The Inside Story of the Lithium Ion Battery

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Outline

- Background - Why this is important
- Electrochemistry/Battery Reactions
- Design of the Cells/Structure
- Manufacturing
- Performance
- Safety
  - Daniel Forbes' Experimental Study

Why This is Important

Portable Electronics

Telecommunications/Personal Computers/Personal Networks

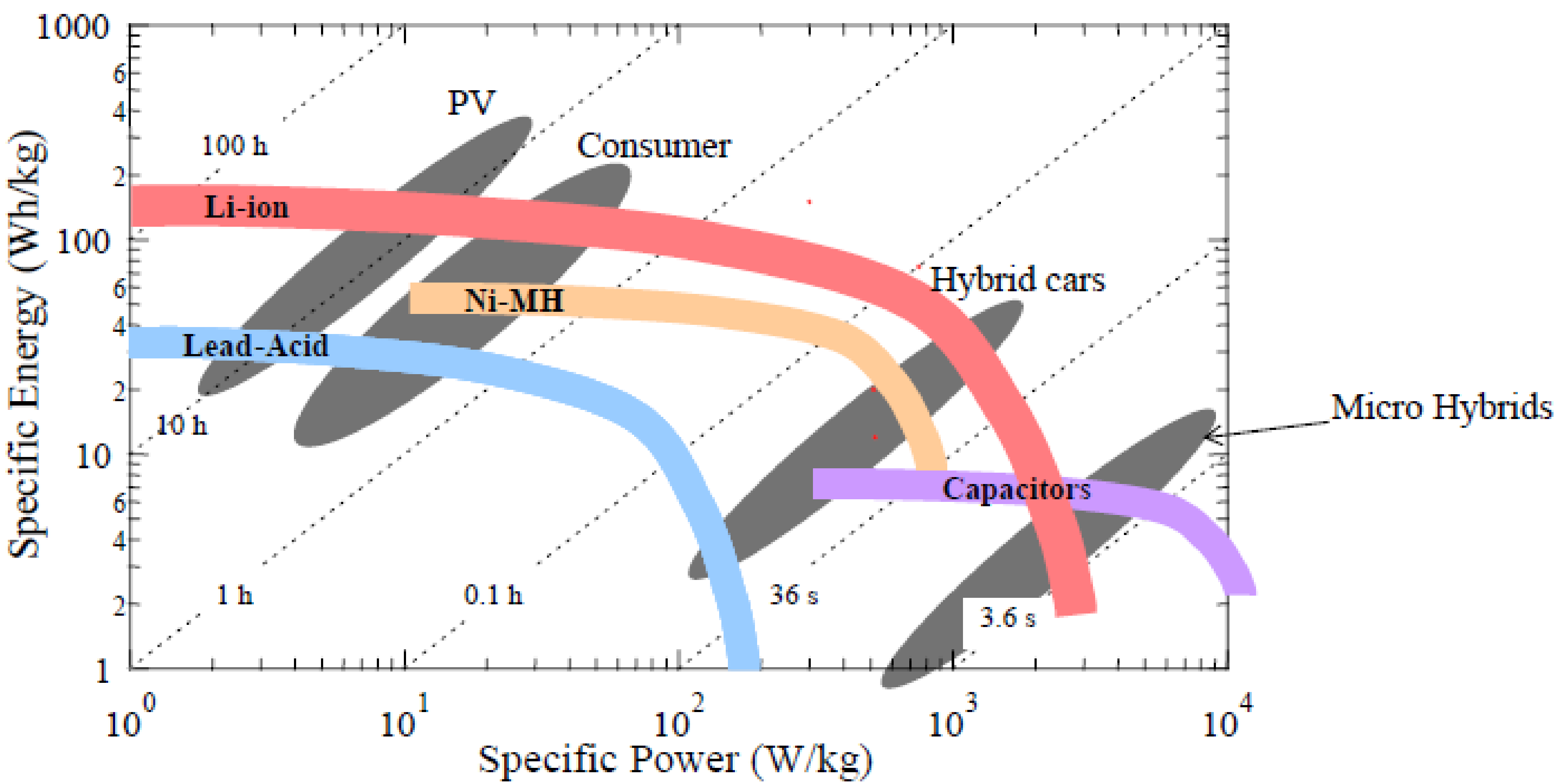
Energy/Transportation

Lithium Ion Battery	Gasoline
~200 Wh/k	~13,000 Wh/kg
~400 Wh/L	~10,000 Wh/L
~ 10 cents/kWh charge	~ 5 cents/kWh refill
FF-->Heat-->Mech-->Elec-->Mech	FF-->Heat--Mech

Historical Context

1791	Galvani (Italy)	Animal Electricity
1800	Alessandro Volta (Italy)	Invention of Voltaic Cell (Cu/brine/Zn)
1833	Micchael Faraday (UK)	Faraday's Law of Electrolysis
1836	John Daniell (UK)	Daniell Cell ($Cu/CuSO_4//ZnSO_{4/}Zn$)
1859	Gaston Plante (France)	PbO_2 (s) + Pb(s) + $2H_2SO_4$ =2 $PbSO_4$ (s) + 2 H_2O
1868	Georges Leclanche (France)	Zn(s) + 2 MnO_2(s) + 2 NH_4Cl(aq) → $ZnCl_2$ + Mn_2O_3(s) + 2 NH_3(aq) + H_2O
1899	Waldemar Jugner (Sweden)	$Cd+2NiO(OH)+2H_2O=Cd(OH)_2+2Ni(OH)_2$
1901	Thomas Edison (USA)	$Fe+2NiO(OH)+2H_2O=Fe(OH)_2+2Ni(OH)_2$
Mid 1960	Union Carbide (USA)	Zn (s) +2MnO_2 (s) → ZnO (s) +Mn_2O_3 (s)
1970s	Various	Valve Regulated Lead Acid Cells
1990	Various	$MH+NiO(OH)=M+Ni(OH)_2$
1991	Yoshio Nishi (Japan)	Lithium Ion Cell

Performance of Various Chemistries



Electrochemical Cell

- Consists of Positive Electrode (Cathode), Negative Electrode (Anode) and Electrolyte
- An open circuit voltage is created by the free energy of reaction of the primary reaction and the influence of side reactions
- In the case of the lithium ion cells, we start with the discharged materials and give the cell a first charge

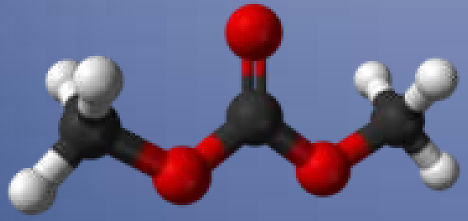
Starting Materials

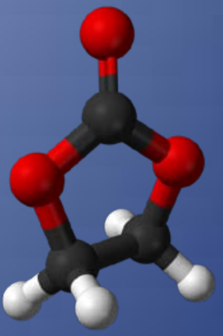
- Anode: Graphite, finely divided
- Cathode: Layered Lithium Metal Oxide, e.g..

  Lithium Cobalt Oxide $LiCoO_2$
- Both Materials are layered materials, through which lithium can move easily due to the layered structures.
- Since water reacts with lithium, we must use nonaqueous electrolytes

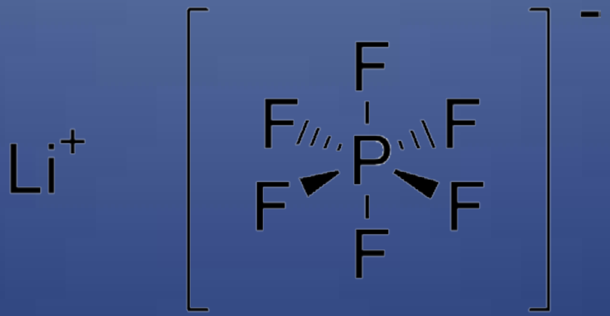
Electrolytes

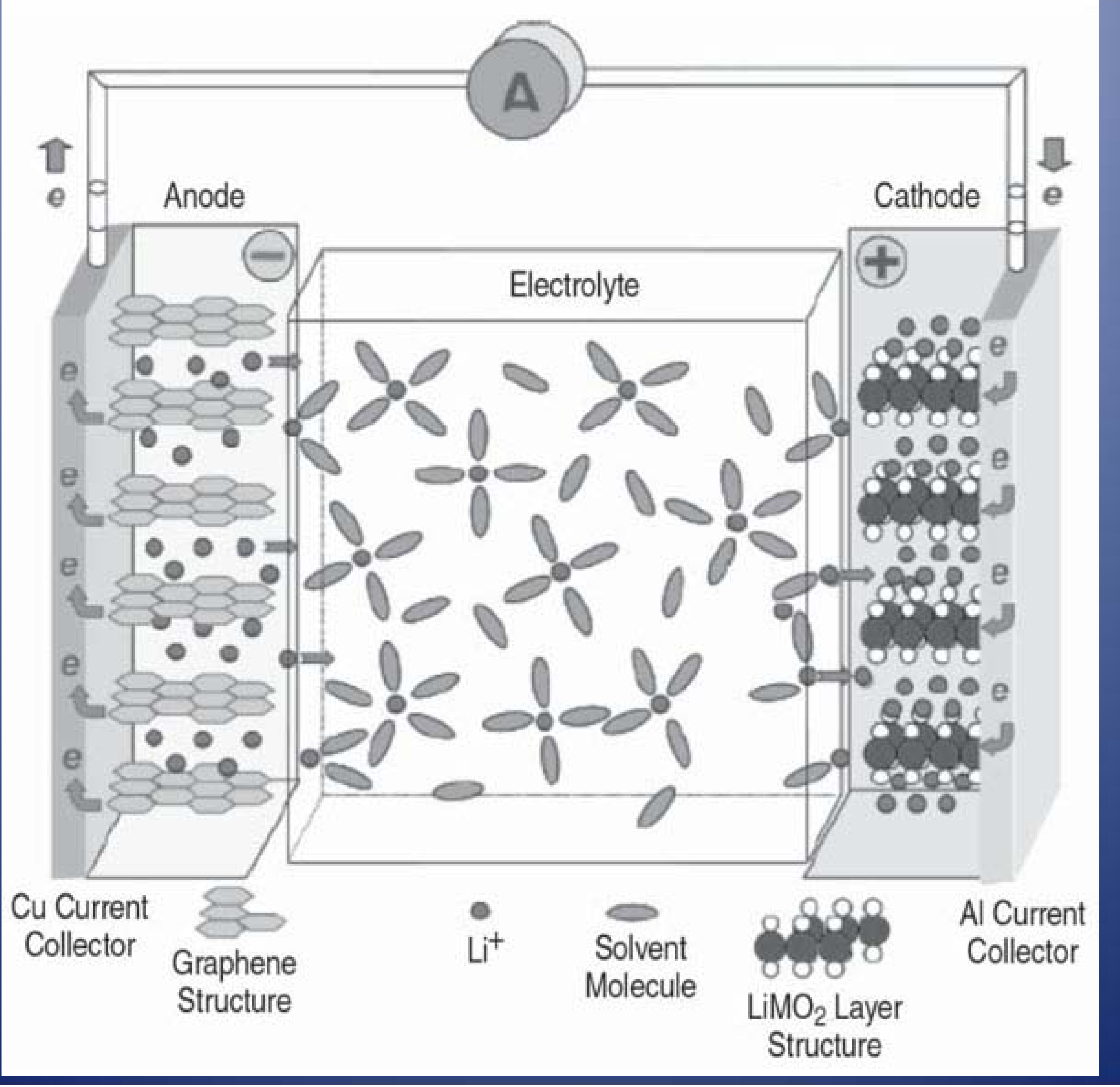
- Solvent: Mixtures of Organic Carbonates such as dimethyl carbonate (DMC) and ethylene carbonate (EC)



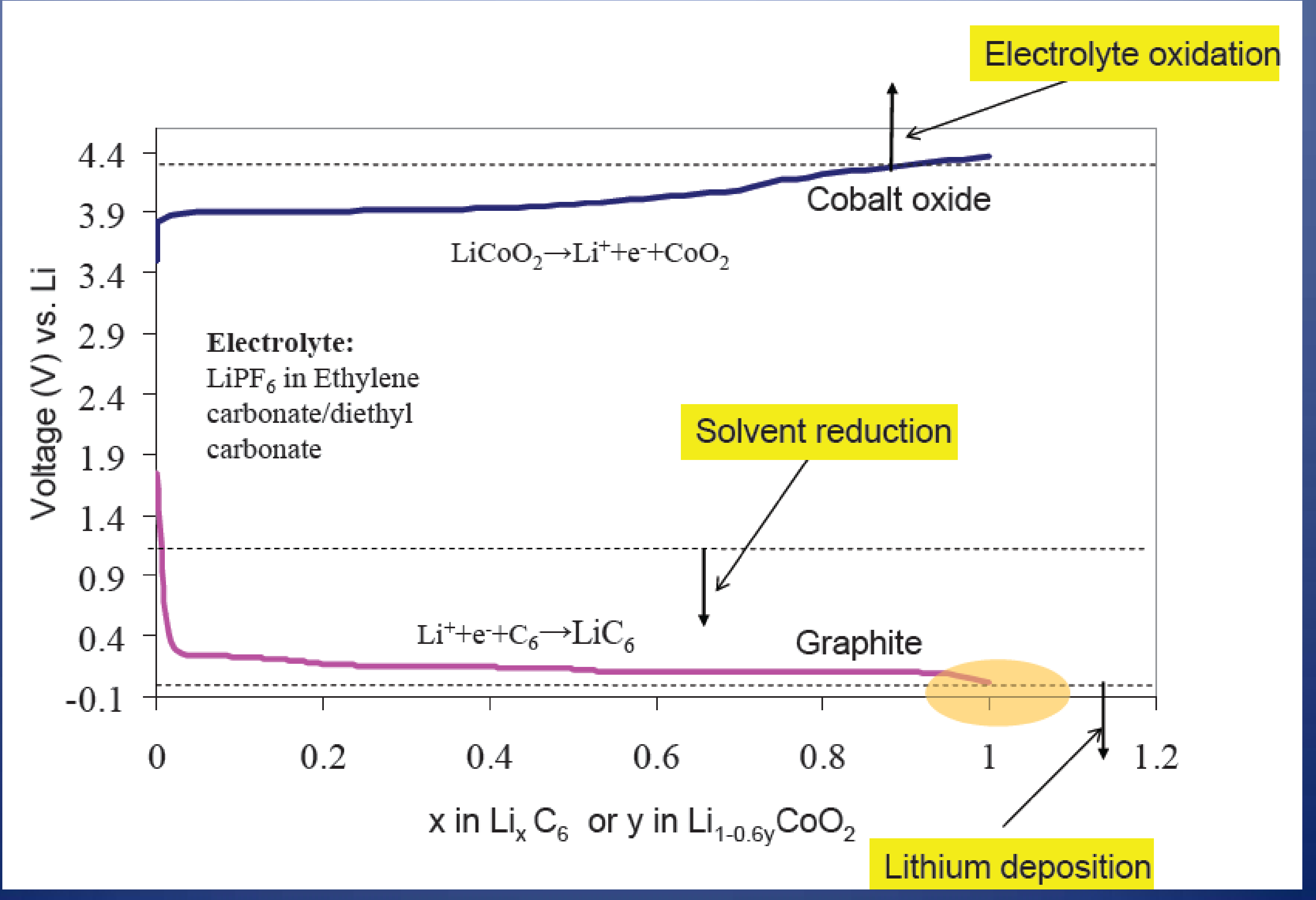


- Salt such as Lithium hexafluoro phosphate




A
e
Anode
Cathode
e
Electrolyte
e
e
e
e
e
e
e
e
e
Cu Current Collector
Graphene Structure
Li+
Solvent Molecule
LiMO2 Layer Structure
Al Current Collector

The First Charge of a Lithium Ion Cell

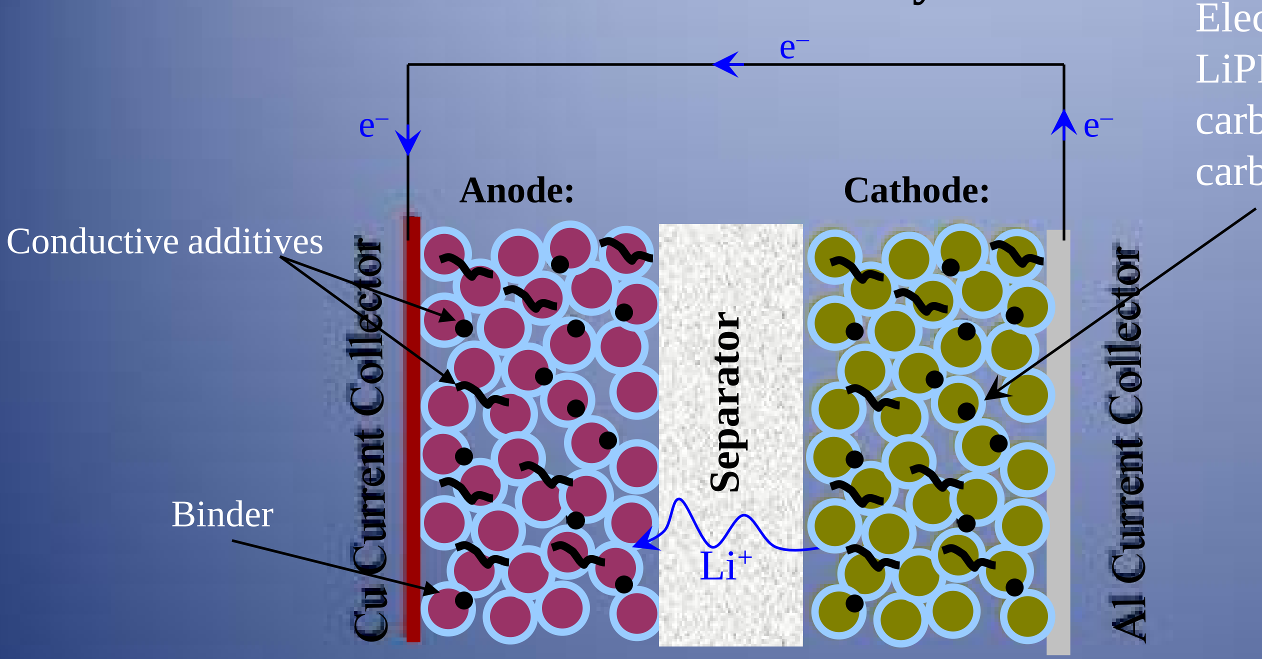


Inconvenient Truths

- On the first charge the carbonates react to form a Solid-Electrolyte Interphase (SEI) layer on the graphite electrode that prevents further decomposition and allows the lithium to intercalate into the graphite.
- The conductivity of the electrolyte is very low relative to acid or alkaline aqueous electrolytes so the electrode spacing must be very small.

Modern Li-ion Battery

Lithium-ion battery



$Li^{+}+e^{-}+C_6 \rightarrow LiC_6$ $\quad$ $LiCoO_2 \rightarrow Li^{+}+e^{-}+CoO_2$

Innovation can occur via new material development, or by better engineering

Manufacturing

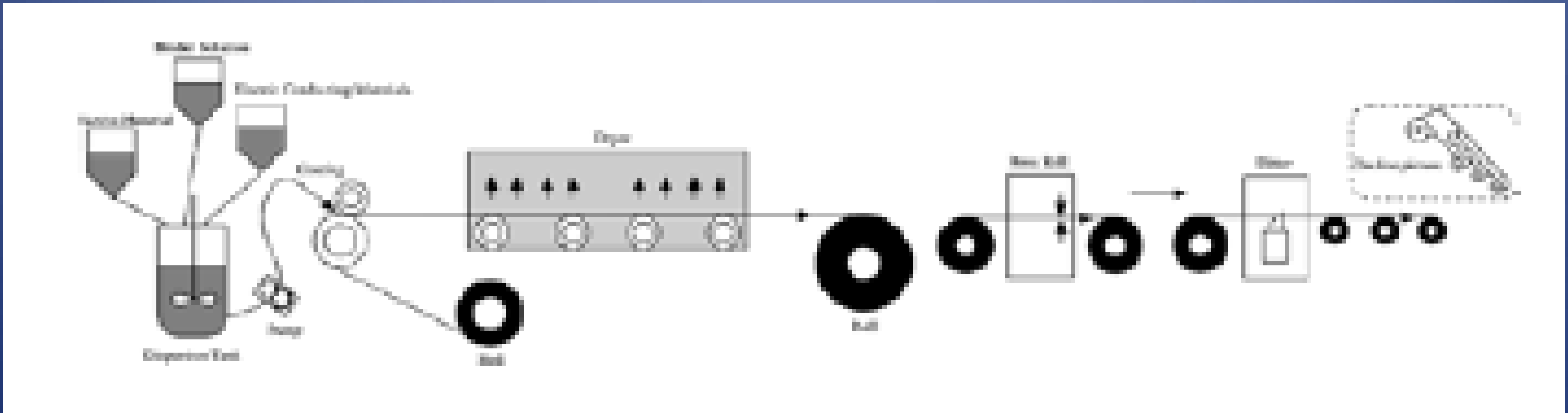
- Slurry Coating
- Calendaring
- Winding
- Cell Assembly
- Electrolyte Fill
- Cap and Seal
- Electrochemical Formation Charge

Starting Materials

Current Collectors
Aluminum foil (Cathode) 20µm
Copper foil (Anode) 14 µm

Separator
Polyethylene
50% porosity, 3-8 µm

Slurry Coating



Manufacturing Equipment

Coating and Drying of Electrodes

Calendaring

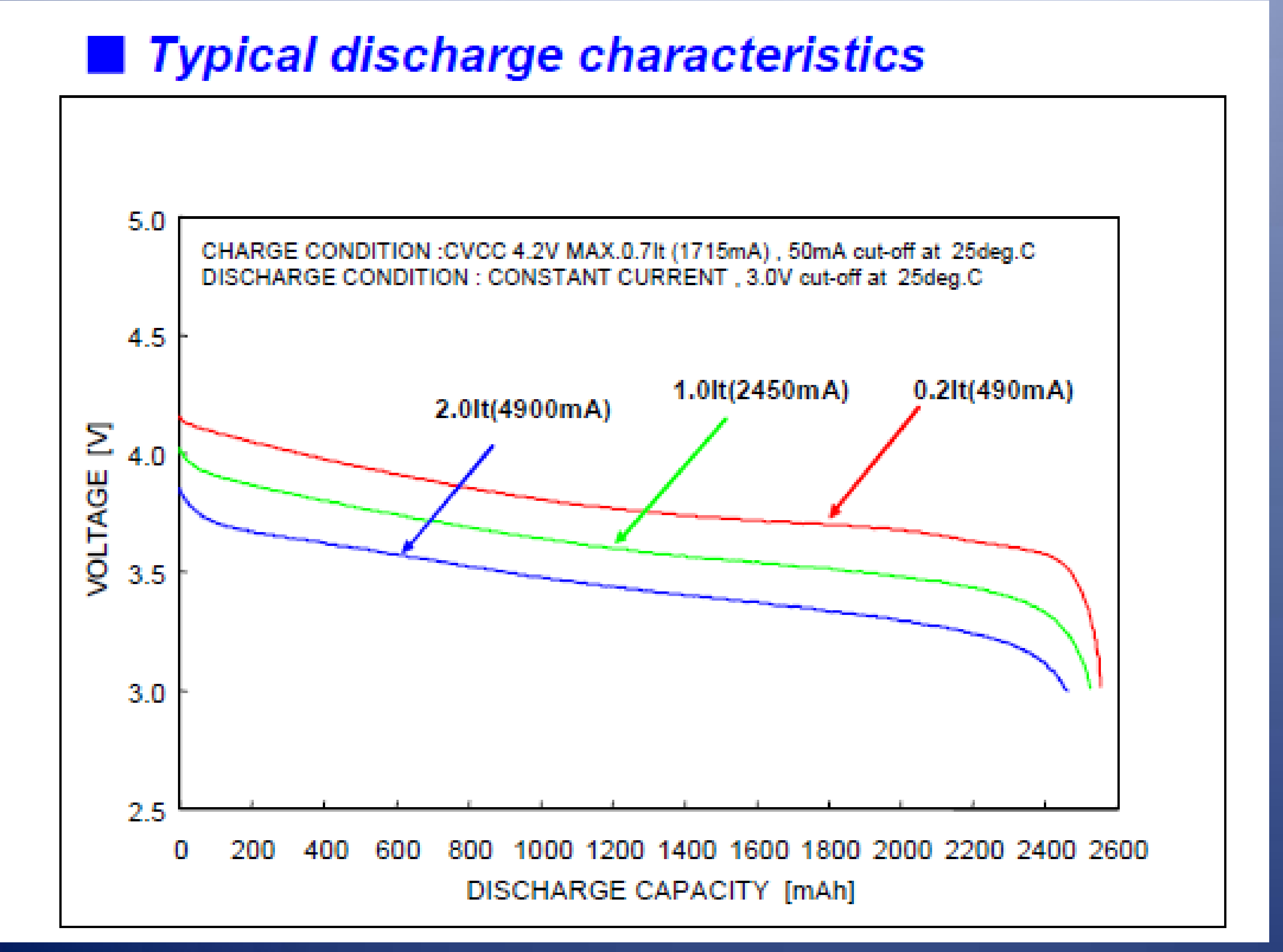
Final Assembly, Filling, Sealing

Cans, Caps, Mandrels

Parts of the Cells

Finished Product

Panasonic CGR18650EA



2.55 Ah Capacity

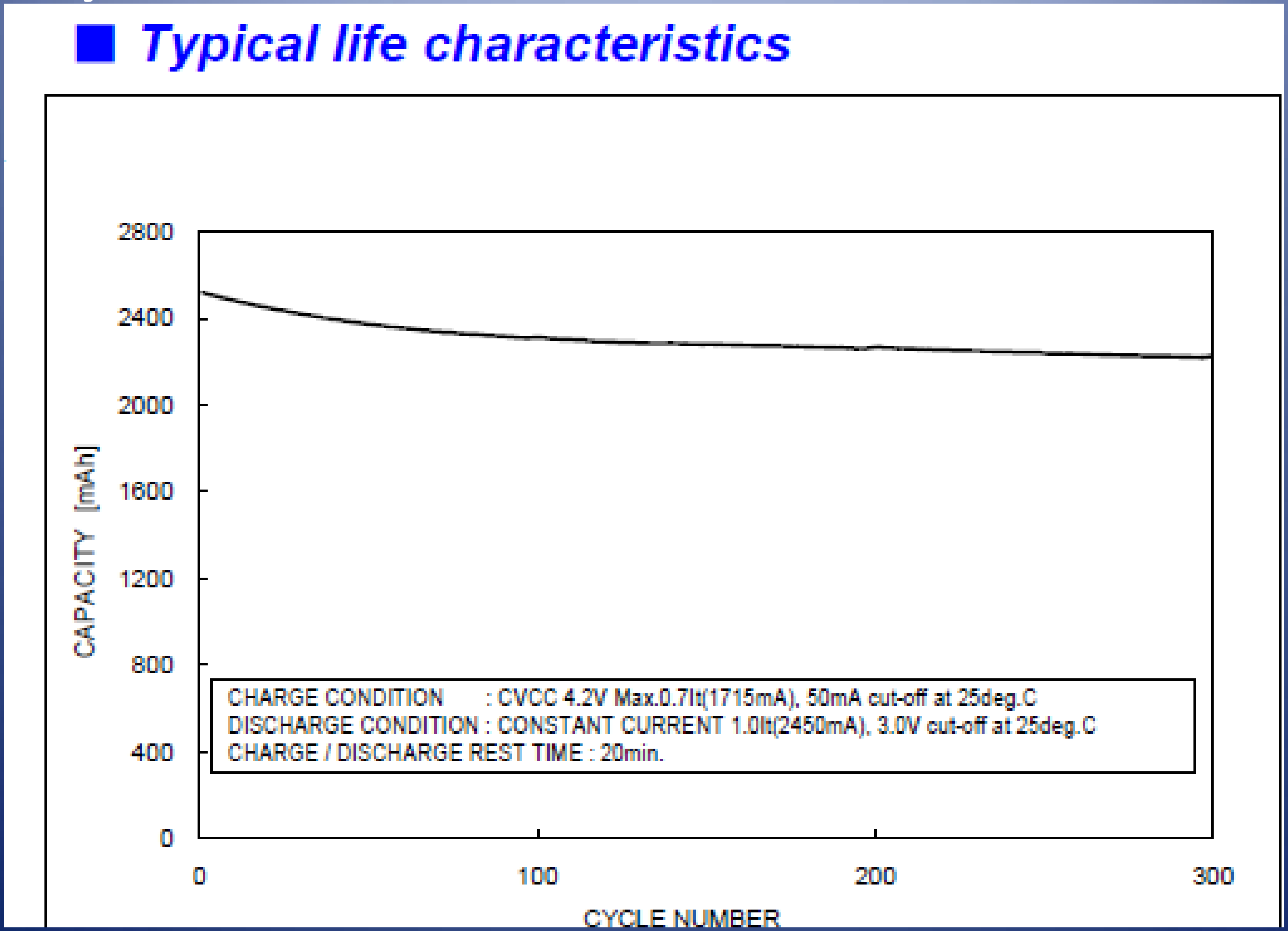
46.5 g Mass

3.7 V Nominal

9.43 Wh

209 Wh/kg

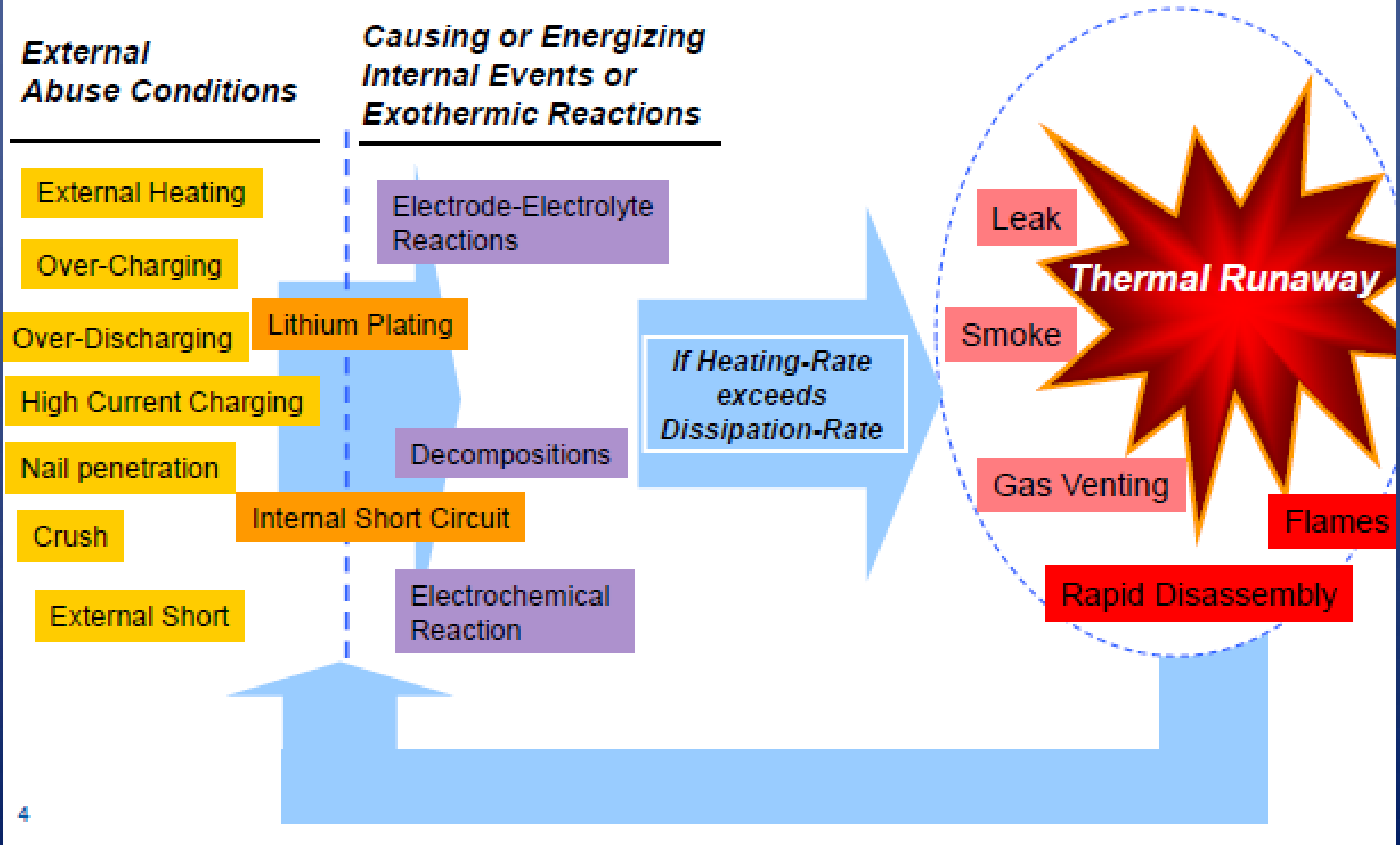
Cycle Life Panasonic CGR18650 EA



Safety

- The lithium ion cell is safe if carefully controlled
- If not controlled serious problems can occur including
  - Venting of flammable electrolyte
  - Fire
  - Explosion

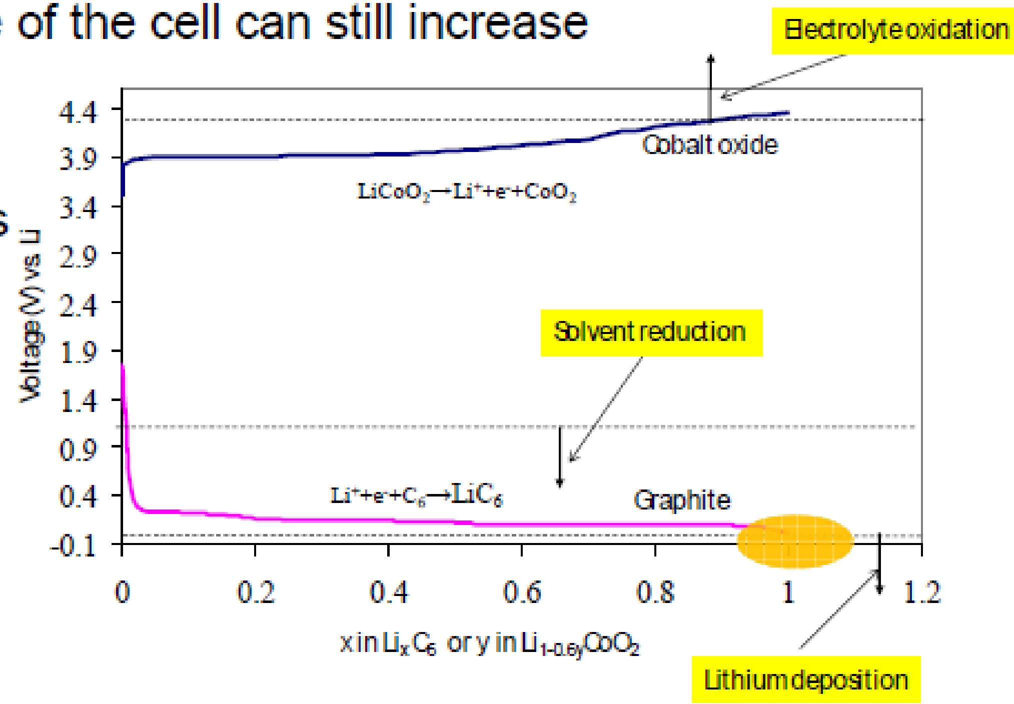
Thermal Runaway Events



Preventing Thermal Runaway

- Use a cathode where oxygen is not released ($LiFePO_4$ cathode from A123)
  - However, note that temperature of the cell can still increase

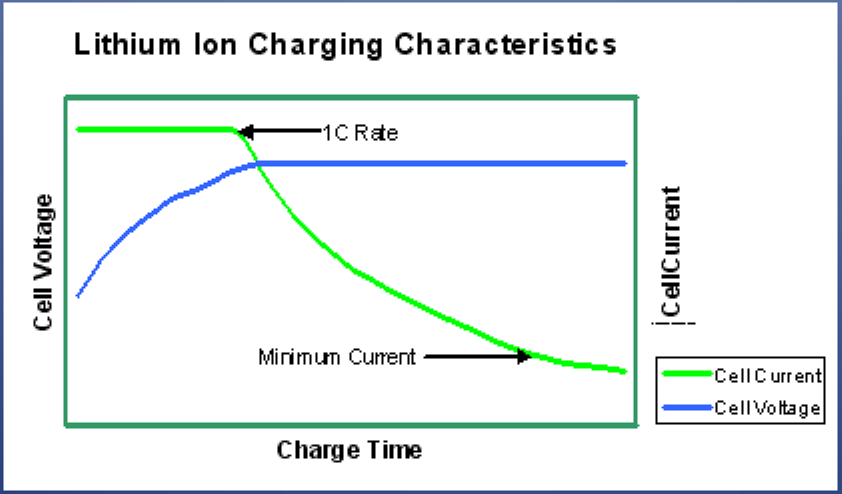
- Move away from a material that forms an SEI on the anode.
  - Anodes do exist that have this feature, but they also have a low voltage ($Li_4Ti_5O_{12}$ from Altair).



- Find a way to provide a overcharge protection similar to lead-acid and Ni-MH cells
  - Attempts are being made to find additives, or redox shuttles, that oxidize on the cathode on overcharge, and reduce on the anode.
  - However, as of today no ideal shuttle mechanism has been found.

Electronic Control

- For Safety
- For Long Life
- For State Of Charge Knowledge
- Daniel Forbes will discuss



Single-Cell Control Circuit Verification

STW 4102 Integrated Circuit for Lithium Ion Cells

Daniel Forbes

Objectives

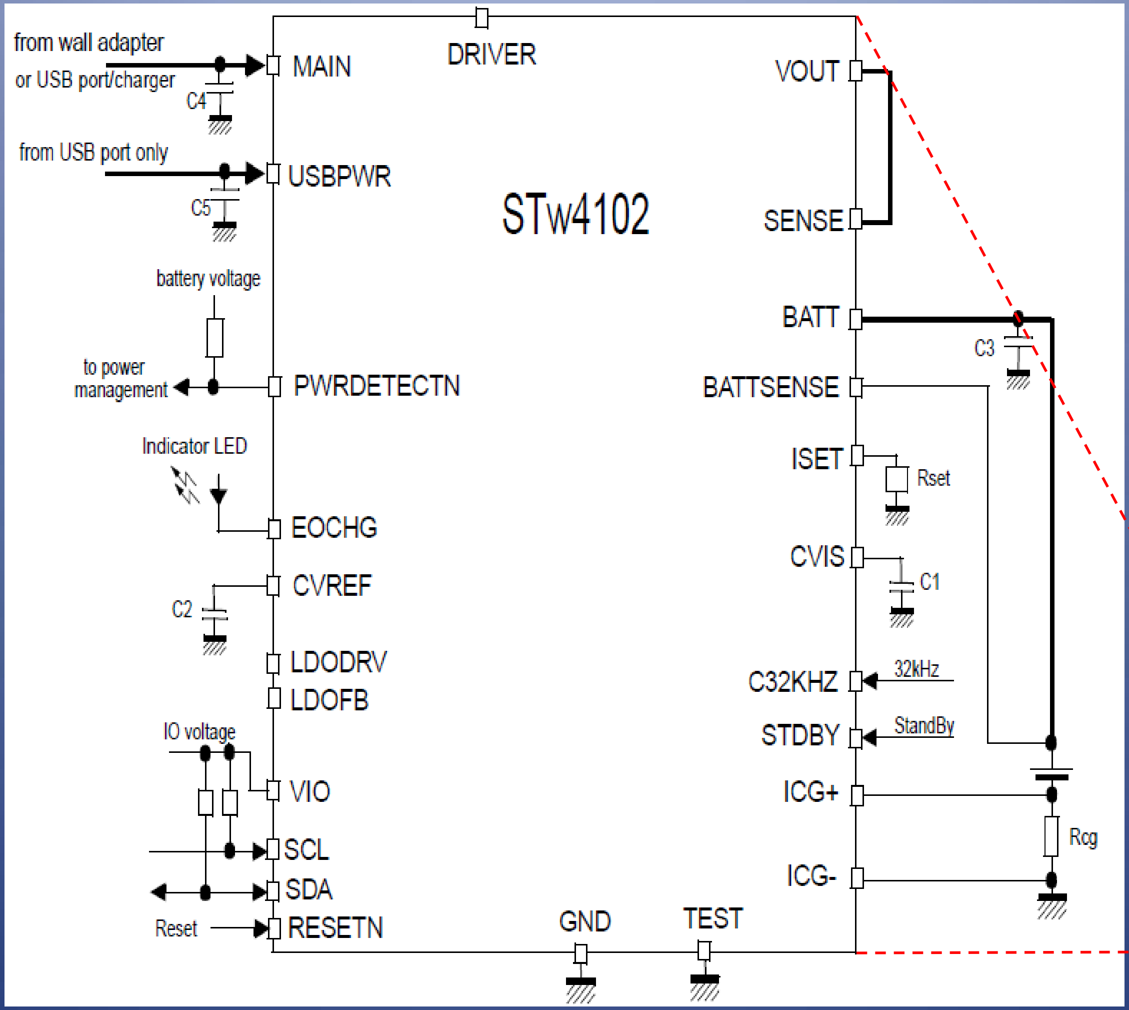
- Experiment with charging and discharging a lithium ion battery
- Research available devices
- Test device to verify operation and learn about cells
- Provide battery lab with simple means to cycle battery while gathering data

Approach

- Surveyed control strategies / available ICs
- Selected control IC
- Designed a test circuit
- Fabricated test board
- Obtained sample cells
- Designed and executed test plan
- Compiled gathered data into graphs for analysis

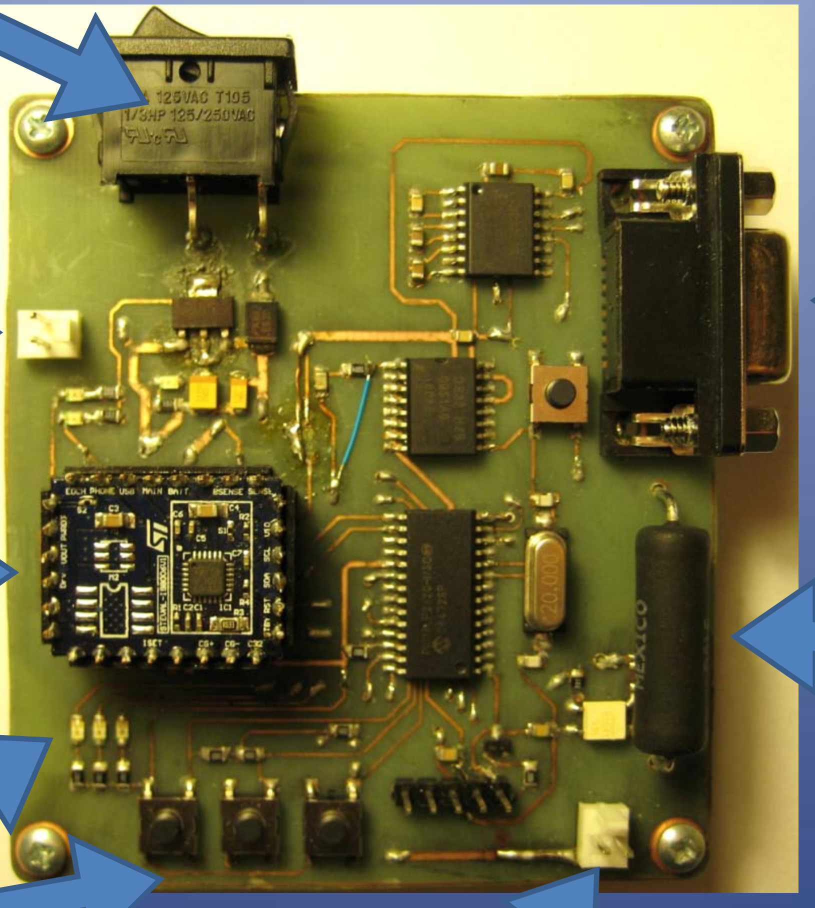
Hardware:

STw4102 Charger and Gas Gauge



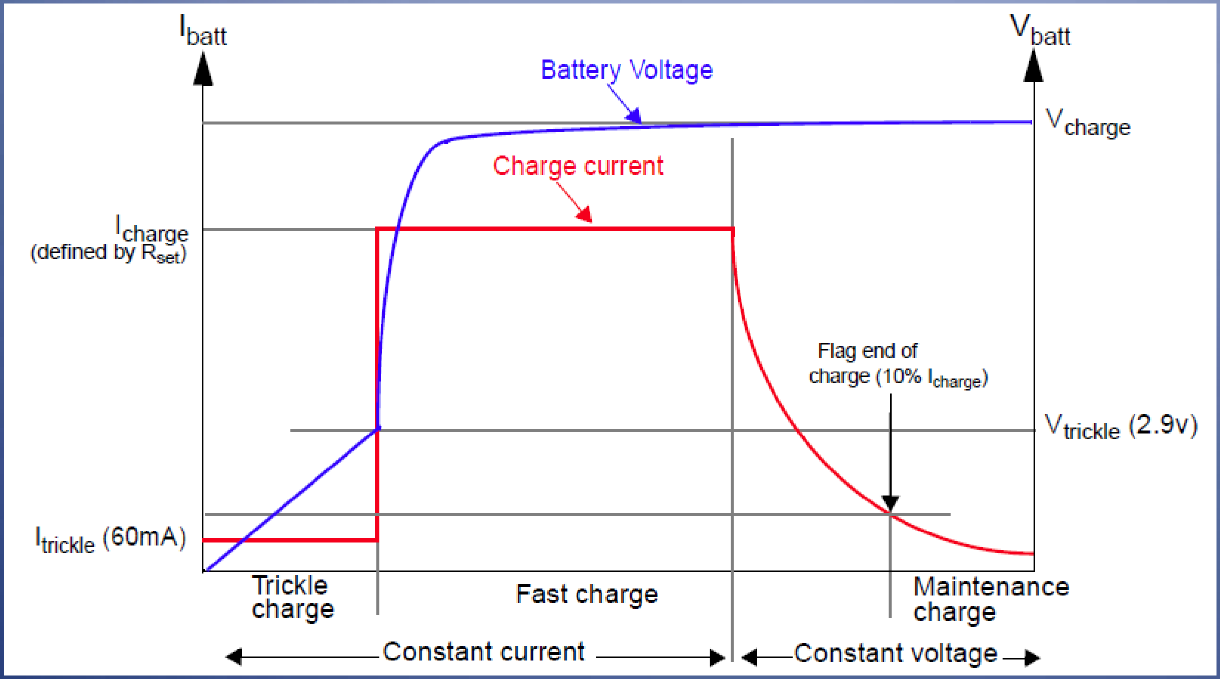
Hardware:

Complete Demonstration Board



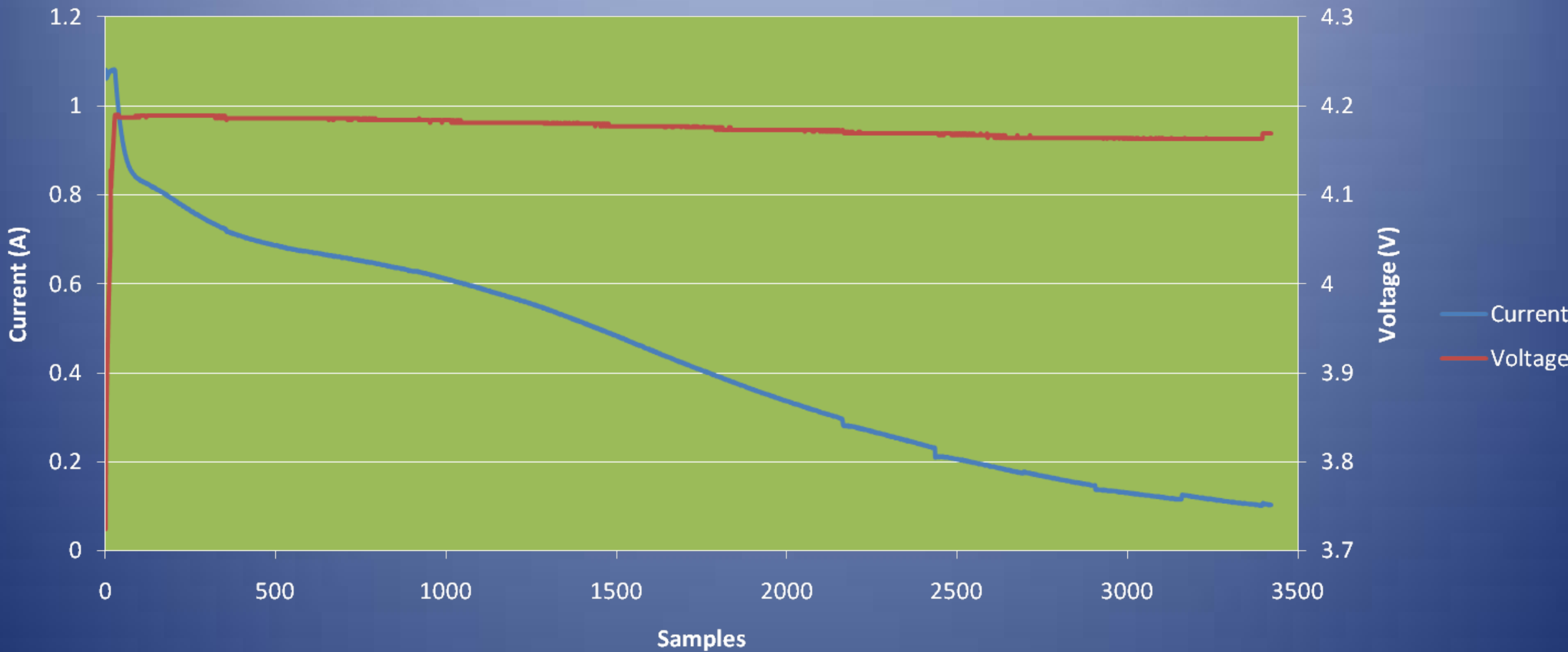
Hardware

Expected Constant-Current Constant-Voltage (CCCV) Charge Curves

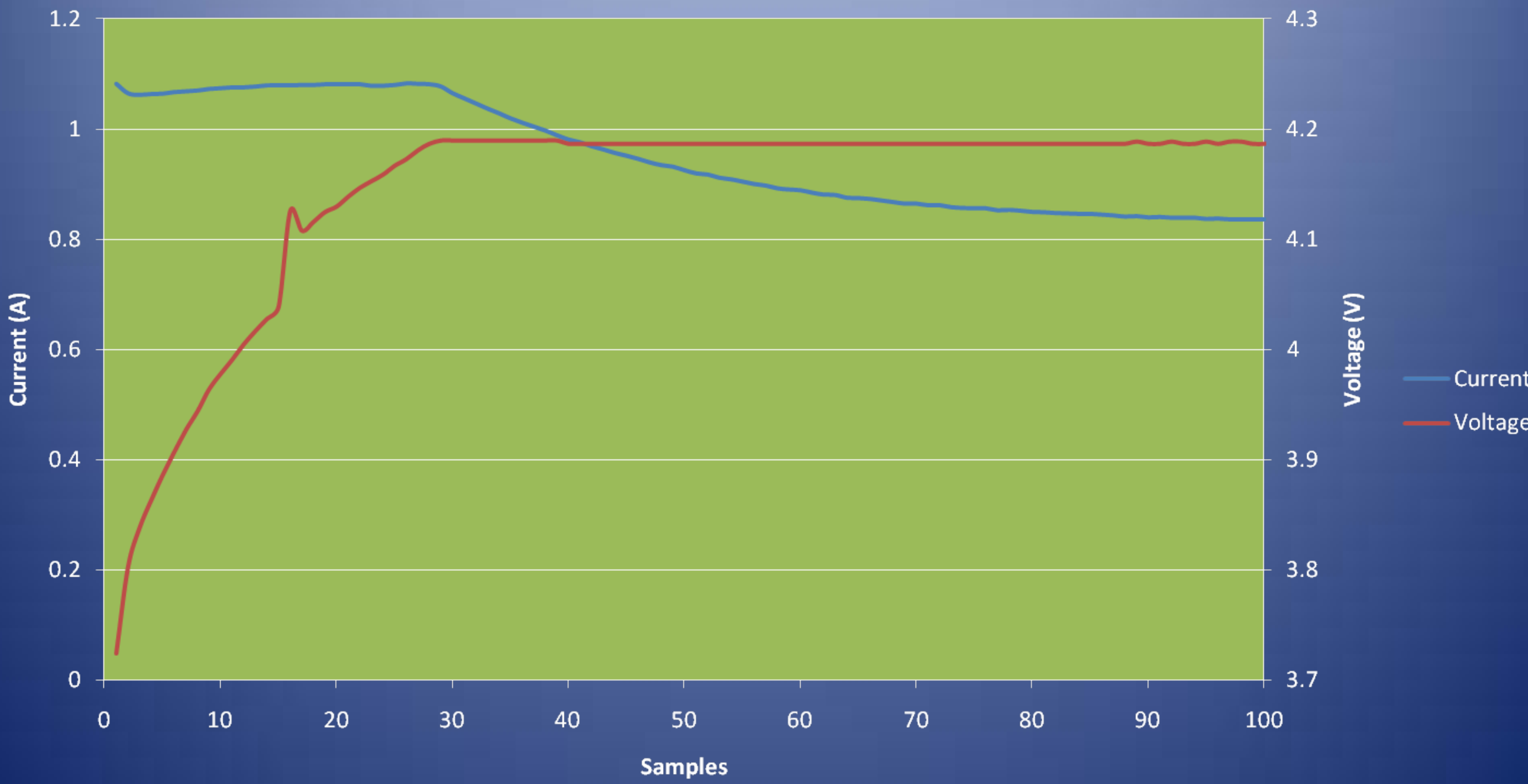


Sample Test Cell:
750 mAh, 3.7 V

Results
Charging (mostly CV)

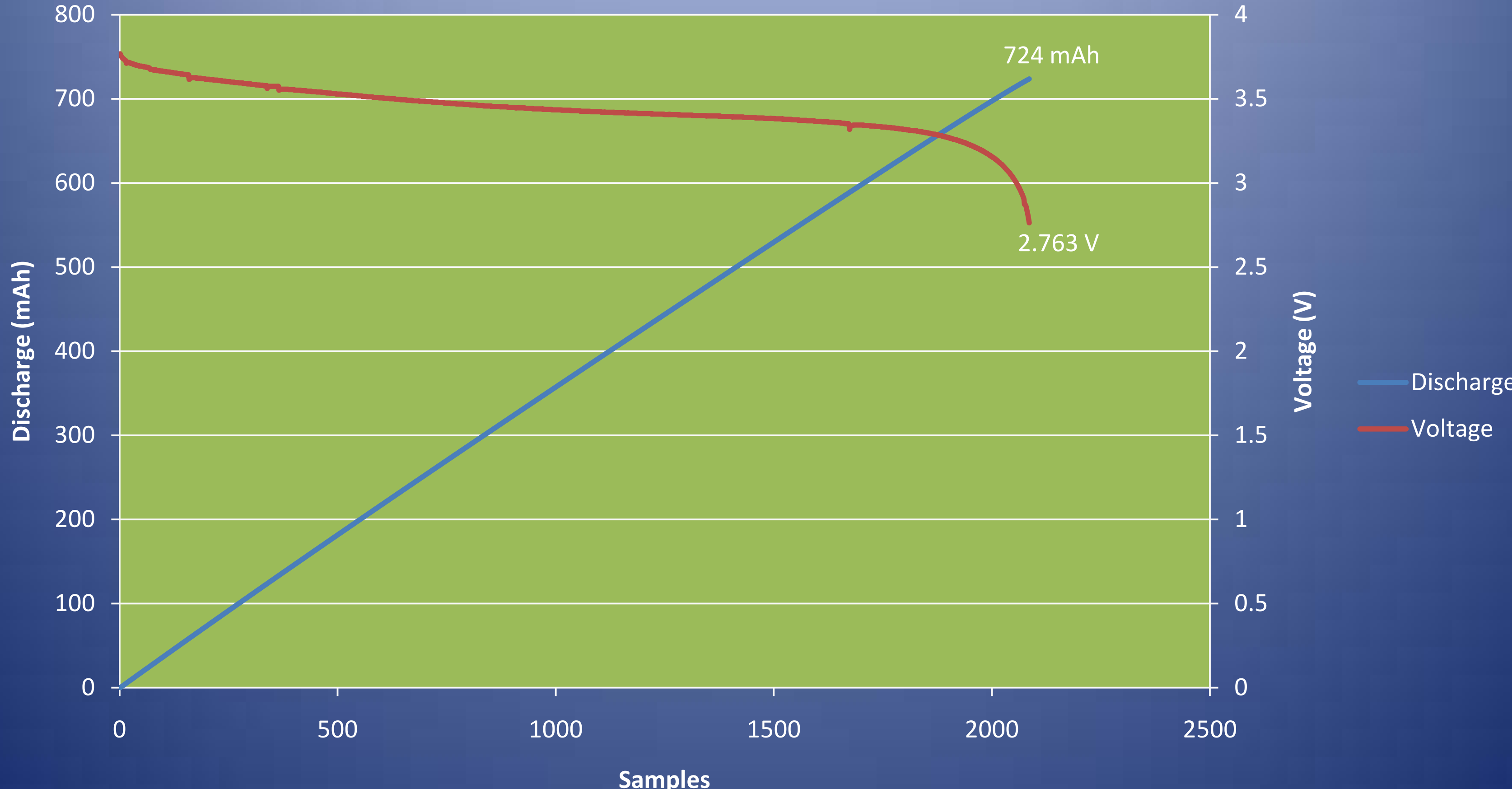


Results
Charging (mostly CV)



Results

Discharging Through a 4.7 Ω Resistor



Conclusions

- STw4102 appears to operate as advertised, providing charging and gas gauging
- Problems encountered
  - I^2C communication debugging
  - PCB quality
  - Loose connection or bad STw4102 demo. board
- Tested test equipment as well as cell
- Tool for battery lab for future use

Recommendation for further work

- Expand system to work with multiple cells
- Build a pack and instrument each cell
- Some fallbacks of STw4102
  - 32 kHz input needed
  - Limited to 914 mAh cell maximum
  - Alternative: TI BQ27541
    - Offers more features (6000 mAh limit, temperature, time-to-empty)
    - Doesn’t integrate charger, separate IC required
- Fix experimental problems (new boards on the way, testing daughter board)
- Automate testing (build a cycler) to increase cell data acquisition speed

Tesla Roadster

Interesting Sites

Electropaedia
http://www.mpoweruk.com/index.htm

Wikipedia
http://en.wikipedia.org/wiki/Lithium-ion_battery

The Battery University
http://www.batteryuniversity.com/index.htm

http://www.meridian-int-res.com/Projects/Lithium_Microscope.pdf

Books

Yoshio, Masaki et al, ed. Lithium Ion Batteries: Science and Technologies. Berlin: Springer, 2009.

Nazri, Gholam-Abbas et al , ed. Lithium Batteries: Science and Technology. Dordrecht: Kluwer Academic Publishers 2004.

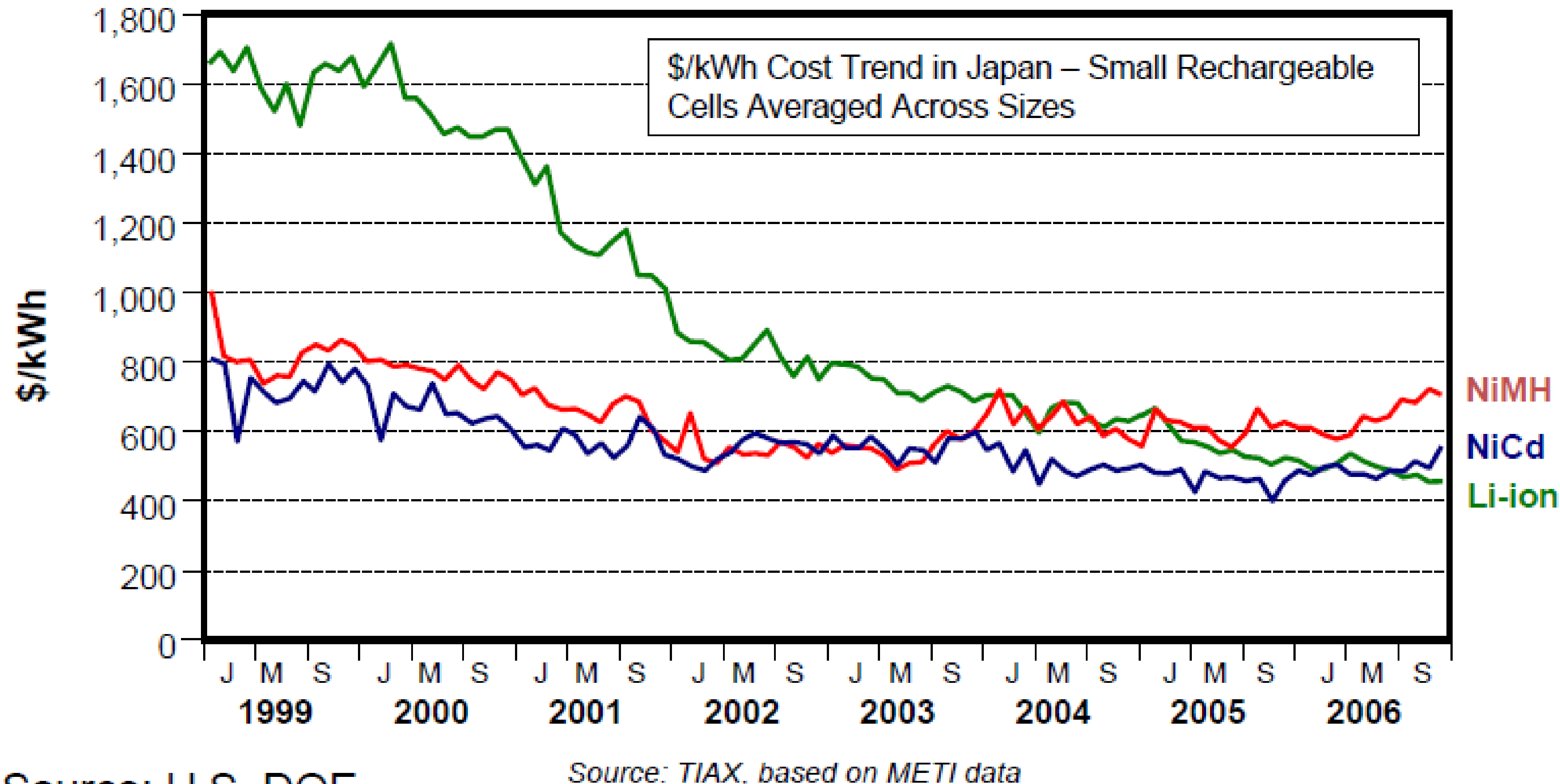
Mathematical Models of John Newman (UC Berkeley)

A Combined Model for Determining Capacity Usage and Battery Size for Hybrid and Plug-in Hybrid Vehicles (with Paul Albertus, Jeremy Couts, and Venkat Srinivasan). *Journal of Power Sources*, **183** (2008), 771-782.

Supplementary Material

- Cost
- Market Growth
- Advanced Chemistries

Cost



Source: U.S. DOE

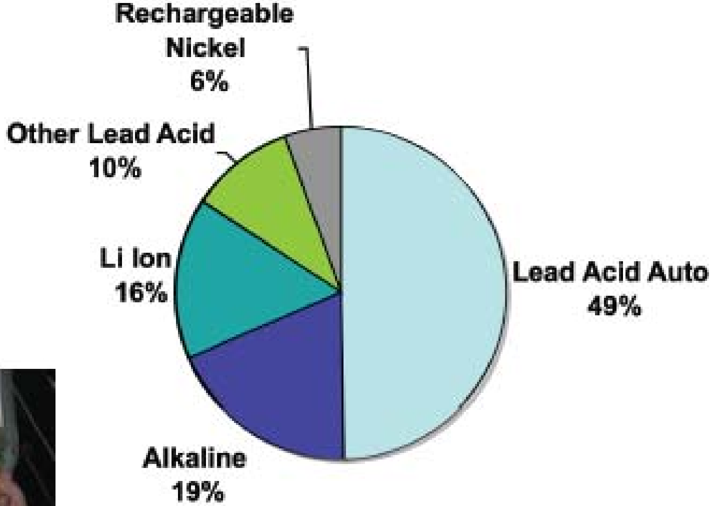
For consumer electronics, energy and cost are the biggest drivers

Battery Market

1867

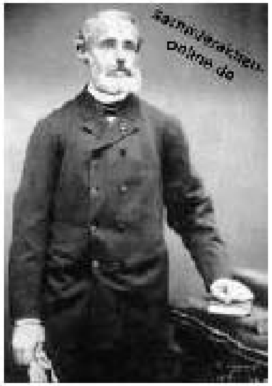
Today

2004 Global Market Share



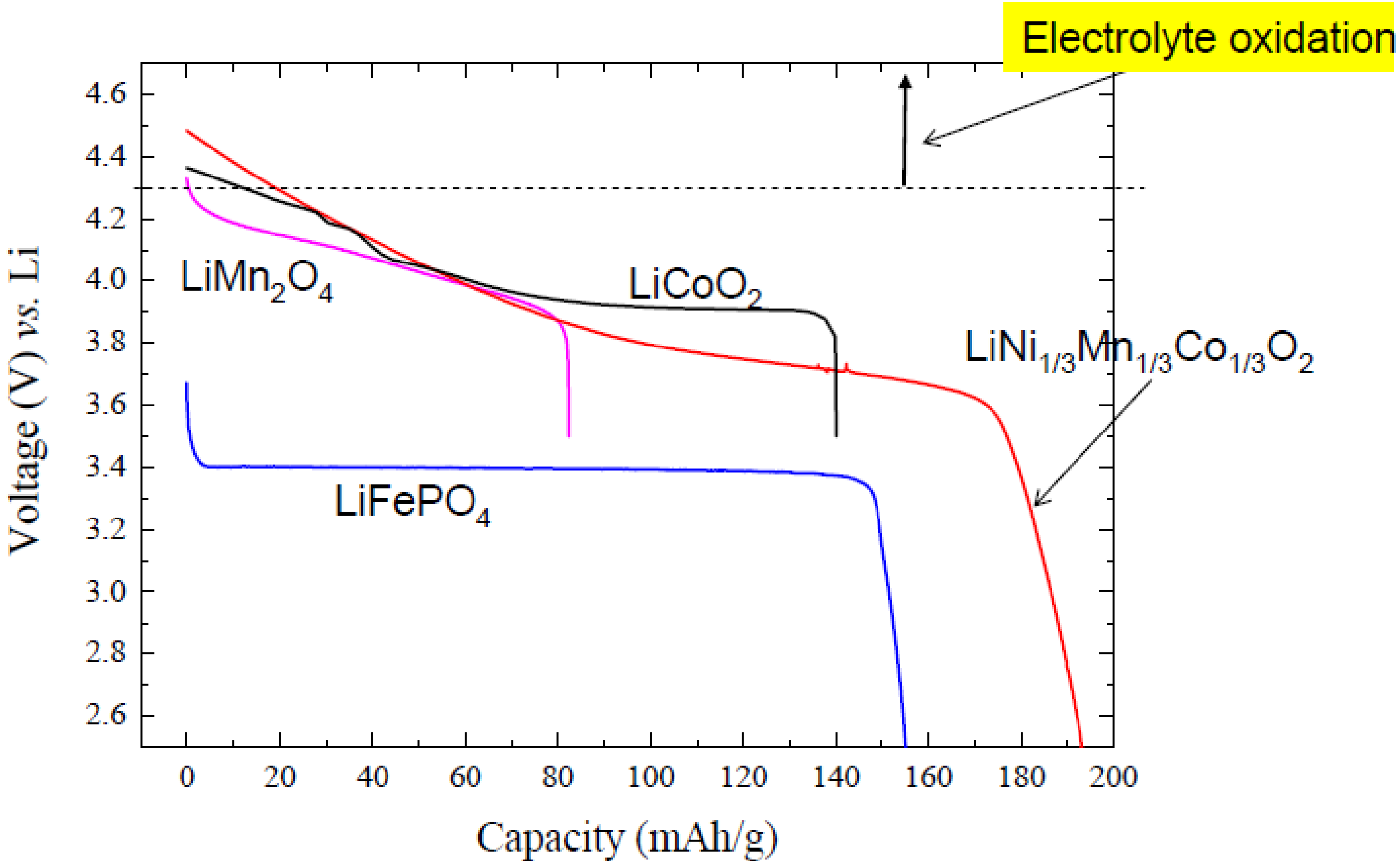
1859

Today



Advanced Chemistries

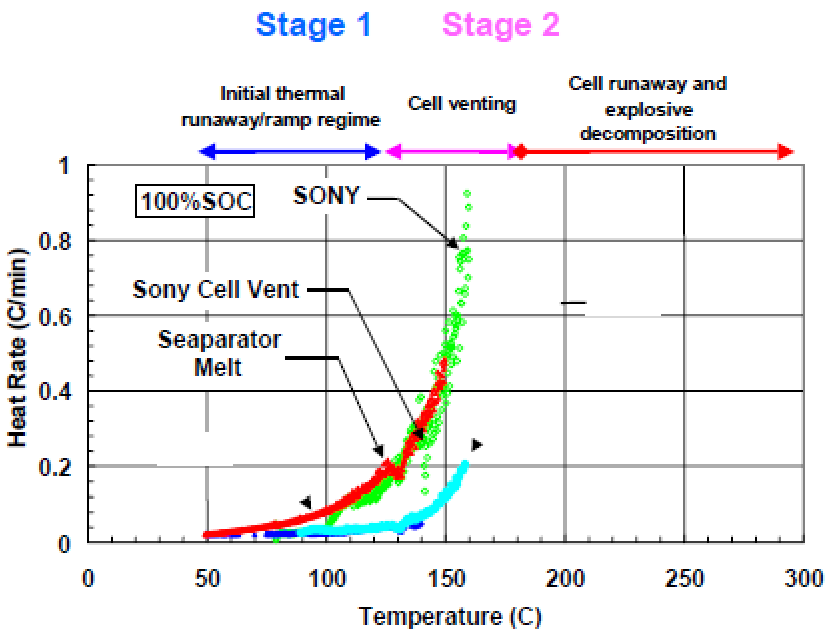
Equilibrium Potential of a Few Cathodes

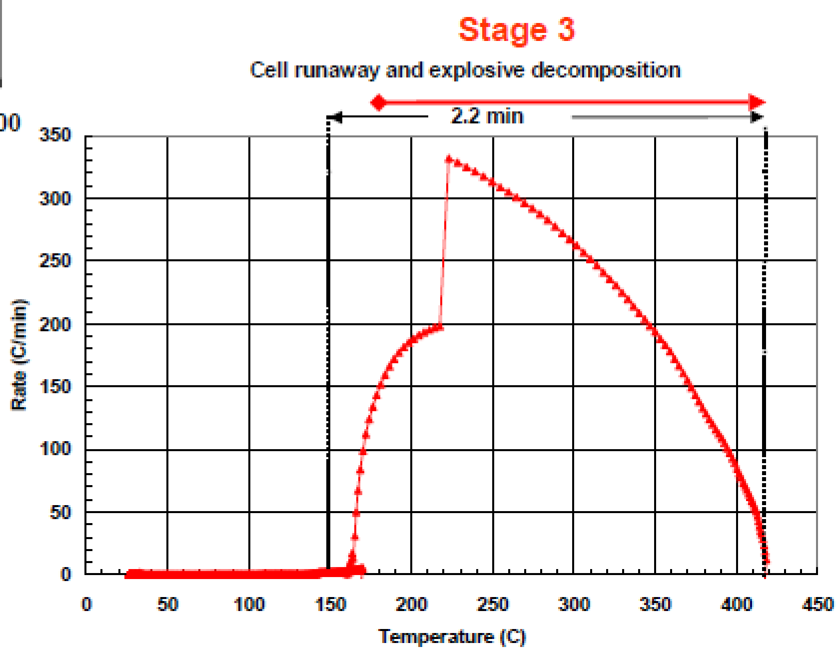


Cathodes have different voltage, different capacity

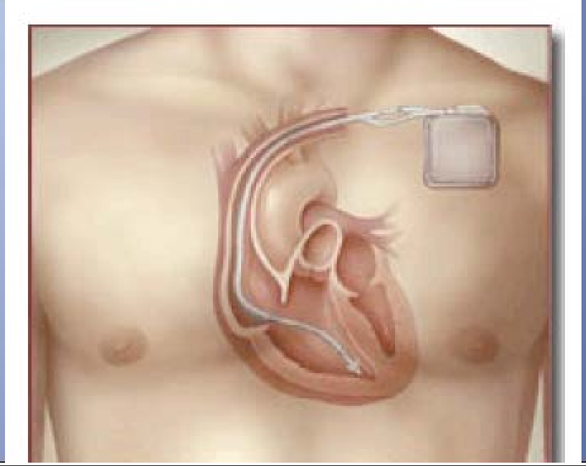
Higher the voltage, or higher the capacity, more energy in the cell

Thermal Runway in Li-ion Cells





Biomedical Applications



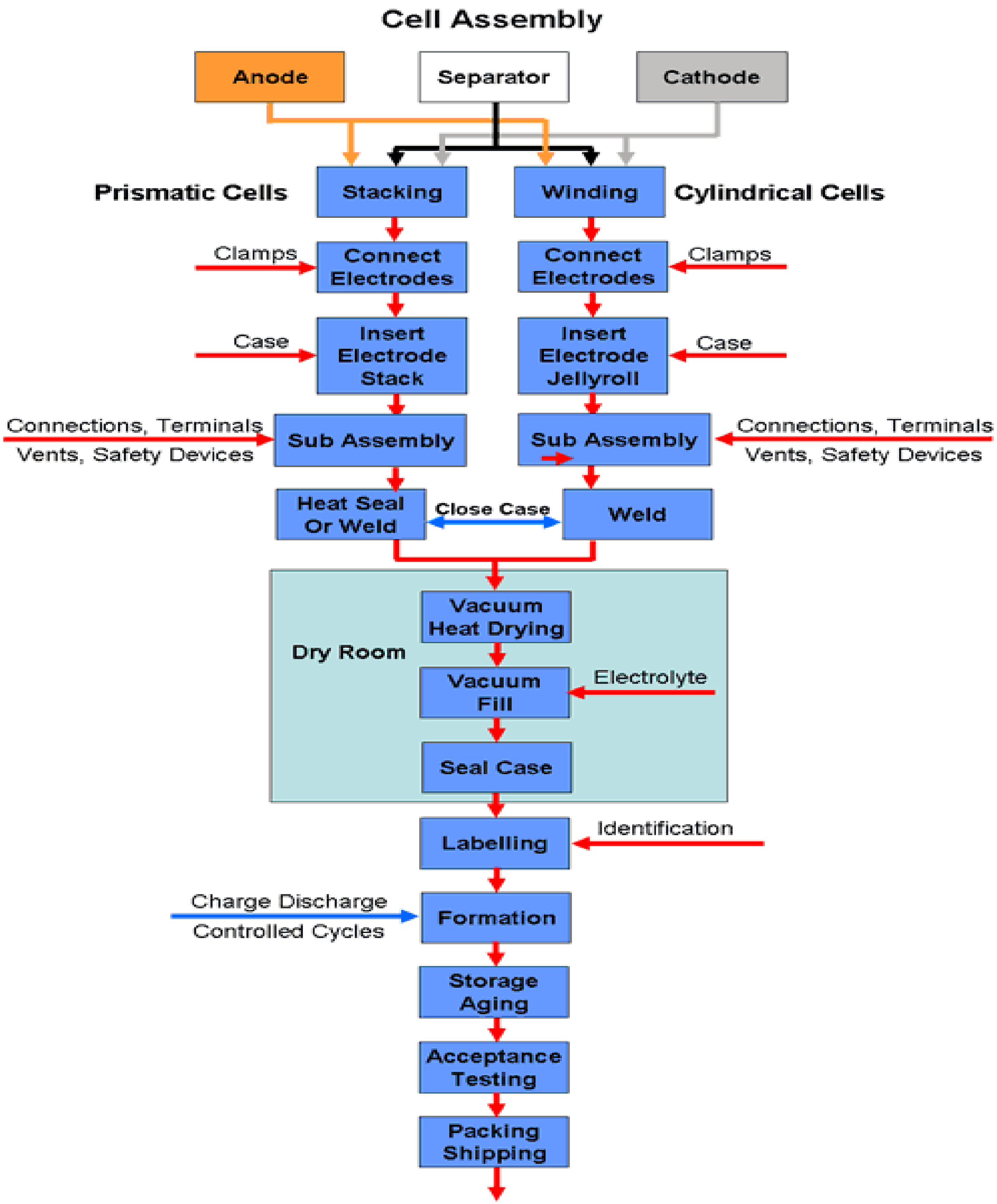
Cardiac Pacemakers	Conduction disorders
Cardiac Defibrillators	Ventricular and atrial tachyarrithmia and fibrillation
Muscle Stimulators	Incontinence
Neurological Stimulators	Essential tremors (Parkinsons disease)
Cochlear Implants	Hearing disorders
Monitoring Devices	Synapse , Seizures
Drug Pumps	Pain caused by cancer and injury Diabetes (insulin pumps) Spasticity (intrathecal baclofen pumps)
Left Ventricle Assist Devices	Heart failure –bridge to transplant or recovery

Candidate Anodes

Anode Material	Average Voltage	Gravimetric Capacity
Graphite (LiC_6)	0.1-0.2 V	372 mA·h/g
Hard Carbon (LiC_6)	? V	? mA·h/g
Titanate ($Li_4Ti_5O_{12}$)	1-2 V	160 mA·h/g
Si ($Li_{4.4}Si$)	0.5-1 V	4212 mA·h/g
Ge ($Li_{4.4}Ge$)	0.7-1.2 V	1624 mA·h/g

Candidate Cathodes

Cathode Material	Average Voltage	Gravimetric Capacity
$LiCoO_2$	3.7 V	140 mA·h/g
$LiMn_2O_4$	4.0 V	100 mA·h/g
$LiNiO_2$	3.5 V	180 mA·h/g
$LiFePO_4$	3.3 V	150 mA·h/g
Li_2FePO_4F	3.6 V	115 mA·h/g
$LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$	3.6 V	160 mA·h/g
$Li(Li_aNi_xMn_yCo_z)O_2$	4.2 V	220 mA·h/g


Cell Assembly
Anode
Separator
Cathode
Prismatic Cells
Stacking
Winding
Cylindrical Cells
Clamps
Connect Electrodes
Connect Electrodes
Clamps
Case
Insert Electrode Stack
Insert Electrode Jellyroll
Case
Connections, Terminals
Vents, Safety Devices
Sub Assembly
Sub Assembly
Connections, Terminals
Vents, Safety Devices
Heat Seal Or Weld
Close Case
Weld
Dry Room
Vacuum Heat Drying
Vacuum Fill
Electrolyte
Seal Case
Labelling
Identification
Charge Discharge
Controlled Cycles
Formation
Storage Aging
Acceptance Testing
Packing Shipping

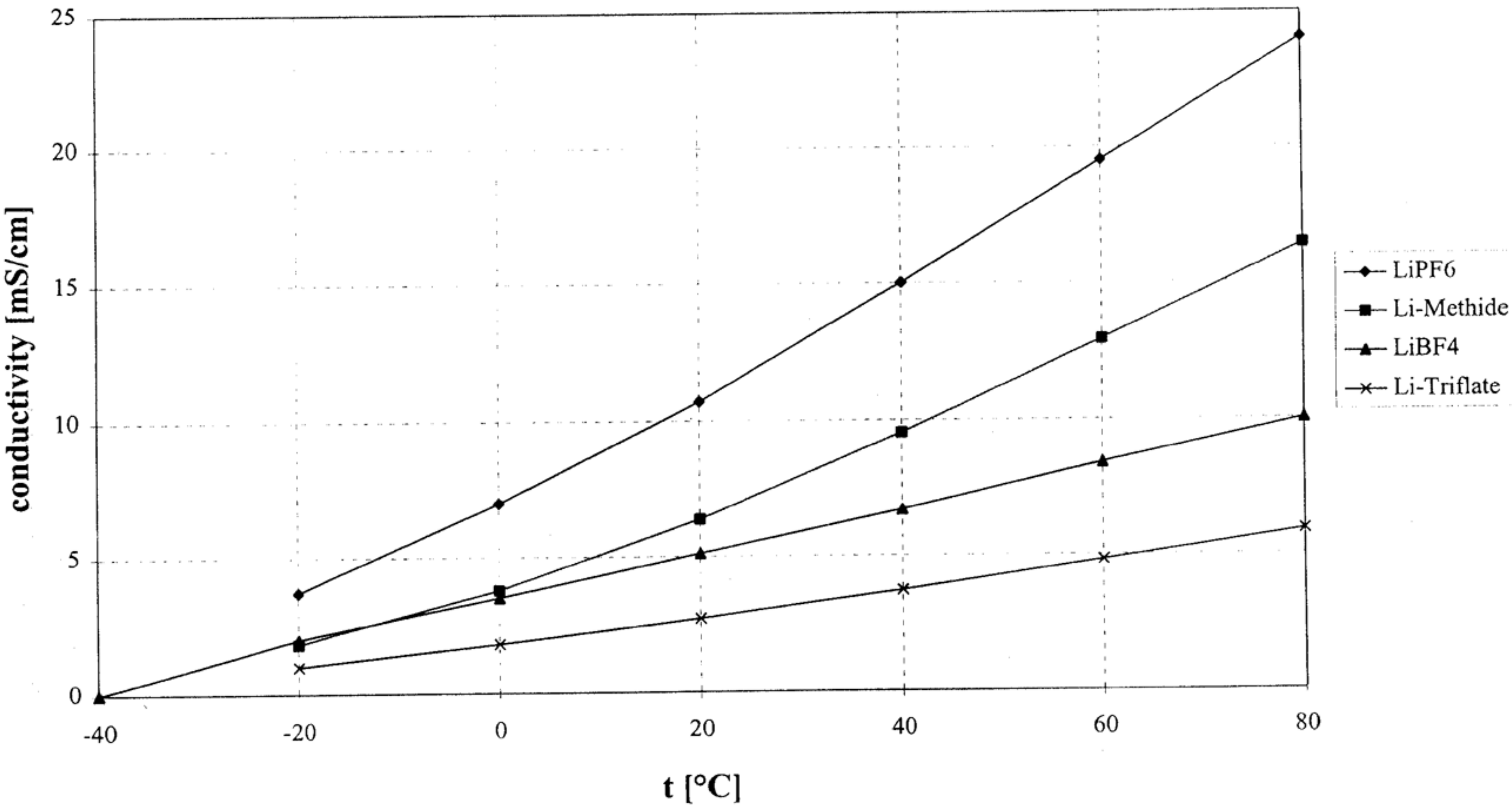


Fig. 1: Comparison of conductivity of 4 different Li-salts (1 M Li-salt in EC:DMC 50:50 wt%)

Electrode Coating