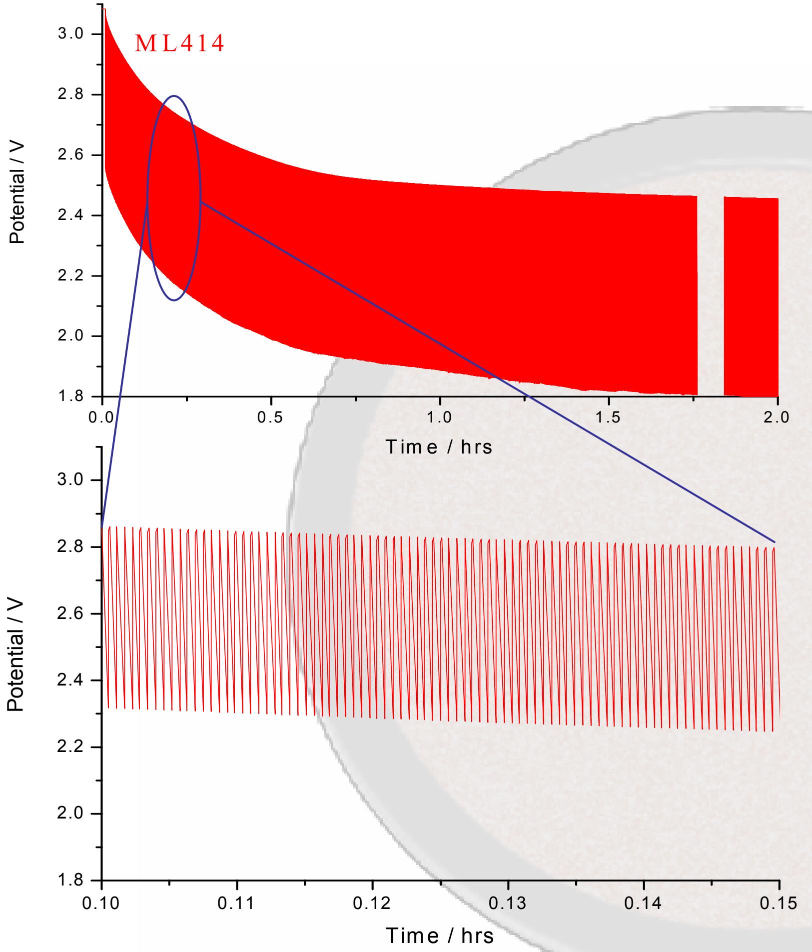
3.shutdown

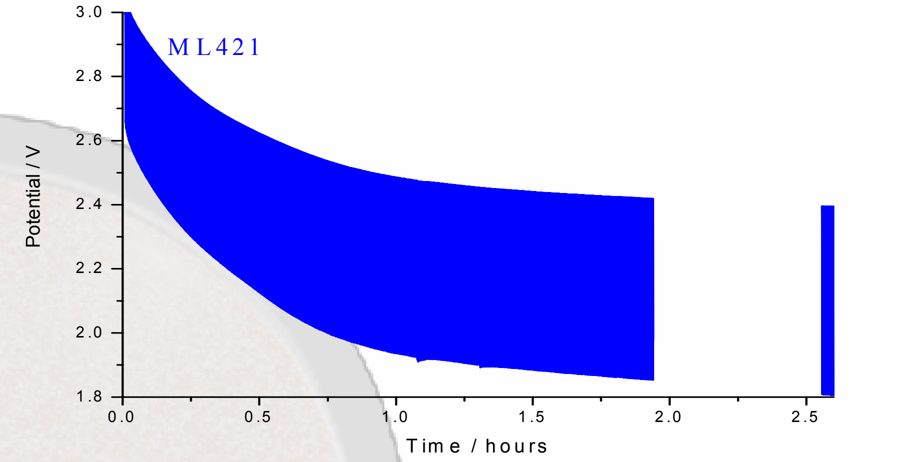
(high power)

- Pulse discharge profile characterisation 4 variables:
- 1 : I_{on} = 0 to 2mA
- 2 : T_{on} = 10ms to seconds
- 3 : I_{off} = 0 to 100’s µA
- 4 : T_{off} = 100ms to minutes



Pulse Discharging Results



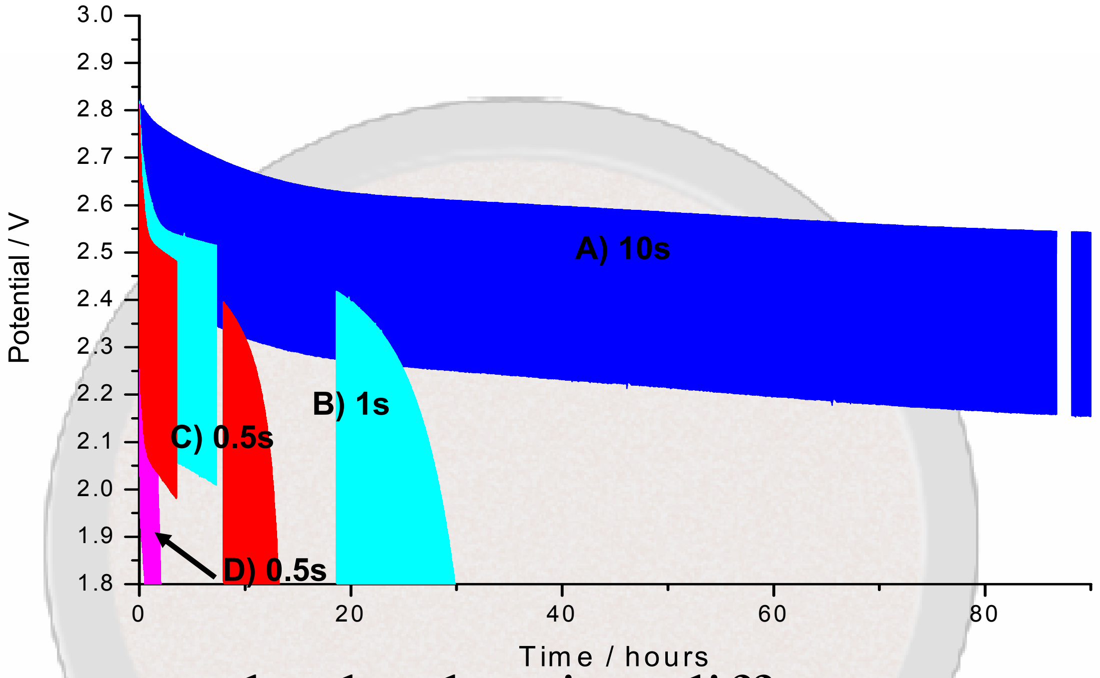


- 10ms @ 2.8mA, 200ms@1µA
- ML414 discharge time ~ 2 hrs
- ML421 discharge time ~ 2.5 hrs
- At high power batteries are concentration gradient and diffusion rate limited

⇒ Electrode surface area

ML421’s for maximum power applications are a “waste of space”

Characterisation : ML414's



Same currents and pulse duration, different recovery times:

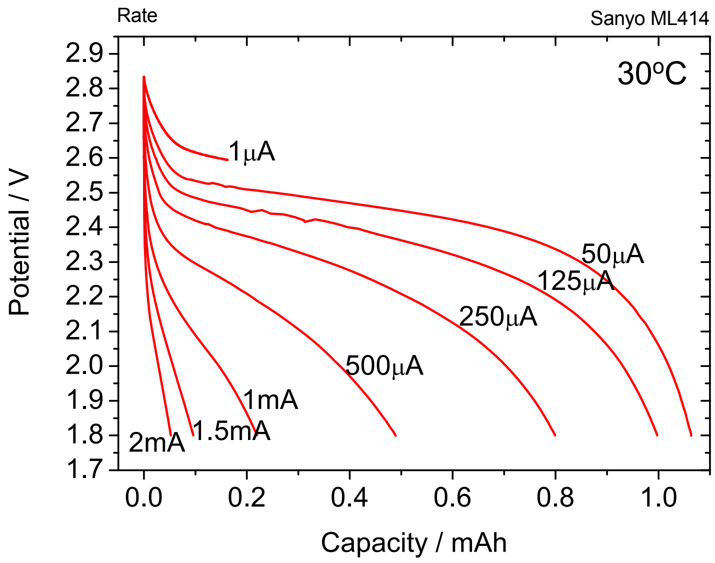
- **A)** "Active" for 10ms @ 2mA, "Sleep" for 10s @ 1µA.
- **B)** "Active" for 10ms @ 2mA, "Sleep" for 1s @ 1µA.
- **C)** "Active" for 10ms @ 2mA, "Sleep" for 0.5s @ 1µA.
- **D)** "Active" for 10ms @ 2mA, "Sleep" for 0.1s @ 1µA.

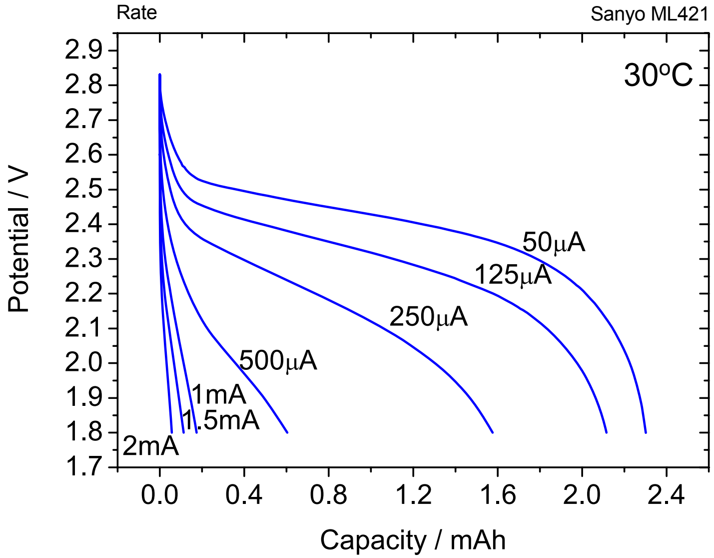
- Pulses short enough and of low enough current then can get high duty cycling and long lifetime, 10,000's pulses.

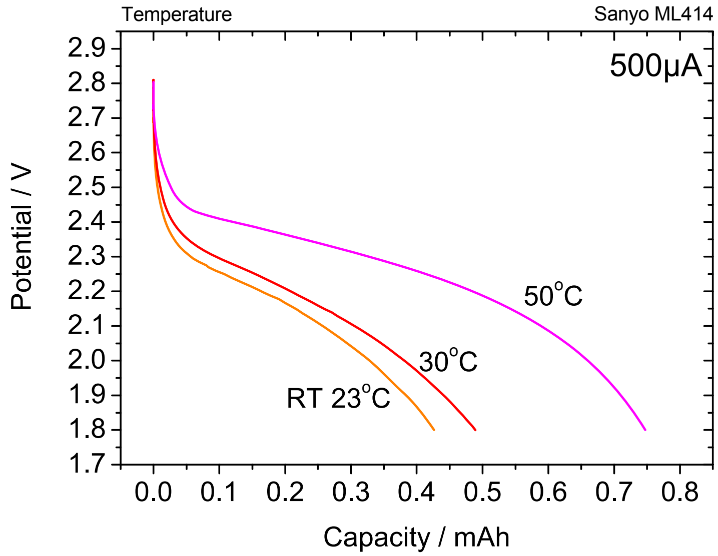
Battery Modeling

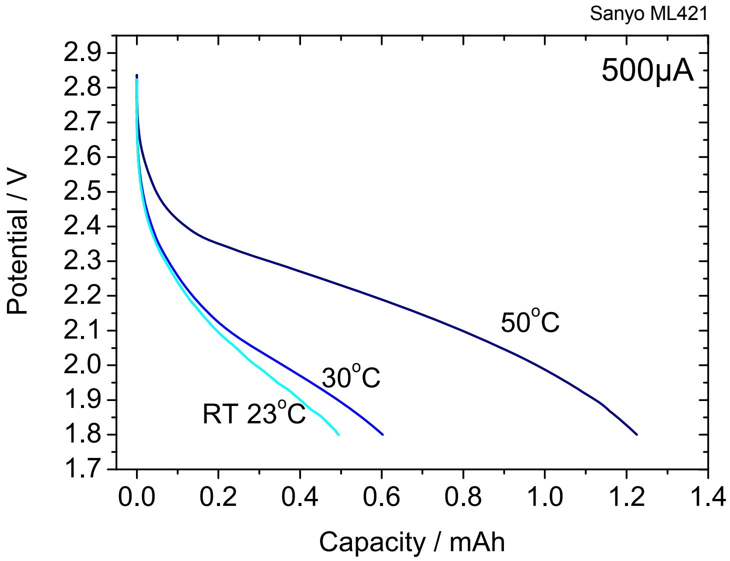
- Detailed Physical models – John Newman
  - Study internal dynamics
  - Generally not suitable for system level design
  - Very intensive ~50 variables, most experimentally determined
- Simple Dynamic models based on Resisters / Capacitors
  - For network type device simulation they are oversimplified
  - Lack interesting bits
    - Non-linear equilibrium potential
    - Rate dependant capacity
    - Temperature effects
- Intermediate-avoid detailed electrochemistry
  - Sufficiently accurate to capture major electrical and thermal properties
  - Avoid detailed calculations of internal electrochemical kinetics
  - Only a few experimental variables required....

Experimental Results



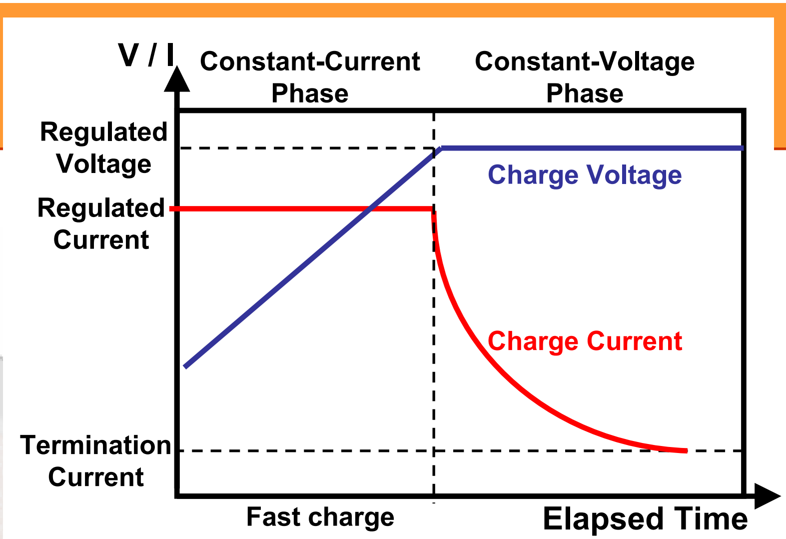


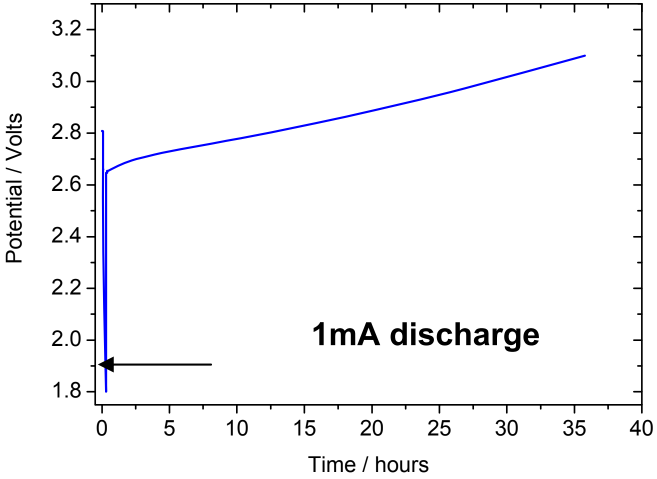


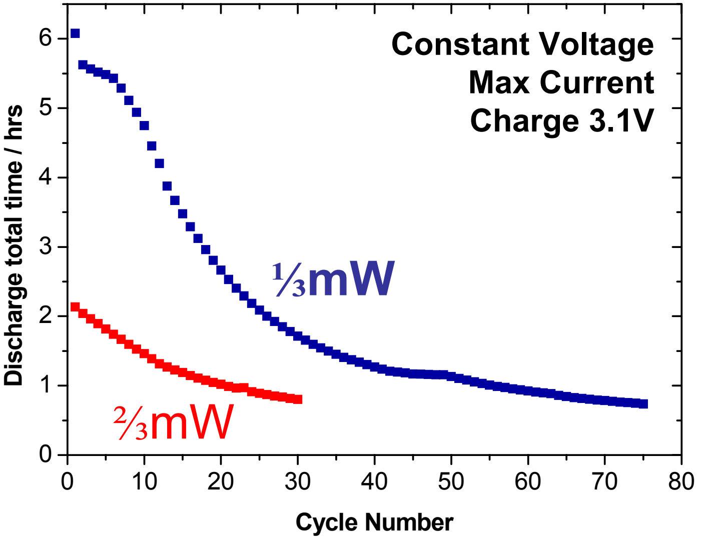


Recharging Sanyo Cells

- Extremely sensitive to conditions
- Constant-current constant-voltage
  - Recharge voltage = 3.1V
  - Standard recharge current = 5µA
- At recommended charge current cell potential rise of 0.01 V per hour

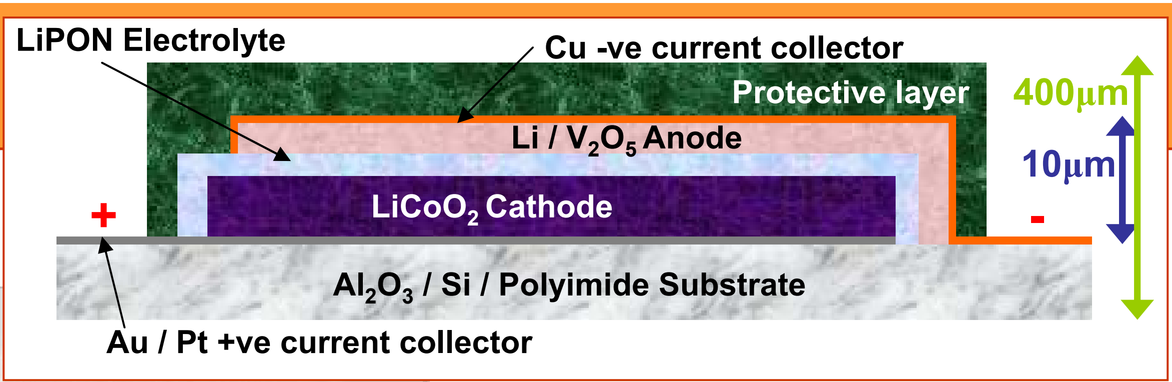






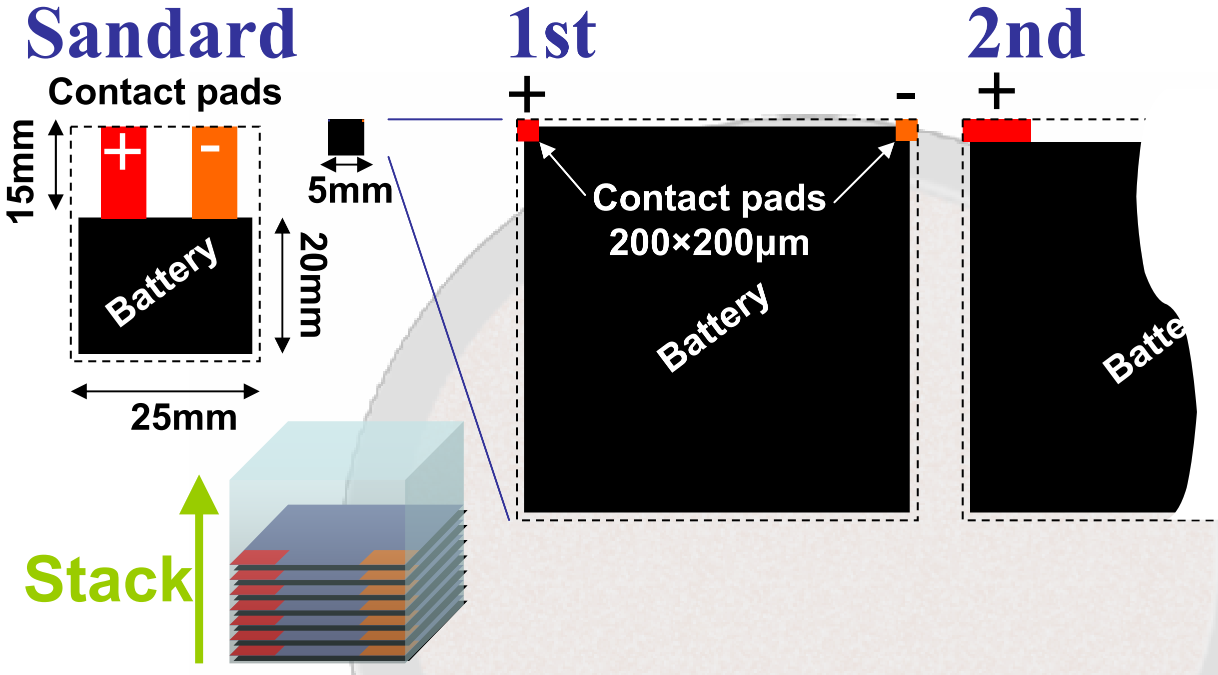
- Fast charge at expense of cyclability
- Low current charge to preserve lifetime
  - Ideal for Speck recharge by Photovoltaic

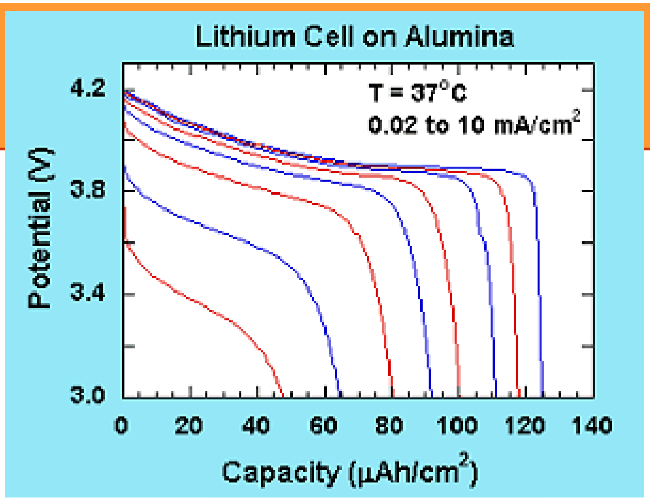
Thin Film

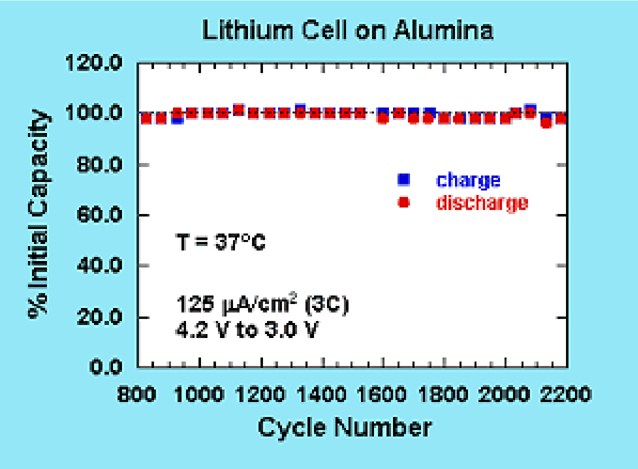


- All-solid-state device
- formed by sputtering
- Key : $Li_{2.9}PO_{3.3}N_{3.6}$ ceramic electrolyte.
- Very thin, light, safe, powerful, any shape, stable, tolerant
- Not fully commercially available, expensive.
- Only viable option for "Specks" smaller than 5 × 5 mm
- Initial work by John Bates
  - Oak Ridge National labs → Oak Ridge Micro Energy Inc.
- Prepared to make us some 5 × 5 mm footprint TF batteries
  - Design from us : created mask set for 4½×4½" substrate
  - Main issue is the location and dimensions of the contact patches
  - Design rules for layer overlap to prevent shorting / cell failure
  - electrochemical performance evaluation and prototype integration

Battery specification



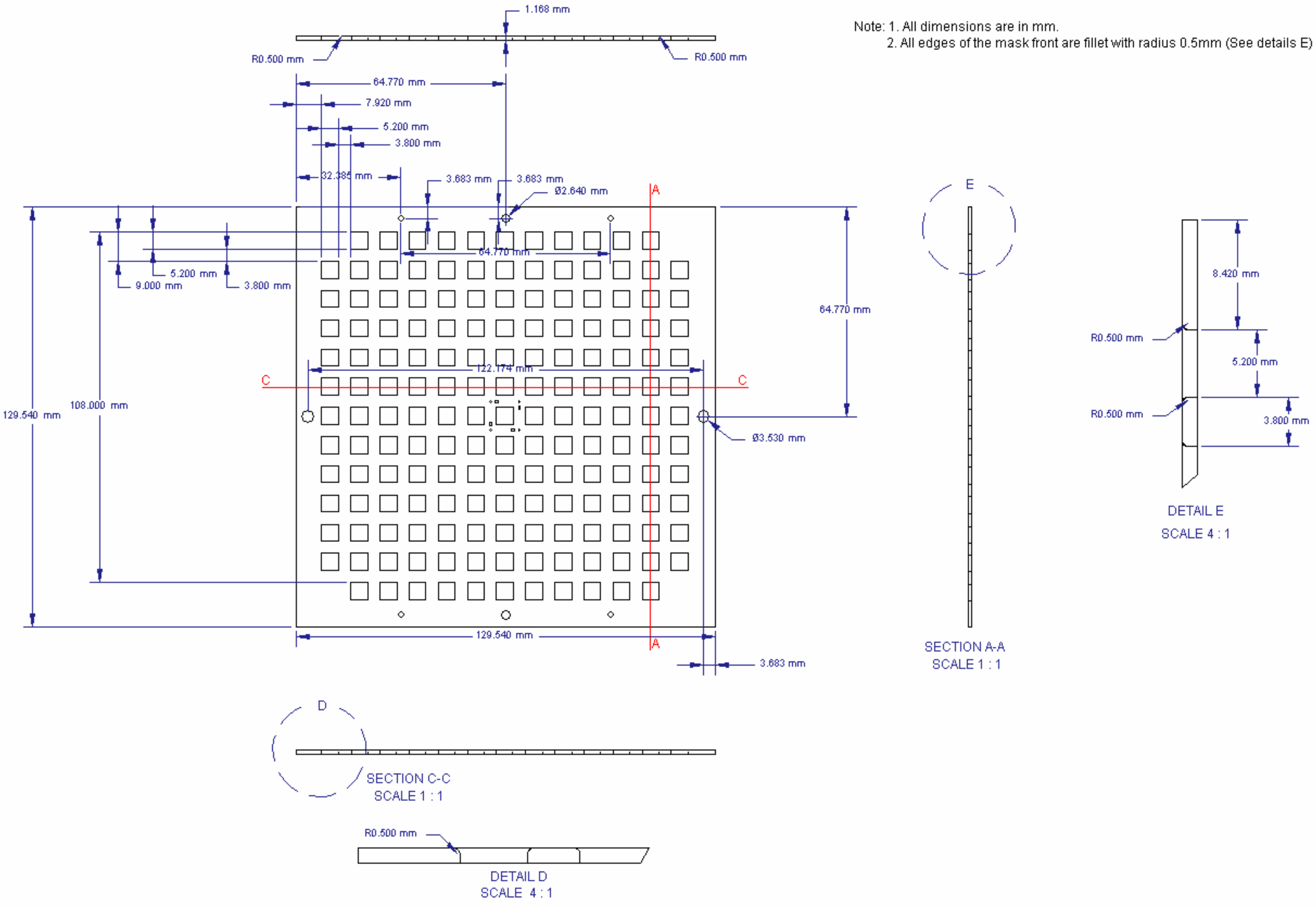




- Size: 0.38×5×5mm ⇒ 4.3×4.5mm cathode
- Total cathode area of ~ 0.20cm^2 ⇒ 40µAh
- Fit ~ 13 in wired parallel ⇒ 500µAh ⇒ 0.5mAh total
- At 1mW drain the 13 cells gives current density of ~ 130µA/cm^2
- No significant capacity reduction from IR loss at room temp.

⇒ Total discharge time of battery stack ~ 2 hours

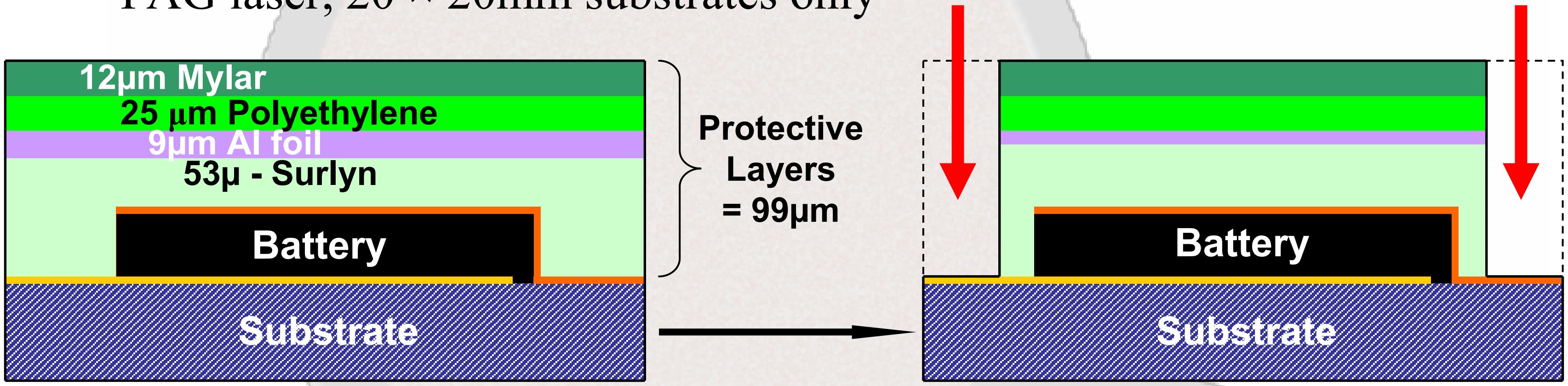
Thin Film – Mask CAD Drawing



Note: 1. All dimensions are in mm.
2. All edges of the mask front are fillet with radius 0.5mm (See details E)

Laser Etching

- Contact pads still too small to mask effectively
- Laser etch to remove protective layers – expose clean surface
- Manfred Buch, St Andrews, Surface science,
  - Laser ablation for creation of micro circuitry
  - YAG laser, 20 × 20mm substrates only



Integration Issues

- Optocap suggested method of connecting was by the use of "ANISOLM" - Anisotropic conductive film - Hitachi
- Used for contact to display interconnects.

Thin Film Centre – University of Paisley

- Collaboration with Prof Frank Placido’s group in Paisley
- Development of a thin film battery system
- Layers deposition by E-beam and RF Sputtering
- Initially very simple system $LiCoO_2$ and solid electrolyte on glass plates. Area masking by Mylar film.
- Require manufacture of $LiCoO_2$ and electrolyte targets for sputtering – Edinburgh Physics Department
- Future
  - Significantly Reduce the packaging costs
  - Lithium free
  - Custom “Speck” battery – back to back and multi-layer
  - Advanced high capacity electrode materials

Lithium Manganse Nickel Oxide

Future Lithium batteries

- Greatest improvement in battery performance achievable through research and development of new and advanced electrodes.

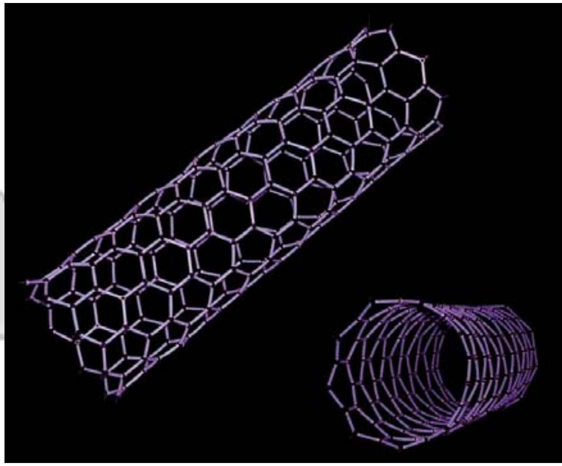
⇒ **Materials chemistry challenge.**

- Advanced "Specknet" electrodes require:

Improved rate capability ⇒ **Nanomaterials**
Higher capacities ⇒ **Advanced Li-Mn-Ni-O**

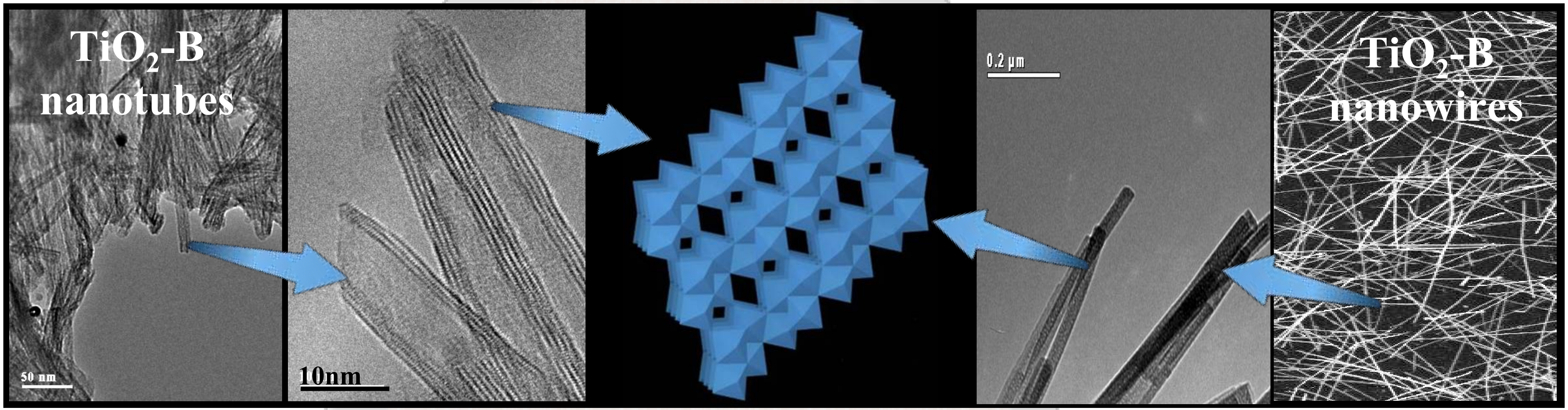
Nanomaterials

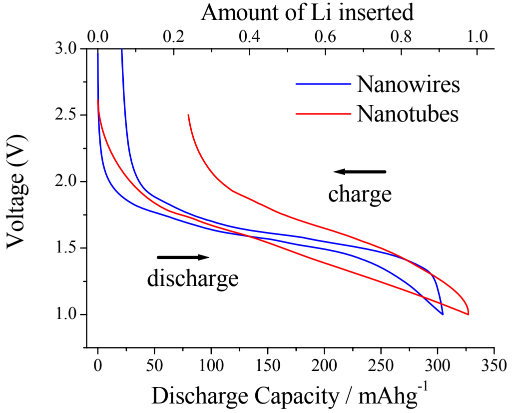
- 1 Nanometre = 1000millionth of a metre
- Simply by making materials small can have a profound influence on their properties.
- Extremely high surface area.
- Inorganic oxide – "Nanotubes" and "Nanowires".



TiO_2-B Nano-tubes / wires*

- TiO_2-B most open polymorph of TiO_2
- 1D morphology & Better particle contact ⇒ High rate capability
- High theoretical capacity 337mAhg^{-1}excelent capacity retention on cycling



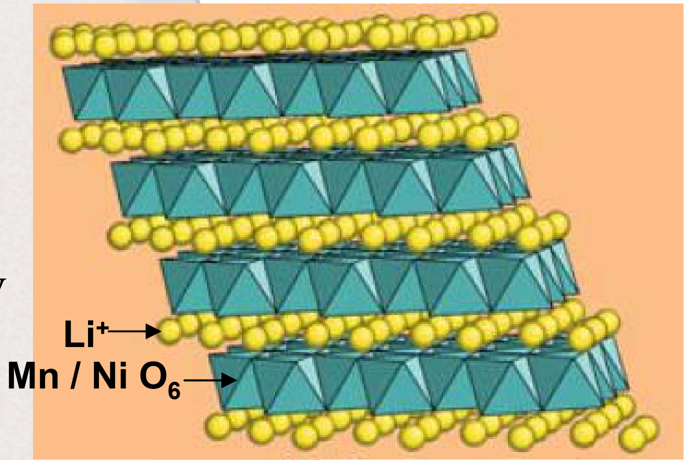


- Poor ionic/electronic conductivity when 1st charged?
- Attempted : Encase active components material in "PEO based electolytic polymer gel"
- Porous electrode with all active material accessible by penetrating electrolyte ⇒ slightly increased conductivity.
- Not optimal ⇒ Si/C coating ⇒ Micro-batteries

* Armstrong, Armstrong, Canales, Bruce *Angew. Chem.* 43, 2286 (2004)

Lithium Manganese Nickel Oxides

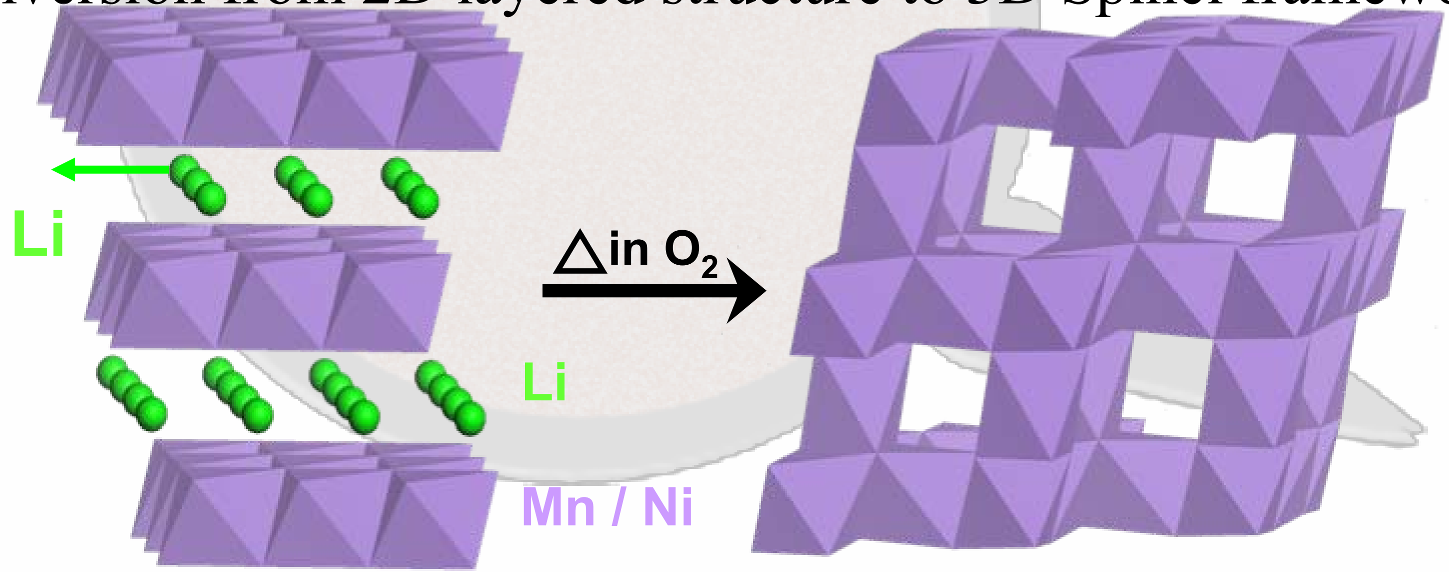
- "Almost ideal" intercalation Electrode = $LiMn_{0.5}Ni_{0.5}O_2$
  - Mn^{4+} in octahedral sites – stabilizes layered structure
  - ½ Ni for electrochemistry $Ni^{2+} \rightleftarrows Ni^{4+} + 2e^-$
  - High capacity to store charge = Theoretical capacity 285mAhg^{-1}
- Manganese materials difficult to synthesise pure phases:
  - Very sensitive to synthesis conditions
  - Which in turn effects electrochemistry
  - Difficult to make all Ni^{2+}
  - Susceptible to ionic mixing



- Standard $LiMn_{0.5}Ni_{0.5}O_2$ electrochemical performance poor
- 8% Ni in Li layers blocking ion flow
- If not 100% Mn^{4+} and Ni^{2+} then creates Mn^{3+}

The Problem with Manganese

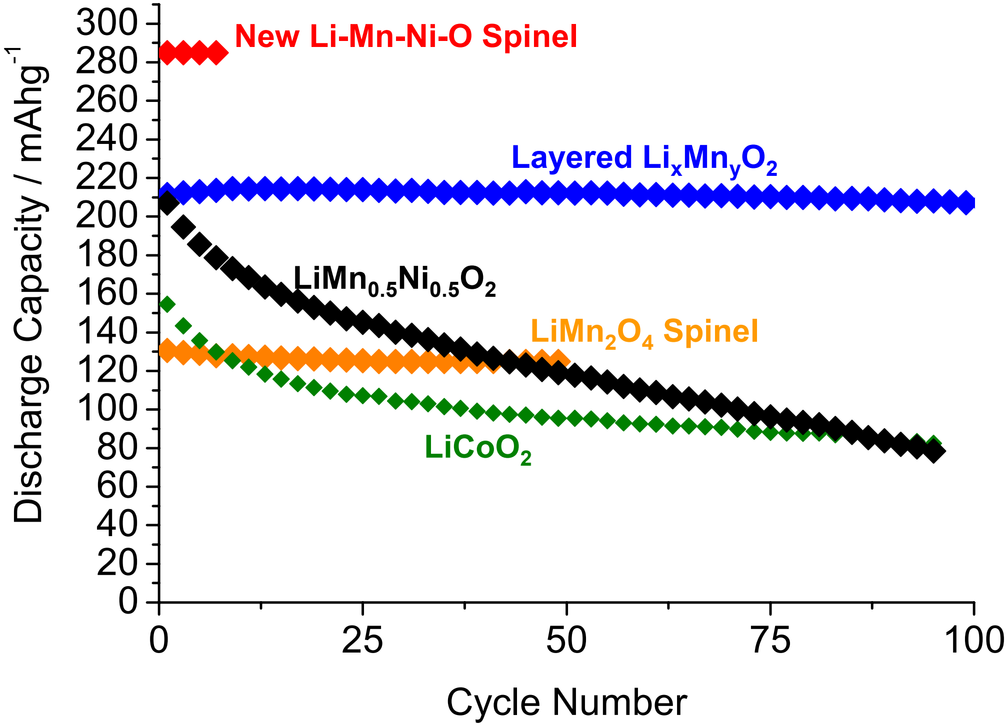
- Mn^{3+} electron config of $3d^4$ (High Spin) = Jahn Teller Active
  - As intercalate / deintercalate Li get anisotropic expansion of crystallites
  - Causing stress / strain within individual particles
  - paticle break up ⇒ loss of inter-particle contact ⇒ poor conductivity
- Structure unstable – can we induce stability and improved performance through structural conversion?
- Conversion from 2D layered structure to 3D Spinel framework



$LiMn_{0.5}Ni_{0.5}O_2$ – ½ Li → $Li_{0.5}Mn_{0.5}Ni_{0.5}O_2$ ($LiMn_2O_4$)

Li-Mn-Ni-O System

- Potentially much higher capacities compared to conventional electrode materials
- Potentially much improved structural stability leading to improved cyclability over Mn only Spinel.–No Mn^{3+}



- $LiMn_{0.5}Ni_{0.5}O_2$ and other Li-Mn-Ni-O are a “hot topic”
- Full understanding of these materials and their structure
- Hope incorporate these materials into future Thin Film batteries
- Optimised synthesis route – make in bulk for sputtering target

Summary and Further Work

- **Batteries**
  - **Sanyo Micro-batteries Cells**
    - Full characterisation of Sanyo micro-batteries
    - Modelling of discharge profile
  - **ThinFilm Li-ion**
    - Performance evaluation and device integration of batteries from Oakridge
    - Development of Thin Film batteries with Paisley University
- Materials
  - **TiO_2-B nanotubes and nanowires**
    - Excellent rate capability but large 1st cycle inefficiency - remove by coating
    - Incorporation into future high power micro-batteries
  - **Li-Mn-Ni-O**
    - Refinement of synthesis process, confirm structural convertion
    - Evaluate electrochemical performance of converted material
    - Incorporation into future Li-Mn-Ni-O based Thin Film batteries
  - **Other new Advanced Materials e.g. $LiFe_2O_4$**