Advanced Secondary Batteries And Their Applications for Hybrid and Electric Vehicles

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Outline

- Introduction to batteries
- Equilibrium and kinetics
- Various secondary batteries
  - Lead acid batteries
  - Nickel metal hydride batteries
  - Lithium ion batteries
- Applications
  - Electric vehicles
  - Hybrid electric vehicles

Introduction to Batteries

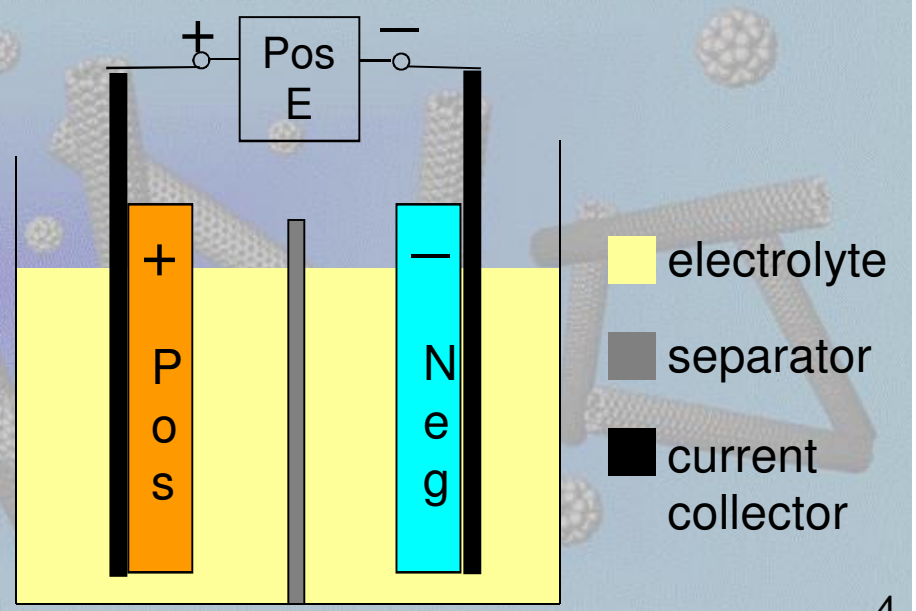
- Battery terminology
  - Primary and secondary batteries
  - Cell voltage (open circuit)
  - Positive and negative electrodes
  - Cathode and anode
  - Power energy and charge
  - Battery cell module and pack
  - Charge and discharge curves
  - Cycle life

Primary and Secondary Batteries

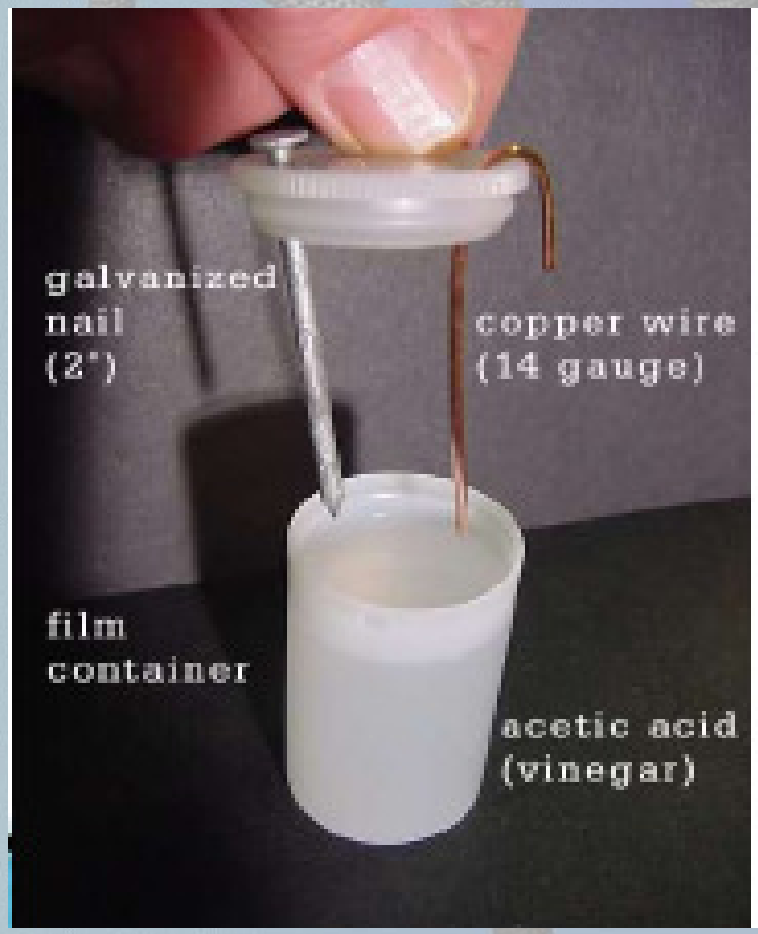
- Primary Battery: not rechargeable (dry cell)
- Secondary Battery: rechargeable (lithium ion batteries)
- Battery is composed of
  - Positive electrode
  - Negative electrode
  - Electrolyte
  - Separator
  - Current collectors

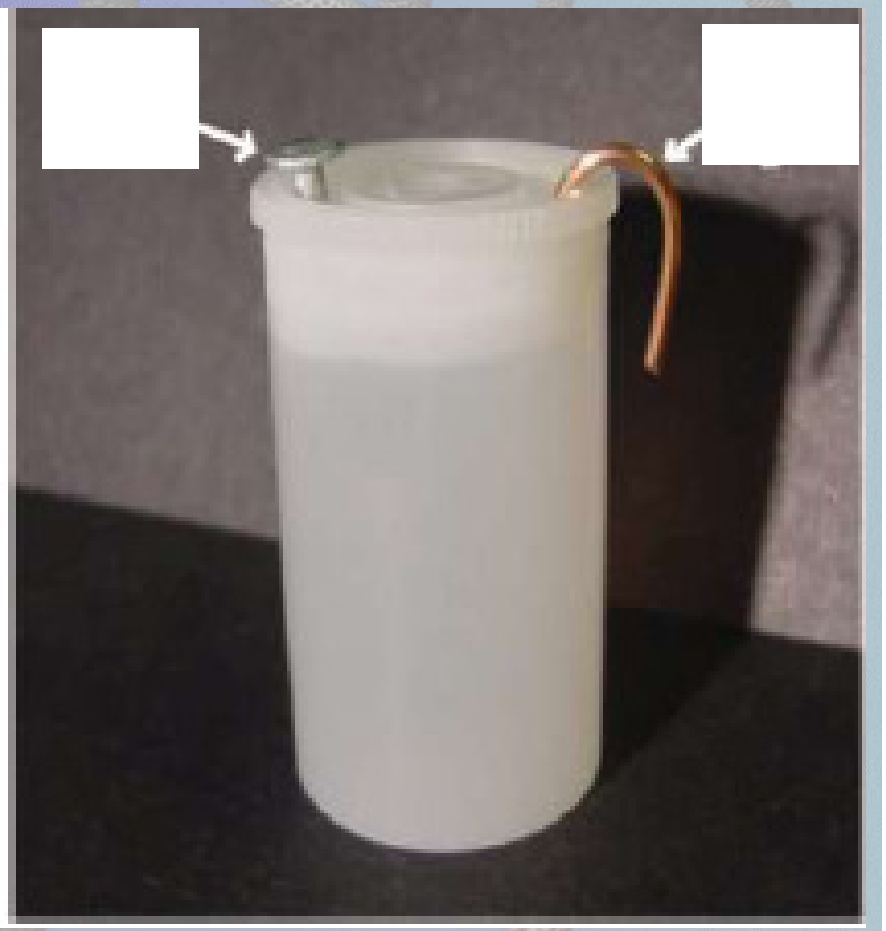
$$E_{oc} = E+ - E-$$

(Cell V) (Half cell V)



How to Determine Positive and Negative Electrodes





How to Calculate Cell Voltage

- Use half cell reduction potentials (25 °C)

Electrode reaction	E°, V
$Li^{+} + e \leftrightarrow Li$	-3.01
$Rb^{+} + e \leftrightarrow Rb$	-2.98
$Cs^{+} + e \leftrightarrow Cs$	-2.92
$K^{+} + e \leftrightarrow K$	-2.92
$Ba^{+2} + 2e \leftrightarrow Ba$	-2.92
$Sr^{+2} + 2e \leftrightarrow Sr$	-2.89
$Ca^{+2} + 2e \leftrightarrow Ca$	-2.84
$Na^{+} + e \leftrightarrow Na$	-2.71
$Mg(OH)_2 + 2e \leftrightarrow Mg + 2OH^{-}$	-2.69
$Mg^{+2} + 2e \leftrightarrow Mg$	-2.38
$Al(OH)_3 + 3e \leftrightarrow Al + 3OH^{-}$	-2.34
$Ti^{+2} + 2e \leftrightarrow Ti$	-1.75
$Be^{+2} + 2e \leftrightarrow Be$	-1.70
$Al^{+3} + 3e \leftrightarrow Al$	-1.66
$Zn(OH)_2 + 2e \leftrightarrow Zn + 2OH^{-}$	-1.25
$Mn^{+2} + 2e \leftrightarrow Mn$	-1.05
$Fe(OH)_2 + 2e \leftrightarrow Fe + 2OH^{-}$	-0.88
$2H_2O + 2e \leftrightarrow H_2 + 2OH^{-}$	-0.83
$Cd(OH)_2 + 2e \leftrightarrow Cd + 2OH^{-}$	-0.81
$Zn^{+2} + 2e \leftrightarrow Zn$	**-0.76**
$Ni(OH)_2 + 2e \leftrightarrow Ni + 2OH^{-}$	-0.72
$Ga^{+3} + 3e \leftrightarrow Ga$	-0.52
$S + 2e \leftrightarrow S^{-2}$	-0.48
$Fe^{+2} + 2e \leftrightarrow Fe$	-0.44
$Cd^{+2} + 2e \leftrightarrow Cd$	-0.40
$PbSO_4 + 2e \leftrightarrow Pb + SO_4^{-2}$	-0.36
$In^{+3} + 3e \leftrightarrow In$	-0.34
$Tl^{+} + e \leftrightarrow Tl$	-0.34
$Co^{+2} + 2e \leftrightarrow Co$	-0.27

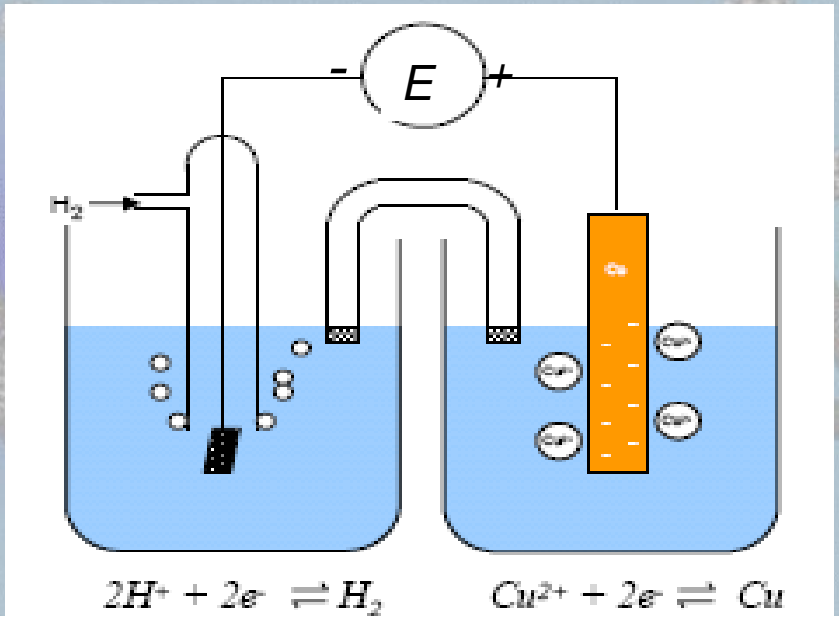
Less stable

Electrode reaction	E°, V
$Ni^{+2} + 2e \leftrightarrow Ni$	-0.23
$Sn^{+2} + 2e \leftrightarrow Sn$	-0.14
$Pb^{+2} + 2e \leftrightarrow Pb$	-0.13
$O_2 + H_2O + 2e \leftrightarrow HO_2^{-} + OH^{-}$	-0.08
$D^{+} + e \leftrightarrow 1/2D_2$	-0.003
$H^{+} + e \leftrightarrow 1/2H_2$	0.00
$HgO + H_2O + 2e \leftrightarrow Hg + 2OH^{-}$	0.10
$CuCl + e \leftrightarrow Cu + Cl^{-}$	0.14
$AgCl + e \leftrightarrow Ag + Cl^{-}$	0.22
$Cu^{+2} + 2e \leftrightarrow Cu$	**0.34**
$Ag_2O + H_2O + 2e \leftrightarrow 2Ag + 2OH^{-}$	0.35
$1/2O_2 + H_2O + 2e \leftrightarrow 2OH^{-}$	0.40
$NiOOH + H_2O + e \leftrightarrow Ni(OH)_2 + OH^{-}$	0.45
$Cu^{+} + e \leftrightarrow Cu$	0.52
$I_2 + 2e \leftrightarrow 2I^{-}$	0.54
$2AgO + H_2O + 2e \leftrightarrow Ag_2O + 2OH^{-}$	0.57
$Hg^{+2} + 2e \leftrightarrow Hg$	0.80
$Ag^{+} + e \leftrightarrow Ag$	0.80
$Pd^{+2} + 2e \leftrightarrow Pd$	0.83
$Ir^{+3} + 3e \leftrightarrow Ir$	1.00
$Br_2 + 2e \leftrightarrow 2Br^{-}$	1.07
$O_2 + 4H^{+} + 4e \leftrightarrow 2H_2O$	1.23
$MnO_2 + 4H^{+} + 2e \leftrightarrow Mn^{+2} + 2H_2O$	1.23
$Cl_2 + 2e \leftrightarrow 2Cl^{-}$	1.36
$PbO_2 + 4H^{+} + 2e \leftrightarrow Pb^{+2} + 2H_2O$	1.46
$PbO_2 + SO_4^{-2} + 4H^{+} + 2e \leftrightarrow PbSO_4 + 2H_2O$	1.69
$F_2 + 2e \leftrightarrow 2F^{-}$	2.87

More stable

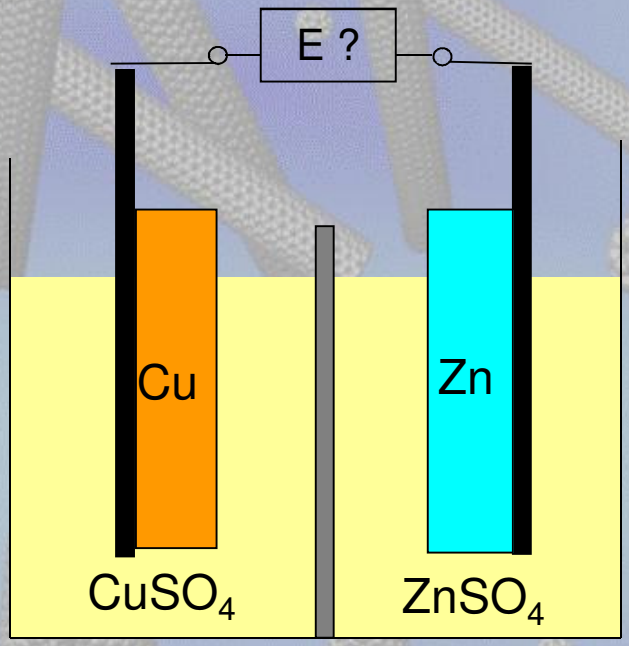
How to Calculate Cell Voltage

- Half cell reduction potentials are measured as follows:
  - Cell voltage is measured between electrode A (Cu) and hydrogen electrode ($E_{oc} = E_A - E_{H2}$)
  - The potential of hydrogen electrode in “acid” is defined as zero volt ($E_{oc} = E_A - 0$)
  - The measured cell voltage is the half cell reduction potential of electrode A



Calculate Cell Voltage (Open circuit)

Chemical reactions?



Chemical reactions?

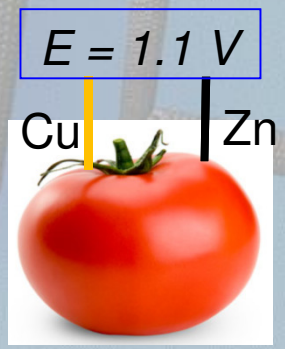
Cell open circuit voltage $E_{oc} = E°_{+} - E°_{-}$

Positive electrode: Cu Negative electrode: Zn

$E°_{+} = 0.34$ V

$E°_{-} = -0.76$ V

$E_{oc} = 0.34 – (- 0.76) = 1.1$ V (**intrinsic**)*



*Current: **extrinsic**

Table
Half Cell Reduction Potentials (25 °C)

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Calculate Cell Voltage (Open Circuit)

- Hydrogen Fuel Cells (with hydrogen and oxygen electrodes)

$O_2 + 4H^+ + 4e \leftrightarrow 2H_2O$	1.23 V
$H^+ + e \leftrightarrow 1/2H_2$	0.00 V
$E_{oc} = 1.23 - 0 =$	**1.23 V**

- Lithium Fluorine Battery

$F_2 + 2e \leftrightarrow 2F^-$	2.87 V
$Li^+ + e \leftrightarrow Li$	-3.01 V
$E_{oc} = 2.87 - (-3.01) =$	**5.88 V**

How to Make High Voltage Batteries

Strong reducing agents

Strong oxidants

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.0079																	2 He 4.0026
3 Li 6.941	4 Be 9.0122											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.065	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.867	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.38	31 Ga 69.723	32 Ge 72.64	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.798
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.96	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57-71 *	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89-103 #	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (270)	109 Mt (268)	110 Ds (281)	111 Rg (272)	112 Uub (285)	113 Uut (284)	114 Uuq (289)	115 Uup (288)	116 Uuh (291)		118 Uuo (294)

* Lanthanide series	57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05	71 Lu 174.97
# Actinide series	89 Ac (227)	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

Cathode and Anode

- Cathode: the electrode where reduction reaction takes place
- Anode: the electrode where oxidation reaction takes place

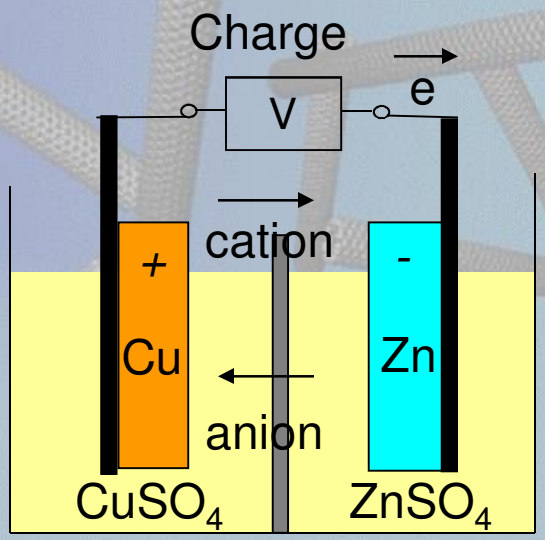
Secondary battery

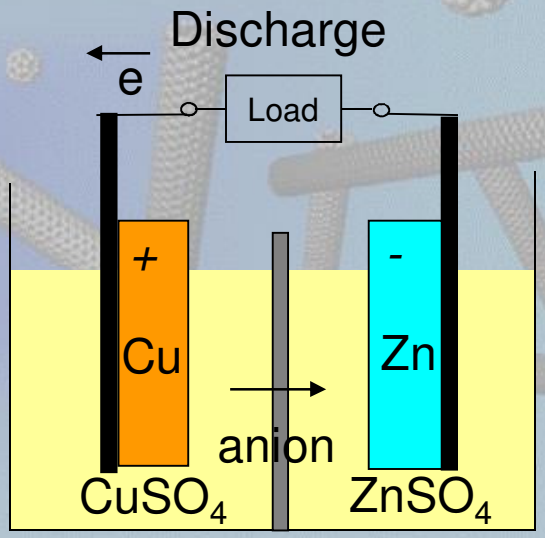
- During charge
  - Negative electrode is the cathode
  - Positive electrode is the anode
- During discharge
  - Positive electrode is the cathode
  - Negative electrode is the anode

Cathode and Anode

Secondary Battery

- During charge
  - Negative electrode is the cathode
    $Zn^{+2} + 2e^- \rightarrow Zn$
  - Positive electrode is the anode
    $Cu \rightarrow Cu^{+2} + 2e^-$
- During discharge
  - Positive electrode is the cathode
    $Cu^{+2} + 2e^- \rightarrow Cu$
  - Negative electrode is the anode
    $Zn \rightarrow Zn^{+2} + 2e^-$





Power Energy and Charge

- Power = Voltage * Current
  - 1 W (watt) = 1 V (volt) * 1 A (ampere)
  - 1 kW = 1000 W
- Energy = Power * Time
  - 1 Wh (watt-hour) = 1 W * 1 h (hour)
  - 1 kWh = 1000 Wh
  - 1 Wh = 3600 J (joules)
- Charge = Current * Time
  - 1 Ah = 1 A * 1 h
  - 1 kAh = 1000 Ah
  - 1 Ah = 3600 C (coulombs)

Power Energy and Charge

- **Specific power**: power withdrawn per unit battery weight
  - W/kg
- Power density: power withdrawn per unit battery volume
  - W/L
- **Specific energy**: energy stored per unit battery weight
  - Wh/kg
- Energy density: energy stored per unit battery volume
  - Wh/L

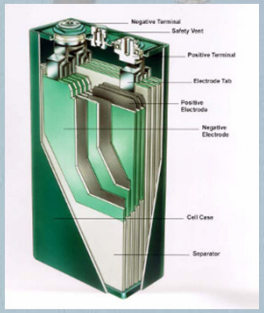
Power Energy and Charge

- Examples
  - AA primary alkaline battery **4.5 Wh**
    - 1.5 V (3 Ah)
  - Lead acid SLI battery **600 Wh**
    - 12 V (50 Ah)
  - Prius battery **1300 Wh (1.3 kWh)**
    - 202 V (6.5 Ah)
  - Lithium ion battery (laptop) **50 Wh**
    - 10 V (5 Ah)
- Gasoline (tank)
  - 600 kWh

Cell Module and Pack

NiMH Cell

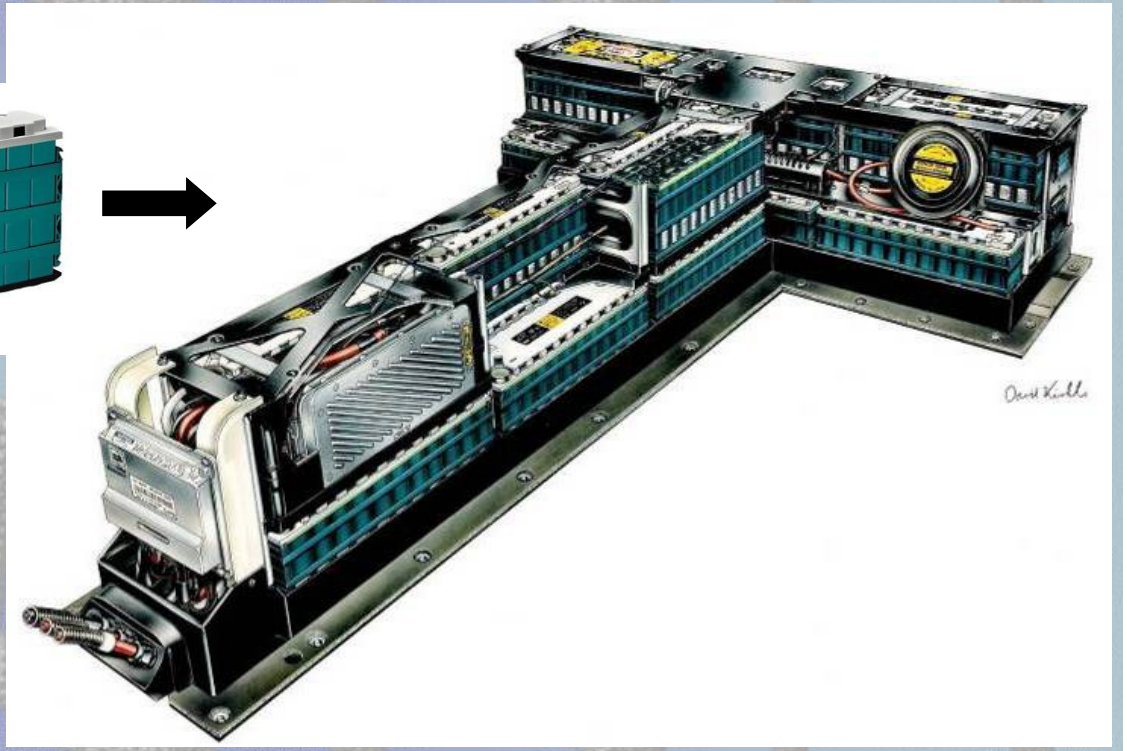
1.2 V



NiMH Module

11 cells

11 x 1.2 = 13.2 V



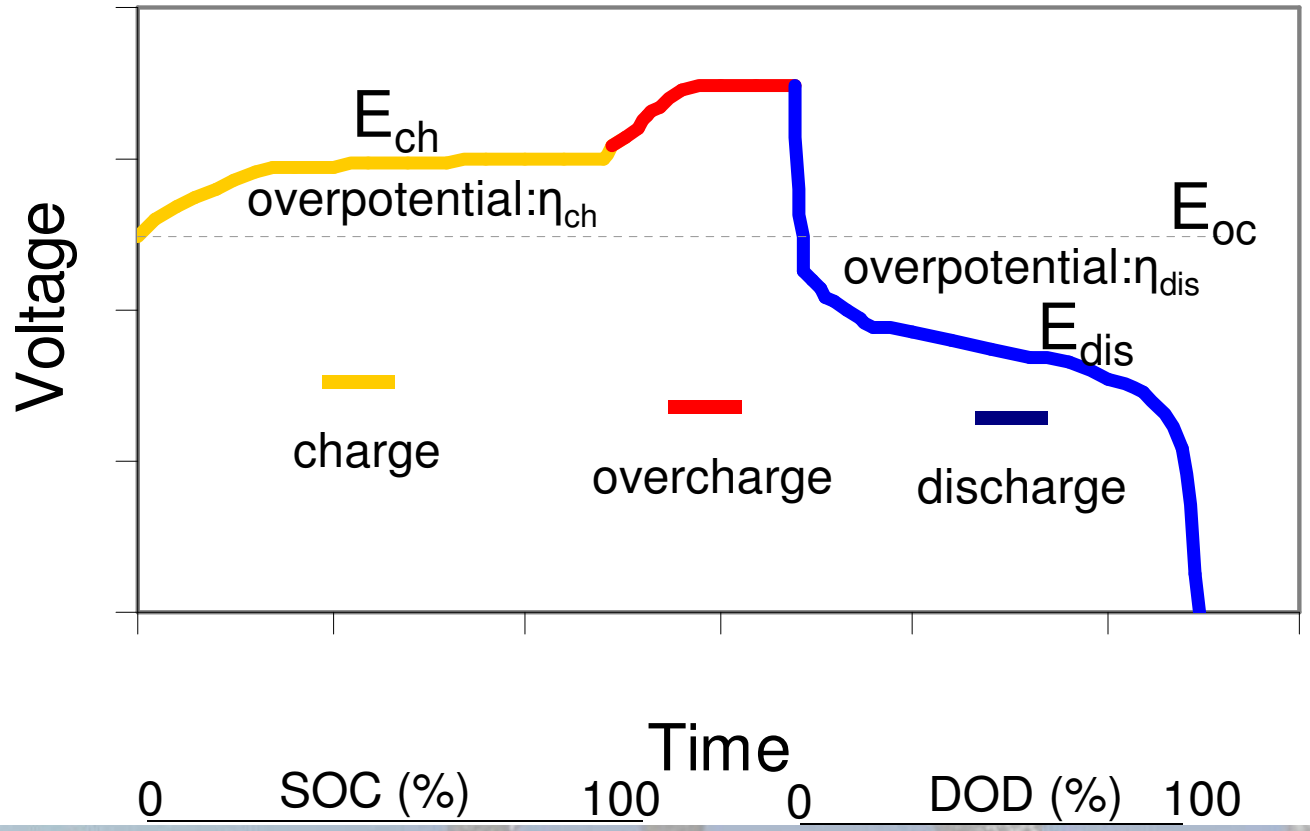
NiMH Pack for EV1

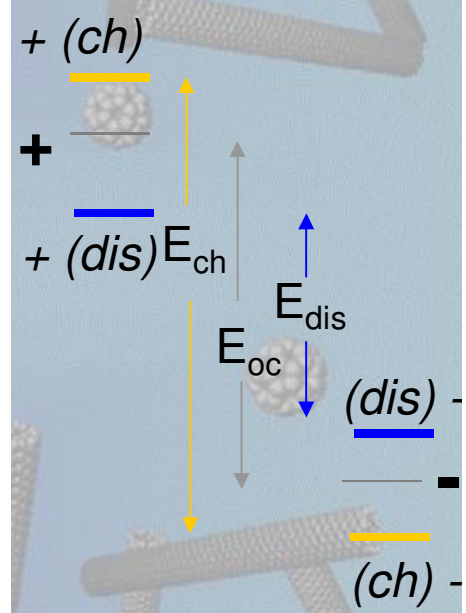
26 Modules

26 x 13.2 = 343 V

Charge and Discharge Curves

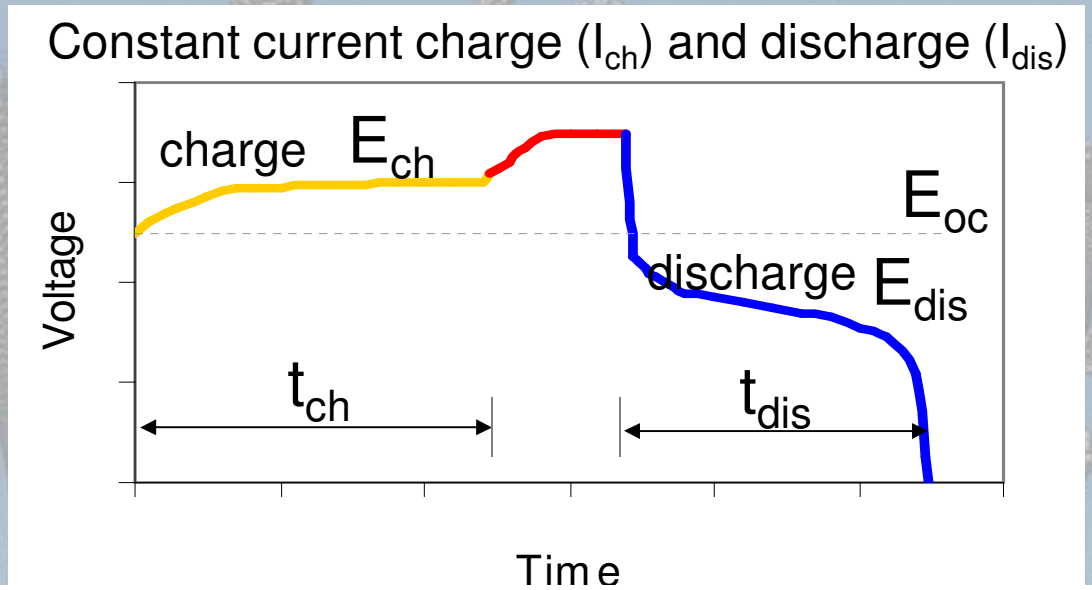
Constant current charge (I_{ch}) and discharge (I_{dis})





Charge and Discharge Curves

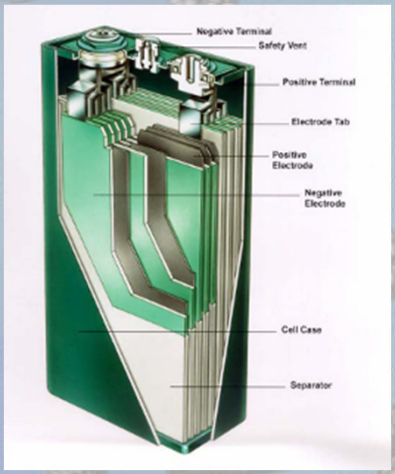
- Charge voltage $E_{ch} > E_{oc}$
- Discharge voltage $E_{dis} < E_{oc}$
- Energy efficiency = (voltaic efficiency * coulombic efficiency) = $(E_{dis} / E_{ch}) * (I_{dis} * t_{dis} / I_{ch} * t_{ch}) < 1$
- The voltage drop is caused by cell resistance
  - $\Delta E_{dis} = E_{oc} - E_{dis} = \eta_{dis} = I_{dis} * R$ (**R: broader resistance**)
  - $\Delta E_{ch} = E_{ch} - E_{oc} = \eta_{ch} = I_{ch} * R$ (R: **extrinsic**)



Battery Component Resistance Distribution

- Nickel metal hydride electric vehicle battery (~300 W/kg)

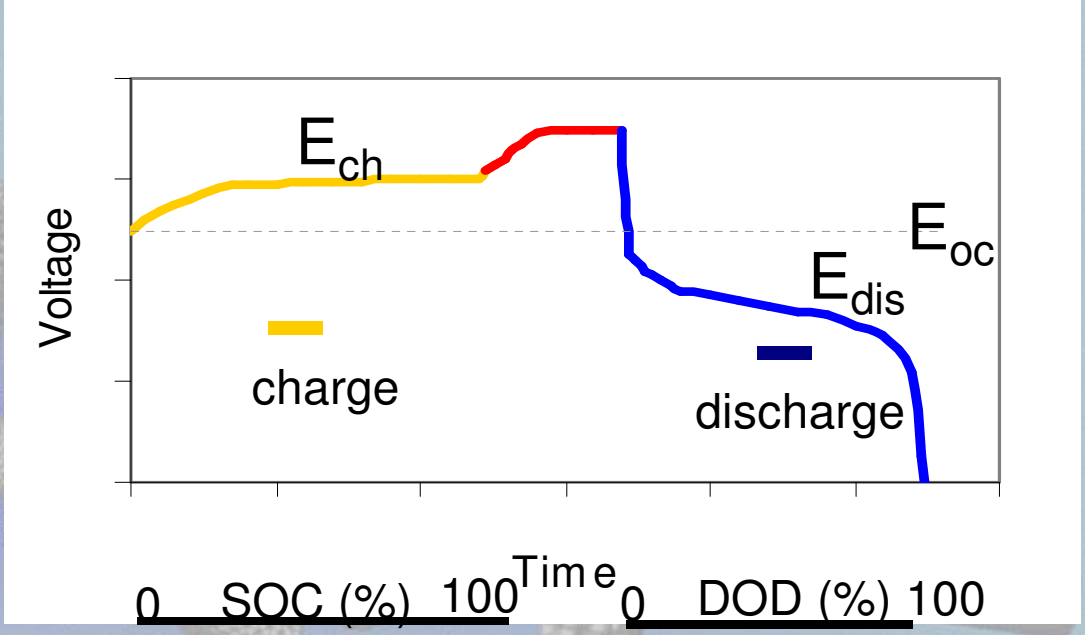
Component	Resistance	Percentage
terminals	0.1 mohm	0.8 %
tabs	0.6 mohm	4.7 %
KOH/separators	3 mohm	23.6 %
positive electrode	1.5 mohm	11.8 %
positive substrate	2.5 mohm	19.7 %
negative electrode	2 mohm	15.7 %
negative substrate	3 mohm	23.6 %
TOTAL	12.7 mohm	100 %



Charge and Discharge

- State of charge (SOC, %)
- Depth of discharge (DOD, %)
- SOC + DOD = 100
- Self discharge
- Discharge
  - "C" rate

    1C, 2C, 1/2C



Cycle Life

- Cycle life is the number of charge-discharge cycles a battery can deliver (has to meet energy and power performance targets)
- Cycle life depends on depth of discharge and temperature
  - Examples
    - lead acid battery
    - nickel cadmium battery

Outline

- Introduction to batteries
- ➢ Equilibrium and kinetics, $E_{oc} > E_{dis}$
- Various secondary batteries
  - Lead acid batteries
  - Nickel metal hydride batteries
  - Lithium ion batteries
- Applications
  - Electric vehicles
  - Hybrid electric vehicles

Equilibrium: Thermodynamics

- ΔG: Free energy change from reactants to products during discharge (J/mole) ➔ negative value
- $\Delta G = - nFE_{oc}$ (nFE_{oc}: electric work) ←**Max.**
  - n: Number of moles of electron transferred
  - F: Faraday's constant (96500 C/mole)
  - E_{oc}: Open circuit cell voltage
- **Theoretical Specific energy**

  ➔ **nFE_{oc} / total weight of reactants**

Theoretical Specific Energy
(Lithium Ion Battery)

- Lithium ion battery half cell reactions

  (+) $CoO_2 + Li^+ + e \leftrightarrow LiCoO_2$ **n = 1**

  $E^o = 1\ V$

  (-) $Li^+ + C_6 + e \leftrightarrow LiC_6$

  $E^o \sim -3\ V$

Theoretical specific energy = nFE_{oc}/ total weight of reactants

- Overall reaction during discharge

  $CoO_2 + LiC_6 \rightarrow LiCoO_2 + C_6$

  $E_{oc} = E^+ - E^- = 1 - (-3) = 4\ V$

E_{oc} = 4 V

Theoretical Specific Energy
(Lithium Ion Battery)

- Free energy change (ΔG) during discharge

  $\Delta G = -nFE_{oc} = -1 * 96500 * 4 = -386000$ J

  $= -386$ kJ $= -107.2$ Wh/mole

- Total weight of reactants

  $CoO_2 + LiC_6 \rightarrow LiCoO_2 + C_6$

  $CoO_2 \rightarrow$ 91 grams

  $LiC_6 \rightarrow 7 + 12 * 6 =$ **79** grams

  Total weight $\rightarrow$ 170 grams (0.17 kg)/mole

- Theoretical specific energy

  107.2 Wh/ 0.17 kg = **630.6 Wh/kg**

- Theoretical energy density

  107.2 Wh/0.055 L = 1949 Wh/L

Practical Specific Energy

- Practical specific energy of a battery is significantly lower than the theoretical value (~30%) ➔ ~ **190 Wh/kg** for lithium battery (USABC target for EV > **150** Wh/kg)
  - Lower discharge voltage (**$E_{dis} < E_{oc}$**)
    - Voltage losses (**broader resistance**)
  - Extra material weight
    - Current collectors
    - Terminals
    - Battery case
    - Separators

Theoretical specific energy = nFE_{oc} / total weight of reactants = 630.6 Wh/kg

Extra Materials

- Battery current collectors and terminals
  - Collect current from electrodes and interconnect to next battery cells
  - Use materials with high electric conductivity and good heat transfer coefficient
- Battery case
  - Contain all battery components
  - Use materials inert with electrolyte and electrodes
  - Need safety release valve with sealed cells
- Separator
  - Separate positive and negative electrodes (prevent short circuit)
  - Made of insulating materials with high porosity

Practical Specific Energy

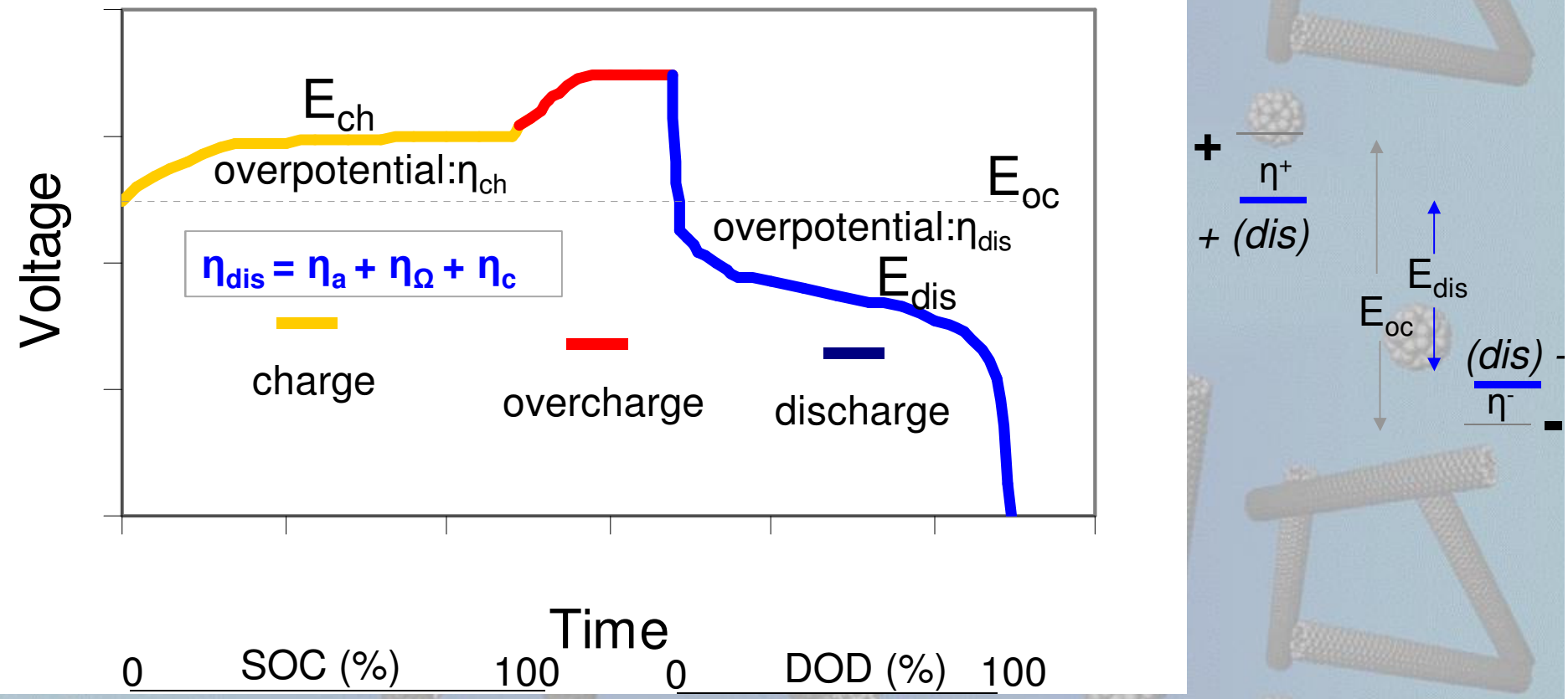
- Practical specific energy of a battery is significantly lower than the theoretical value (<30%)
  - Lower discharge voltage ($E_{dis} < E_{oc}$)
    - Activation polarization losses
    - Ohmic losses
    - Concentration polarization losses
  - Extra material weight
    - Current collectors
    - Terminals
    - Battery case
    - Separators

Kinetics in Batteries

- Source of voltage losses (**broader resistance**)
  - Electrode activation polarization losses (η_a)
    - Butler-Volmer equation
      - Depends on electrode reactions
  - Ohmic losses (η_Ω)
    - Ohm's law (**Ohmic resistance**)
      - Electronic resistance (electrode current collector, tabs. and terminals)
      - Ionic resistance (electrolyte and separator)
      - Temperature effects
  - Concentration polarization losses (η_c)
    - Nernst equation
      - Depends on diffusion in electrolyte and solid state

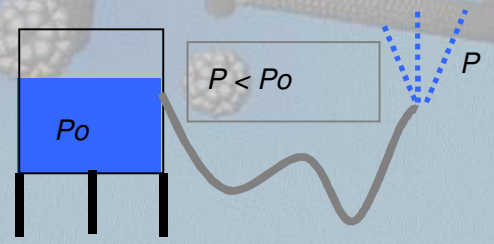
Charge and Discharge Curves

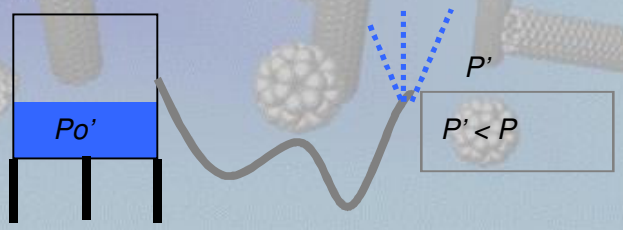
Constant current charge (I_{ch}) and discharge (I_{dis})



Kinetics in Batteries

- Sources of voltage losses ($E_{oc} - E_{dis}$):
  - Electrode activation polarization losses
    - Butler-Volmer equation
  - Ohmic losses
    - Ohm's law
      - Electronic resistance (electrode current collector, tabs. and terminals)
      - Ionic resistance (electrolyte and separator)
  - Concentration polarization losses
    - Nernst equation

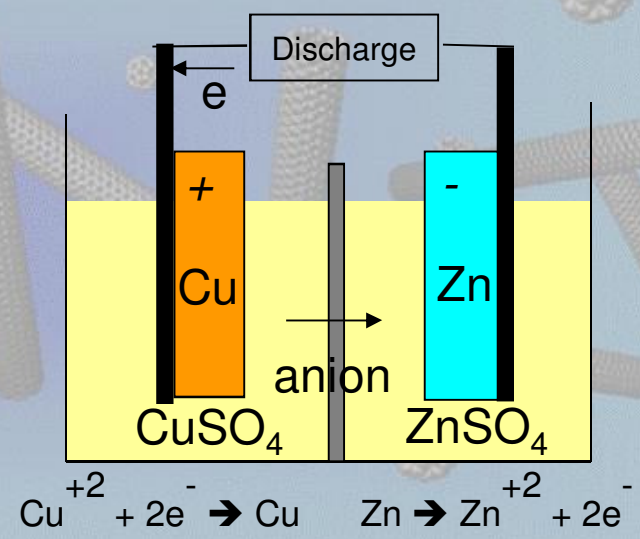




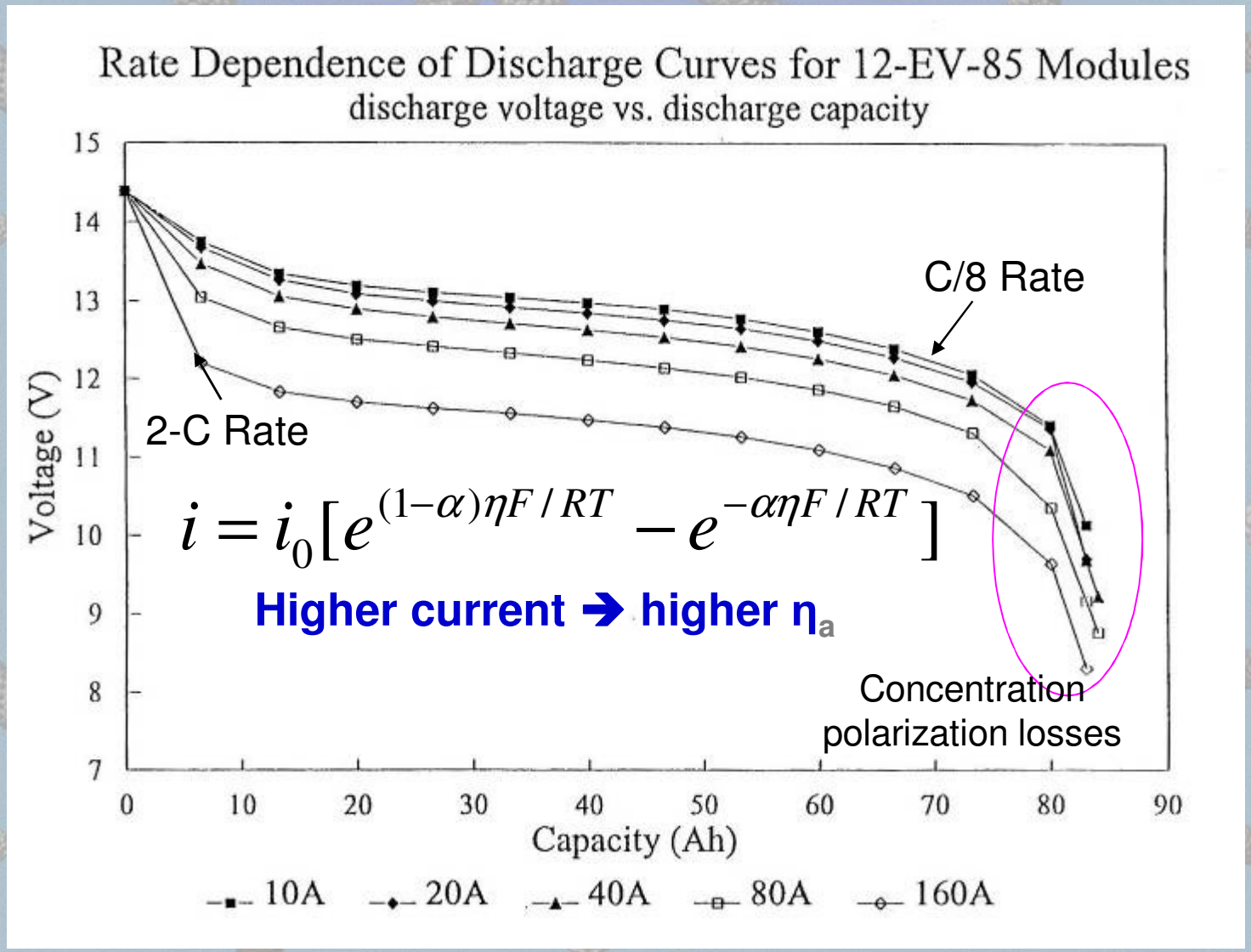
Activation Polarization Losses
(Butler-Volmer Equation)

$$i = i_0[e^{(1-\alpha)\eta F/RT} - e^{-\alpha\eta F/RT}]$$

- Current density i (electrochemical reaction at electrode/electrolyte interface) is a function of:
  - η_a : Activation polarization loss
  - i_0 : Exchange current density
  - α : The symmetry factor
  - F : Faraday's constant
  - R : Molar gas constant
  - T : Temperature



Effect of Rate on Discharge

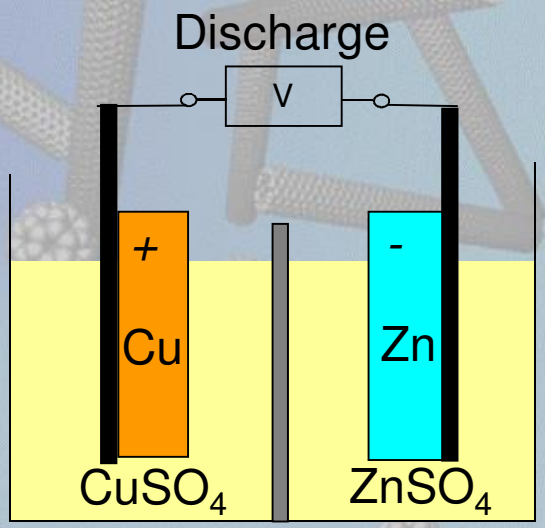


$$i = i_0[e^{(1-\alpha)\eta F/RT} - e^{-\alpha\eta F/RT}]$$

Higher current ➔ higher η_a

Concentration Polarization Losses (Nernst Equation)

- During discharge
  - Reaction at the positive electrode:
    $Cu^{+2} + 2e^{-} \rightarrow Cu$
  - Reaction at the negative electrode:
    $Zn \rightarrow Zn^{+2} + 2e^{-}$
  - Cell reaction:
    $Zn + Cu^{+2} \rightarrow Cu + Zn^{+2}$



- Nernst equation

η_c

$$E_{oc,real} = E_{oc,table} + \frac{RT}{nF} Ln \frac{(A)^a}{(B)^b}$$

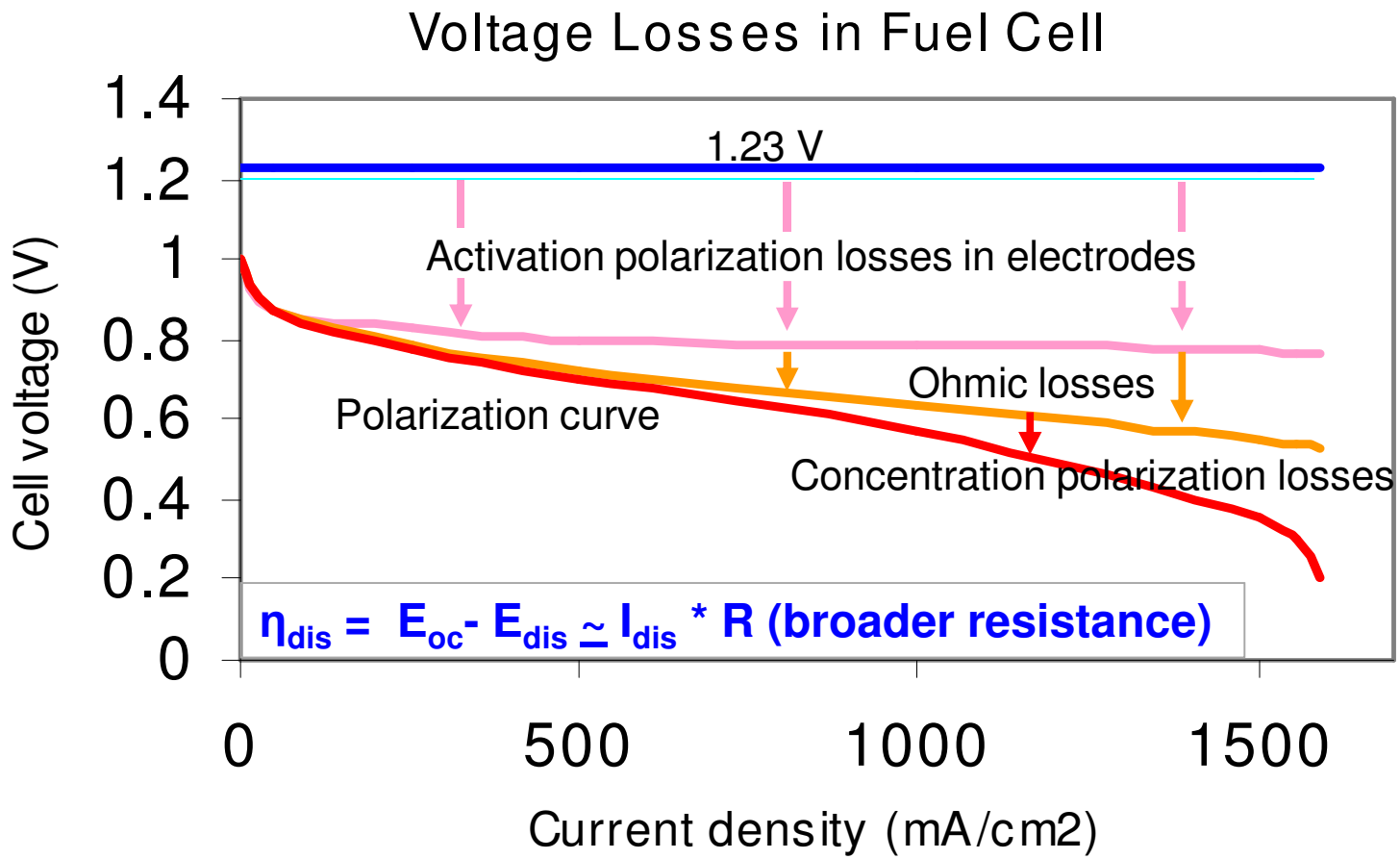
  - A: Concentration of Cu^{+2}
  - B: Concentration of Zn^{+2}
  - a and b (= 1): factor for Cu^{+2} and Zn^{+2}
  - R : Molar gas constant
  - T : Temperature
  - F : Faraday's constant

$$E_{oc,real} = E_{oc,table} + \frac{RT}{nF} Ln \frac{(Cu^{+2})}{(Zn^{+2})}$$

(If $Zn^{+2} = Cu^{+2} = 1M$)

Total Voltage Losses

- $E_{oc} - E_{dis}$ = Total voltage losses (η_{dis}, extrinsic) = Activation losses (η_a) + Ohmic losses (η_Ω) + Concentration losses (η_c)



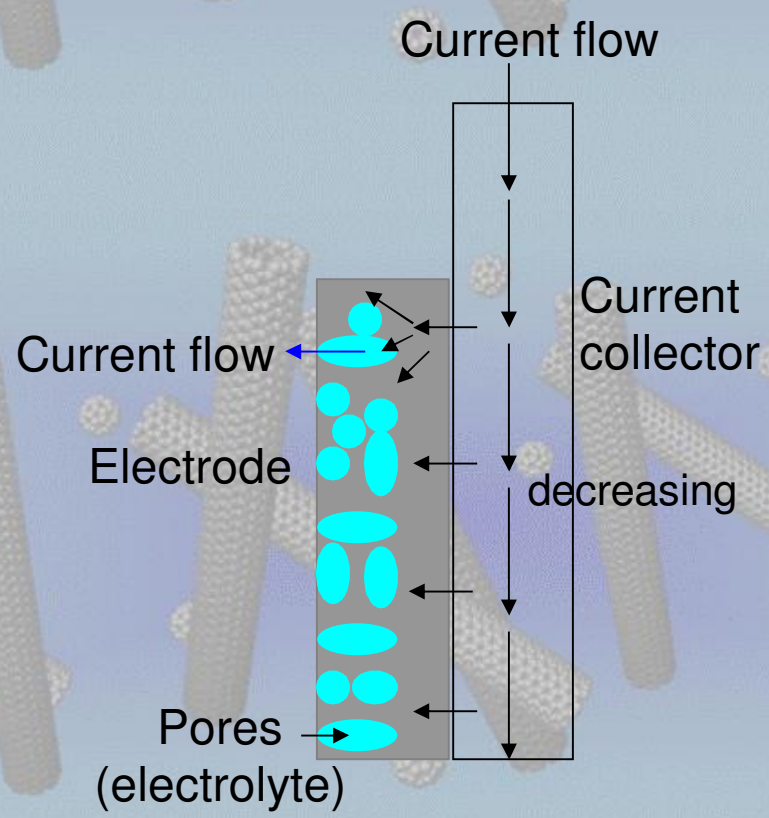
Model: Porous Electrode Theory

- Porous electrode theory
  - Butler-Volmer equation
  - Ohm's law

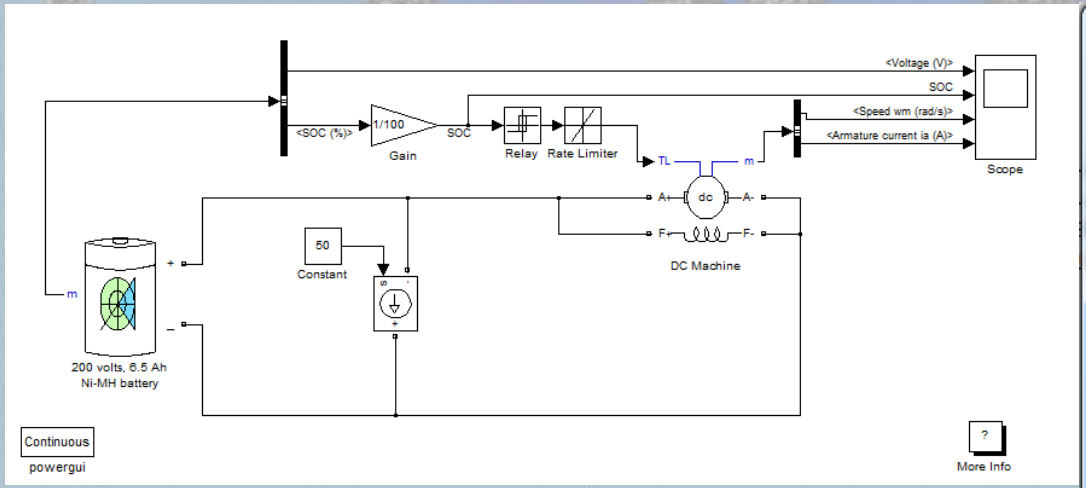
For a battery cell

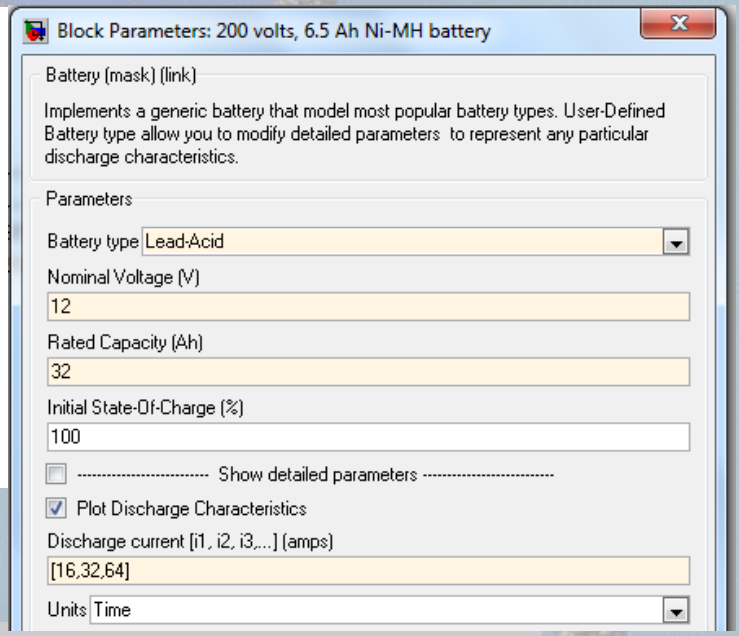
Power = f (1/R)

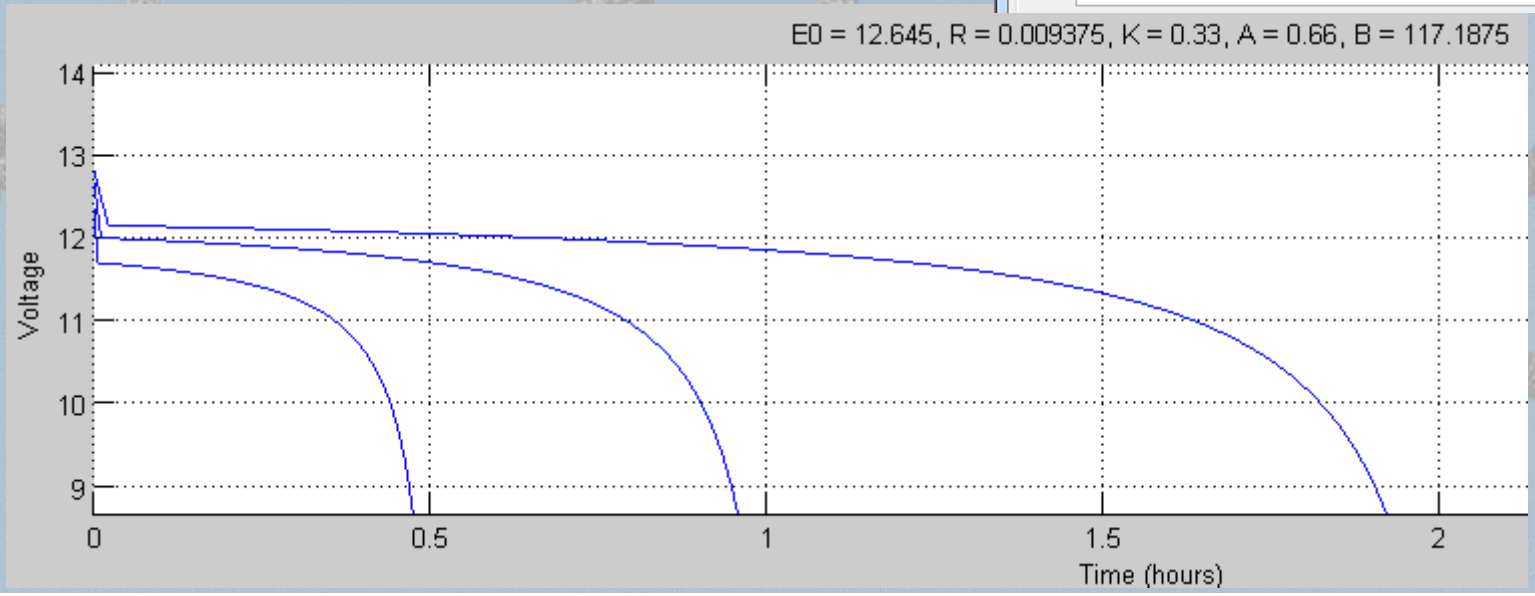
R = f (1/surface area)



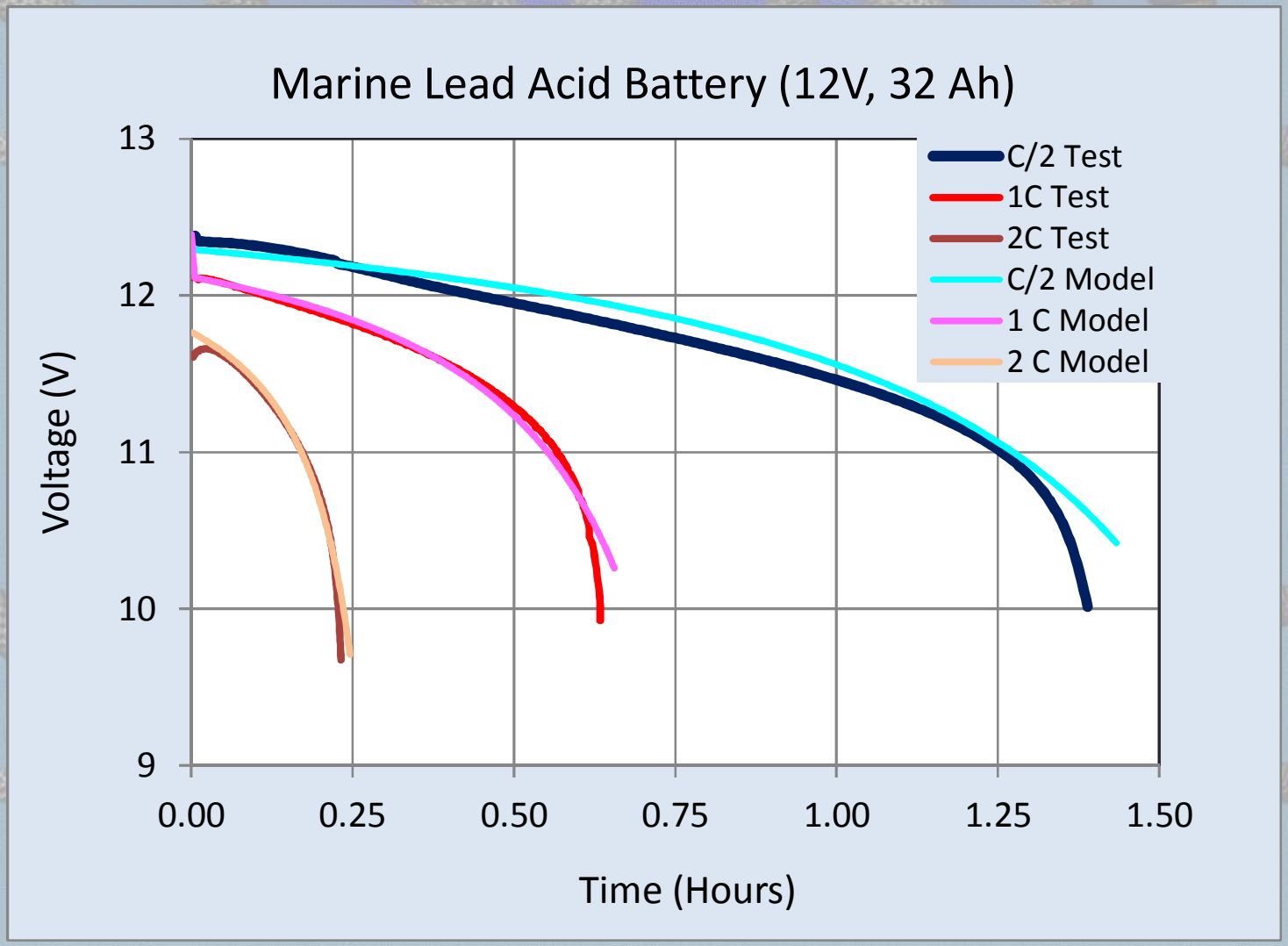
MATLAB Model







Experimental Results V.S. MATLAB Model



Outline

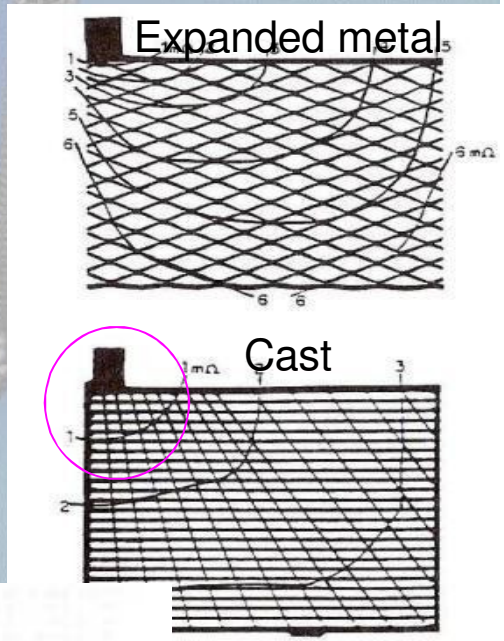
- Introduction to batteries
- Equilibrium and kinetics
- Various secondary batteries
  - Lead acid batteries
  - Nickel metal hydride batteries
  - Lithium ion batteries
- Applications
  - Electric vehicles
  - Hybrid electric vehicles

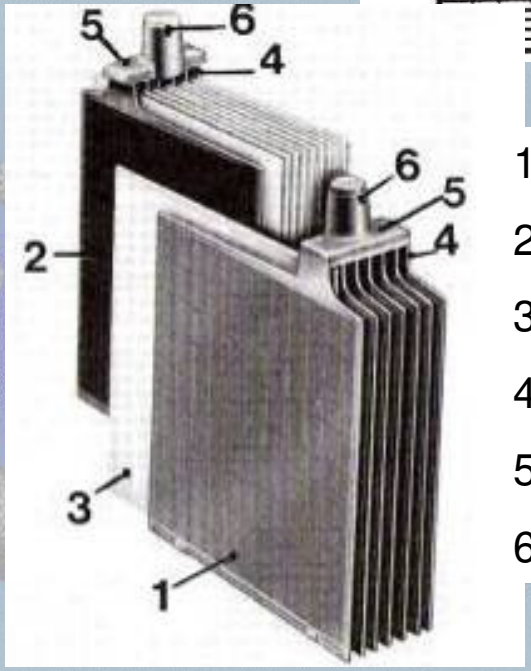
Lead Acid Batteries

- Invented by Planté in 1860
- Lead acid starter batteries are enabling technology for gasoline powered IC engine cars
- Almost all vehicles use lead acid batteries for starter lighting and ignition (SLI) systems
- It is 20 billion dollars industry (total battery industry ~ 30 billion dollars)

Lead Acid Batteries

- Positive electrodes
  - PbO_2
- Negative electrodes
  - Pb
- Current collectors
  - **Lead** (or alloy) grids
- Separators
  - Porous or glass mat
- Electrolyte
  - **5M H_2SO_4** aqueous solution





1. Positive
2. Negative
3. Separator
4. Tab
5. Bus bar
6. Terminal

Theoretical Specific Energy

- Lead acid battery half cell reactions

$PbO_2 + SO_4^{2-} + 4\ H^+ + 2\ e \leftrightarrow PbSO_4 + 2\ H_20$

$E° = 1.69\ V$

$PbSO_4 + 2\ e \leftrightarrow Pb + SO_4^{2-}$

$E° = -0.36\ V$

- Overall reaction during discharge

$PbO_2 + Pb + 2H_2SO_4 \rightarrow 2\ PbSO_4 + 2\ H_20$

$V_{oc} = V_+ - V_- = 1.69 – (-0.36) = 2.05\ V$

Theoretical Specific Energy

- Free energy change (ΔG) during discharge

  $\Delta G = -nFE = -2 * 96500 * 2.05 = -395700$ J

  $= -395.7$ kJ $= -109.9$ Wh/mole

- Total weight of reactants

  $PbO_2 + Pb + 2H_2SO_4 \rightarrow 2\ PbSO_4 + 2\ H_20$

  $PbO_2 \rightarrow$ 239 grams

  $Pb \rightarrow$ 207 grams

  $2H_2SO_4 \rightarrow 98 * 2 = 196$ grams

  Total weight $\rightarrow$ 642 grams (0.642 kg)/mole

- Theoretical specific energy

  109.9 Wh/ 0.642 kg = **171 Wh/kg**

- Theoretical energy density

  109.9 Wh/0.1 L = 1099 Wh/L

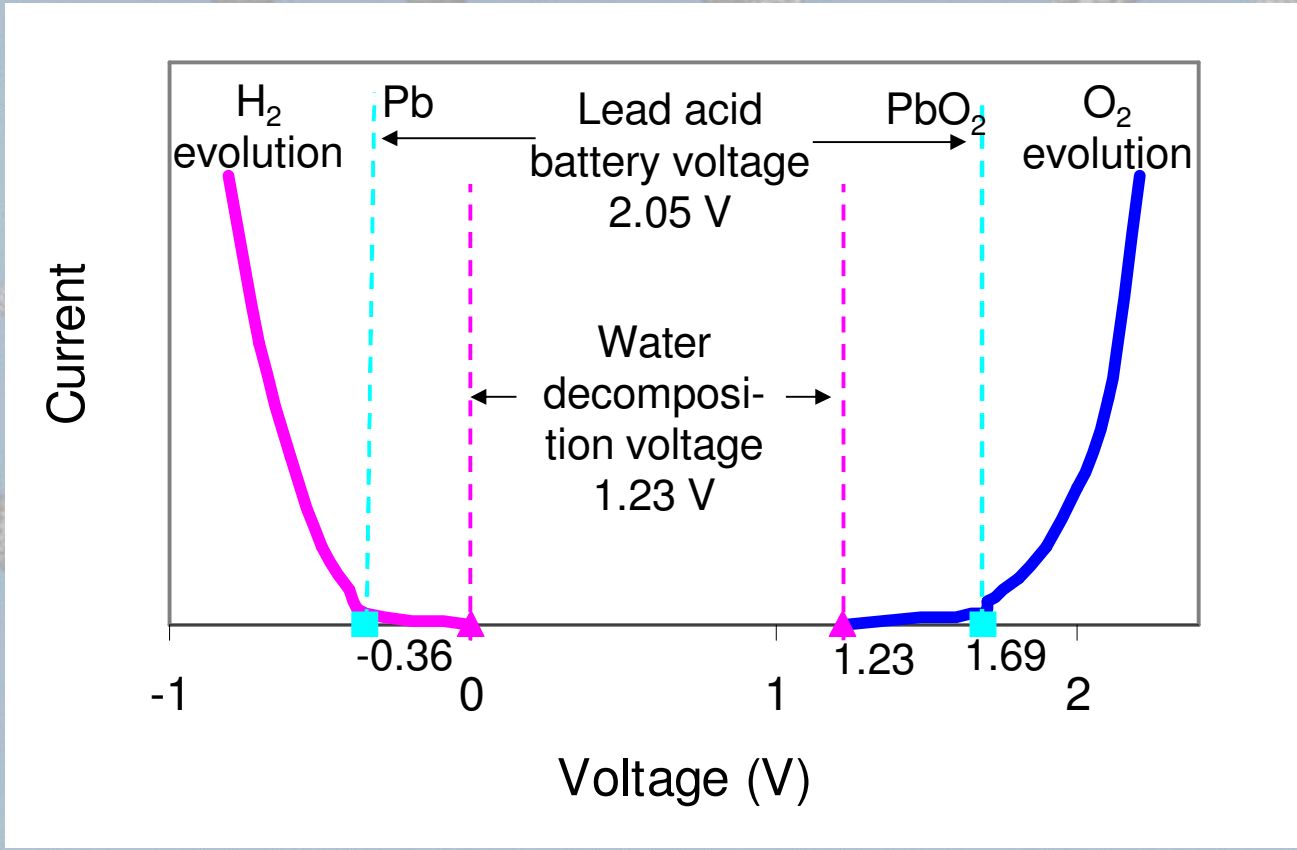
Practical Specific Energy

- Practical specific energy < 20 % theoretical specific energy (171 Wh/kg)➔ ~ **34** Wh/kg due to:
  - Voltage losses (up to 10%)
  - Inactive weight (~75%)
    - Current collectors
    - Tabs and terminals
    - Solvent (water) in electrolyte
  - Low utilization of active material

USABC target for EV applications: > **150** Wh/kg

Charge Lead Acid Batteries

- During charge:
  - $2\ PbSO_4 + 2\ H_20 \rightarrow PbO_2 + Pb + H_2SO_4$ **(2.05 V)**
  - Competing reaction: $\mathbf{2H_2O} \rightarrow O_2 + 2H_2$ **(1.23 V)**



Electrolyte (H_2SO_4) Concentration

- Overall reaction during charge

  $2\ PbSO_4 + 2\ H_20 \rightarrow PbO_2 + Pb + H_2SO_4$

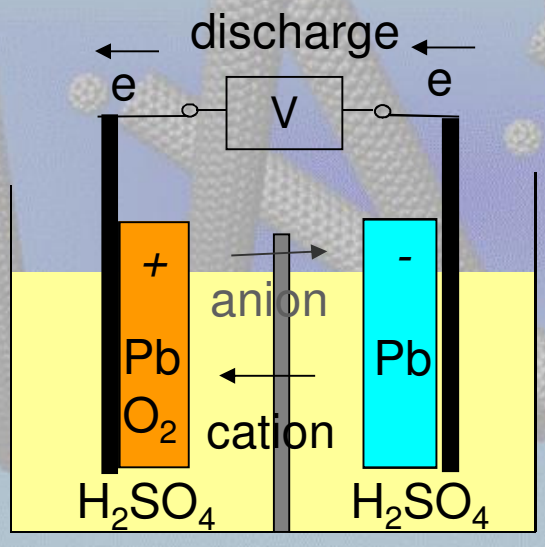
  The concentration of sulfuric acid increases to 5 M

- Overall reaction during discharge

  $PbO_2 + Pb + \mathbf{H_2SO_4} \rightarrow 2\ PbSO_4 + 2\ H_20$

  The concentration of sulfuric acid decreases

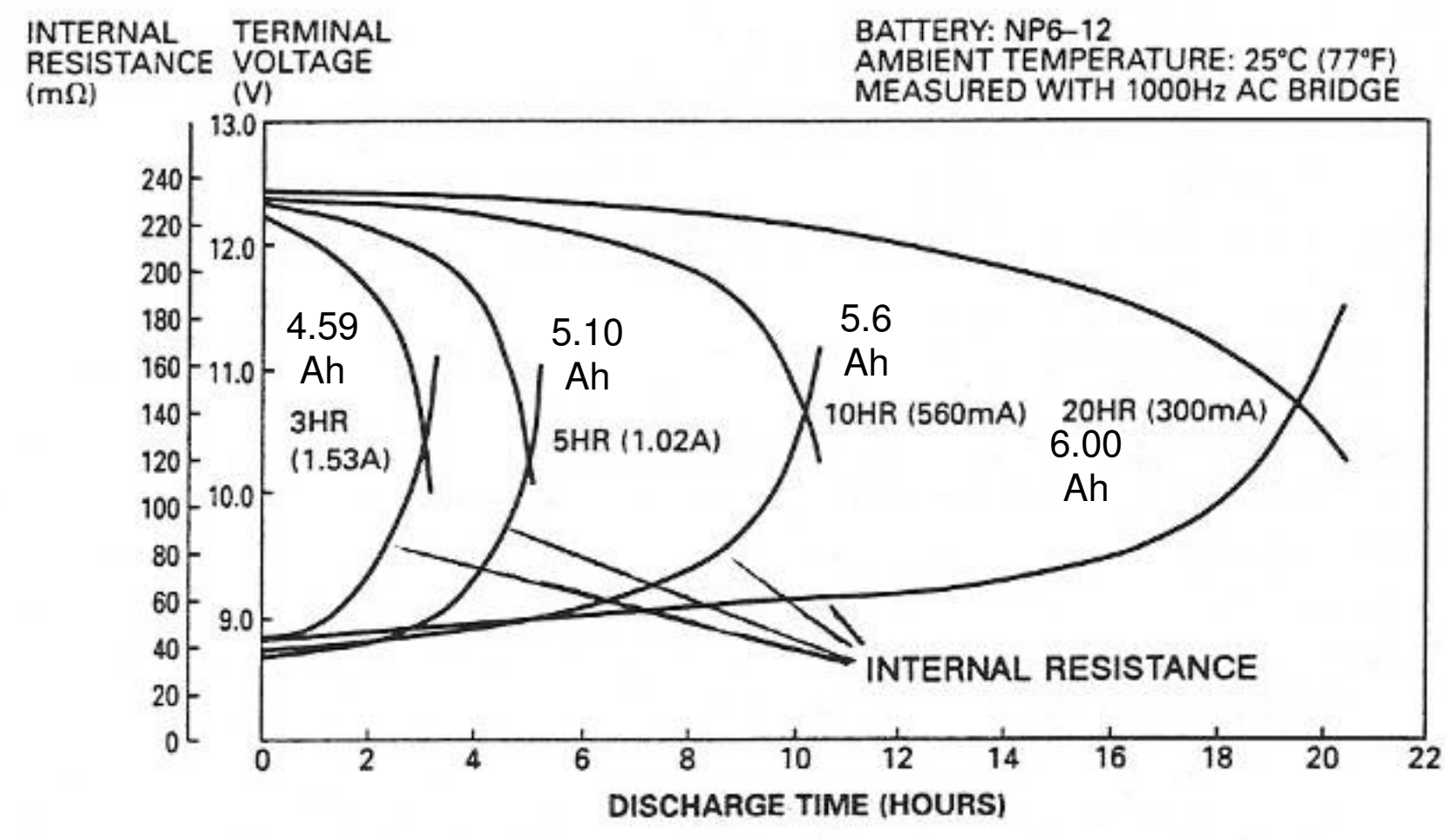
Diffusion!
Power?



Cation: H^+

Anion: SO_4^{-2}

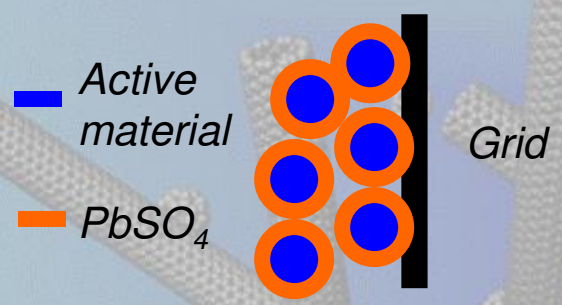
Cell Capacity Under Different Discharge Rates

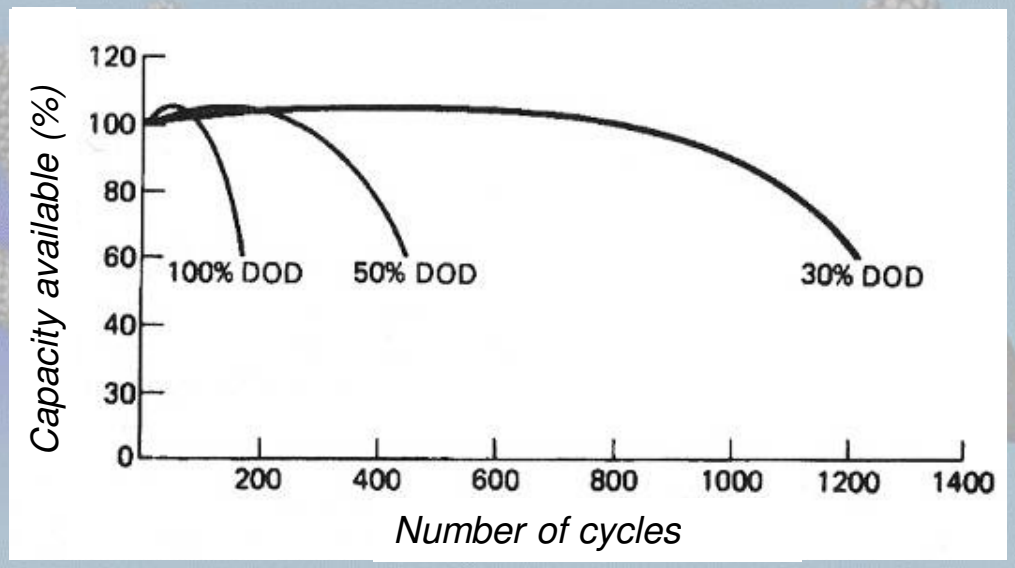


Failure Mode

- Positive electrode
  - Lead grid corrosion

    $PbO_2 + Pb + H_2SO_4 \rightarrow 2\ PbSO_4 + 2\ H_20$
  - Shedding
    - 70% volume change from PbO_2 to $PbSO_4$ (discharge)
- Negative electrode
  - Sulfation (the formation of $PbSO_4$)
- Cycle life depends on DOD and temperature





Outline

- Introduction to batteries
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  - ➢ Nickel metal hydride batteries
  - Lithium ion batteries
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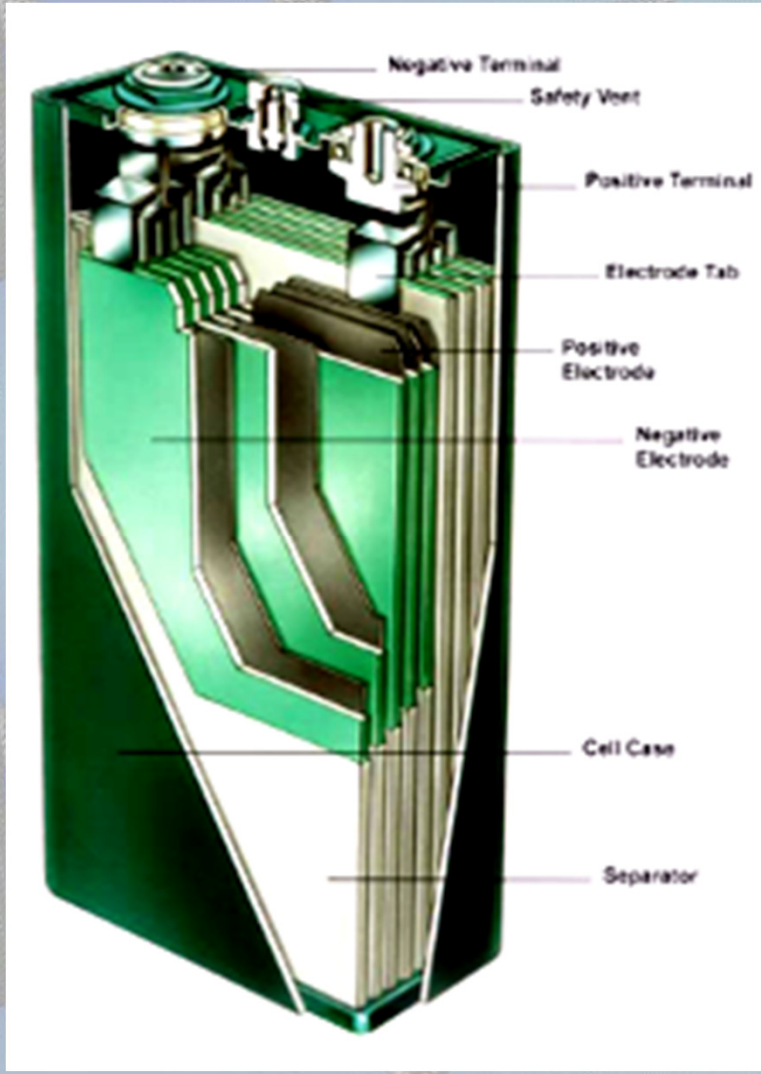
Nickel Metal Hydride Batteries

- Became commercially available around 1992
- Metal hydride is actually a solid phase hydrogen intercalation electrode
- Nickel metal hydride battery has **high power** and good cycle life for **HEV** applications
- It is > 1 billion dollars industry (total battery industry ~ 30 billion dollars)

Nickel Metal Hydride Batteries

- Positive electrodes
  - Nickel hydroxide pasted onto nickel foam or sheet substrate
- Negative electrodes
  - Most common material is **AB_5** or **$MmNi_{3.55}Co_{0.75}Al_{0.2}Mn_{0.5}$** where Mm is misch metal, an alloy consisting of 50% cerium, 25% lanthanum, 15% neodymium, and 10% other rare-earth metals and iron
- Separators
  - Polymer with submicron pores
- Electrolyte
  - 30% KOH aqueous solution



Theoretical Specific Energy

- Nickel metal hydride battery half cell reactions

$$NiOOH + H_2O + e \leftrightarrow Ni(OH)_2 + OH^-$$

$$E^o = 0.45\ V$$

$$M + H_2O + e \leftrightarrow MH + OH^-$$

$$E^o = -0.83\ V$$

- Overall reaction during discharge

$$NiOOH + MH \rightarrow Ni(OH)_2 + M$$

$$E_{oc} = E_+ - E_- = 0.45 - (-0.83) = \mathbf{1.28\ V}$$

Theoretical Specific Energy

- Free energy change (ΔG) during discharge

  $\Delta G = -nFE = -1 * 96500 * 1.28 = -123520$ J

  $= -123.5$ kJ $= -34.3$ Wh/mole

- Total weight of reactants

  $NiOOH + MH \rightarrow Ni(OH)_2 + M$

  NiOOH ➔ 92 grams

  MH ➔ 70 grams

  Total weight ➔ 162 grams (0.162 kg)/mole

- Theoretical specific energy

  34.3 Wh/ 0.162 kg = **212 Wh/kg**

- Theoretical energy density

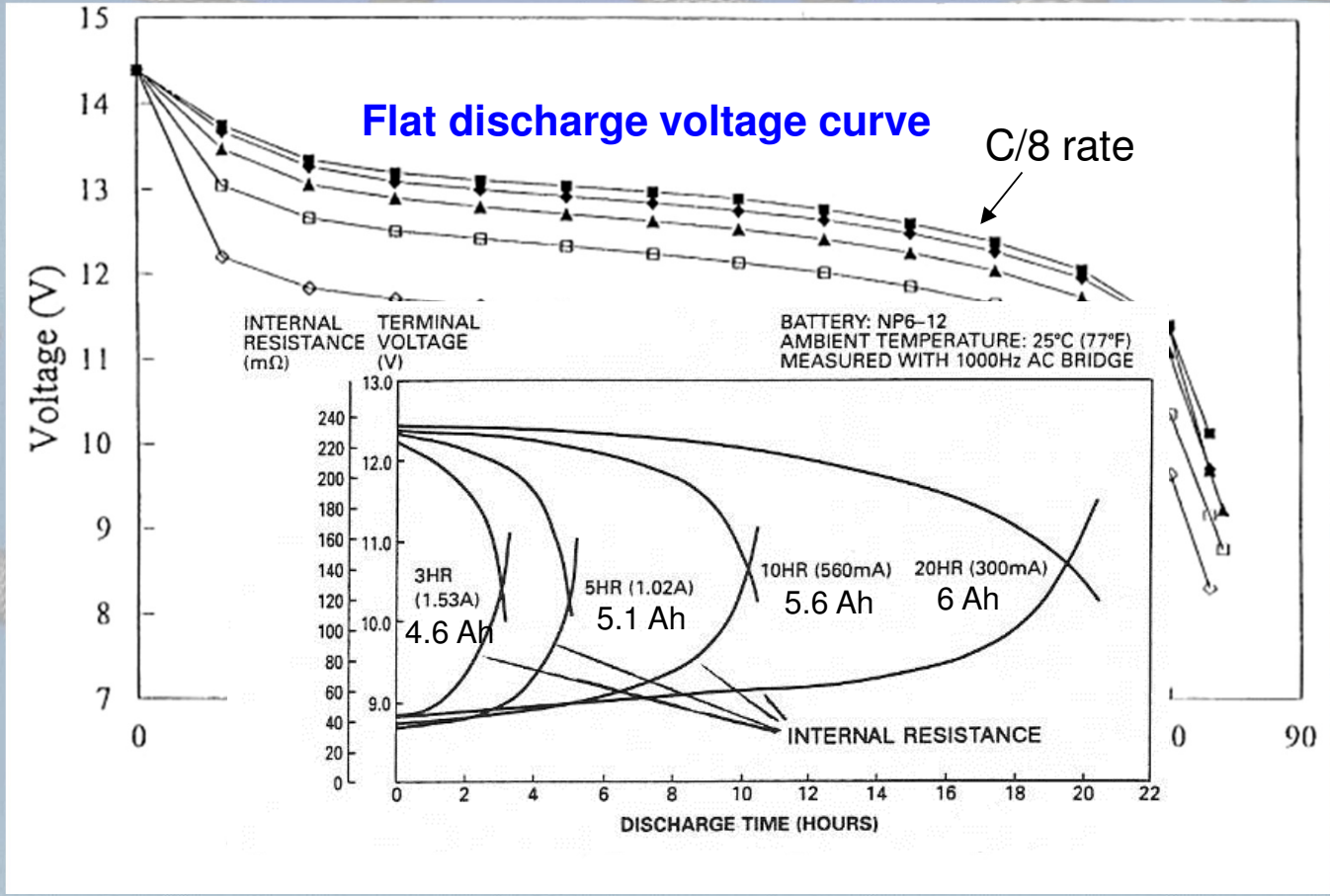
  34.3 Wh/0.02 L = 1715 Wh/L

Practical Specific Energy

- Practical specific energy up to 45% theoretical specific energy (212 Wh/kg)➔up to **90** Wh/kg due to:
  - Voltage losses (up to 10%)
  - Less inactive weight (~50%)
    - Current collectors
    - Tabs and terminals
    - Solvent (water) in electrolyte
  - High utilization of active material (~90%)

Effects of Discharge Rate on Capacity

- Capacity least affected by discharge rate among commonly used batteries (best abuse tolerance)



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Lithium Ion Batteries

- Invented by Dr. Goodenough at U. Texas in 1982 and became commercially available in 1991 (Sony)
- Both lithium cobalt oxide and carbon electrodes are intercalation electrodes
- Have safety issues for applications in HEV and plug-in HEV
- It is 5 billion dollars industry for applications in portable electronics (total battery industry ~ 30 billion dollars)

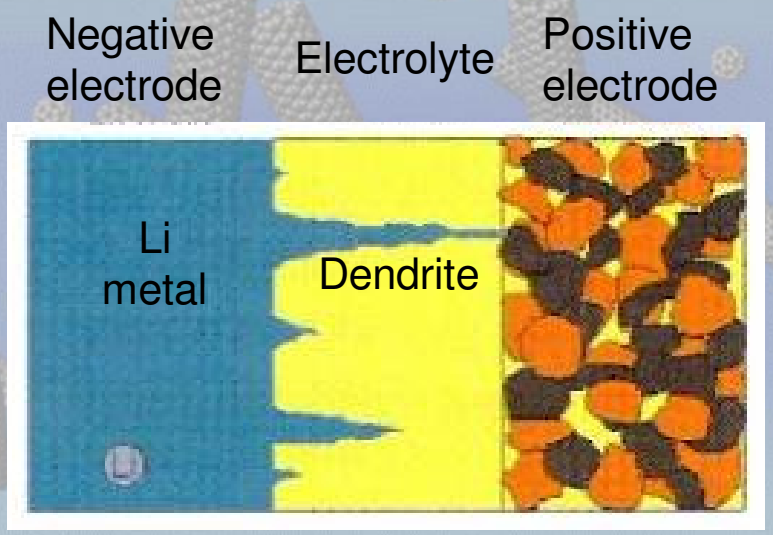
Lithium Ion Batteries

- Positive electrodes
  - Layered lithium metal oxide ($LiMO_2$, M = **cobalt**, nickel, manganese, aluminum, or combination of two to three metals), spinel lithium manganese oxide ($LiMn_2O_4$), and lithium iron phosphate ($LiFePO_4$) on aluminum current collector
- Negative electrodes
  - **Carbon** or **graphite** on copper current collector
- Separators
  - Celgard microporous, polyethylene, or ceramic separators
- Electrolyte
  - $LiPF_6$ dissolved in ethylene carbonate (EC)
    - Solvent with high dielectric constant (89.6 at 40°C)
    - Lithium salt with high conductivity
    - 0.005 S/cm as compared to 0.5 S/cm for aqueous electrolyte

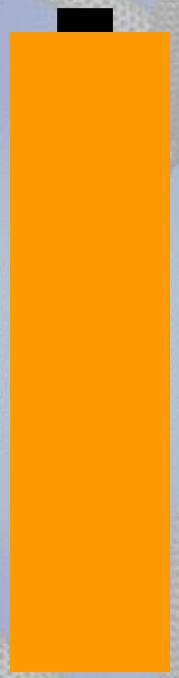
59

Carbon Negative Electrode

- Prevent **lithium metal deposition** (or formation of lithium **dendrite**)
  - Lithium metal deposition could still happen during rapid charge when Temp < 5℃
  - Dendrite could cause short circuit and **thermal runaway**



Lithium Ion Batteries



Lithium ion battery18650

3.6 V, 2 Ah

7.2 Wh

Alkaline AA battery

1.5 V, 1.5 Ah

2.25 Wh

Theoretical Specific Energy

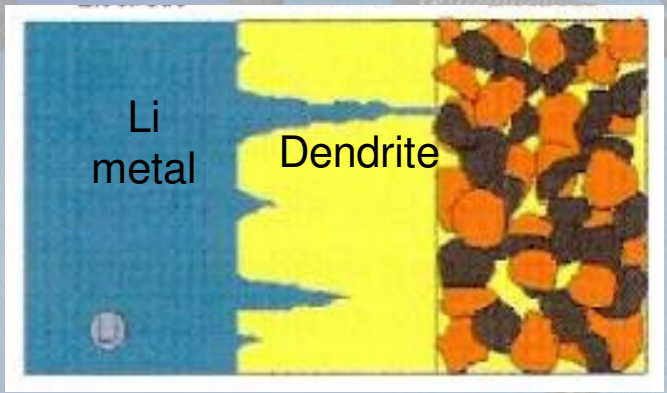
- Lithium ion battery half cell reactions

$$CoO_2 + Li^+ + e \leftrightarrow LiCoO_2$$

$$E^o = 1\ V$$

$$Li^+ + C_6 + e \leftrightarrow LiC_6$$

$$E^o \sim -3\ V$$



- Overall reaction during discharge

$$CoO_2 + LiC_6 \rightarrow LiCoO_2 + C_6$$

$$E_{oc} = E_+ - E_- = 1 - (-3.01) = 4\ V$$

Theoretical Specific Energy

- Free energy change (ΔG) during discharge

  $\Delta G = -nFE = -1 * 96500 * 4 = - 386000$ J

  $= -386$ kJ $= -107.2$ Wh/mole

- Total weight of reactants

  $CoO_2 + LiC_6 \rightarrow LiCoO_2 + C_6$

  $CoO_2 \rightarrow$ 91 grams

  $LiC_6 \rightarrow$ **79** grams

  Total weight $\rightarrow$ 170 grams (0.17 kg)/mole

- Theoretical specific energy

  107.2 Wh/ 0.17 kg = **630.6 Wh/kg**

- Theoretical energy density

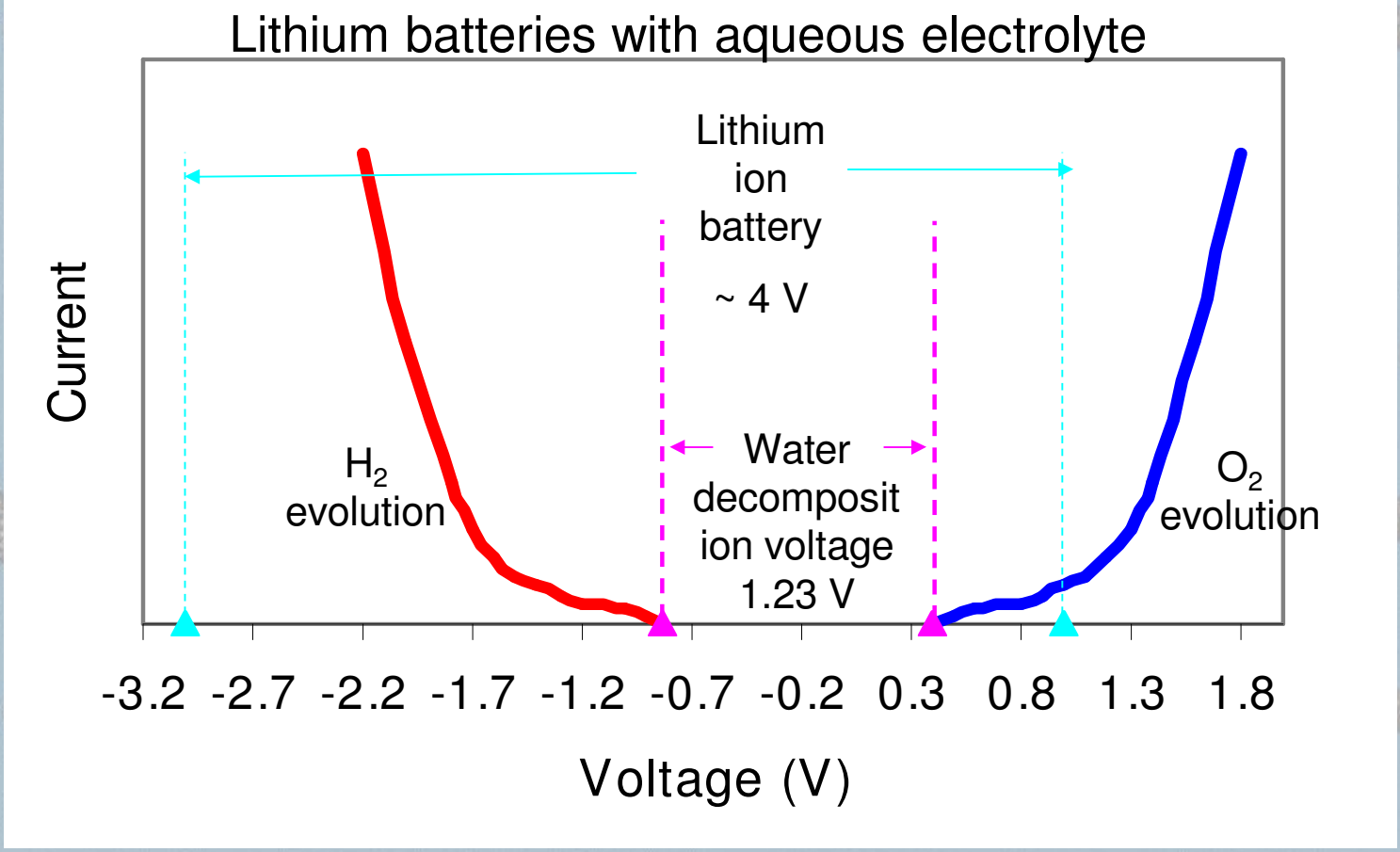
  107.2 Wh/0.055 L = 1949 Wh/L

Practical Specific Energy

- Practical specific energy up to 30% theoretical specific energy (630.6 Wh/kg)➔ ~**190** Wh/kg due to:
  - Voltage losses (up to 10%)
  - Less inactive weight (~35%)
    - Current collectors
    - Tabs and terminals
    - Electrolyte
    - **Carbon** in negative electrode
  - Utilization of active material (~50%)
    - Intercalation electrodes

Charge and Discharge

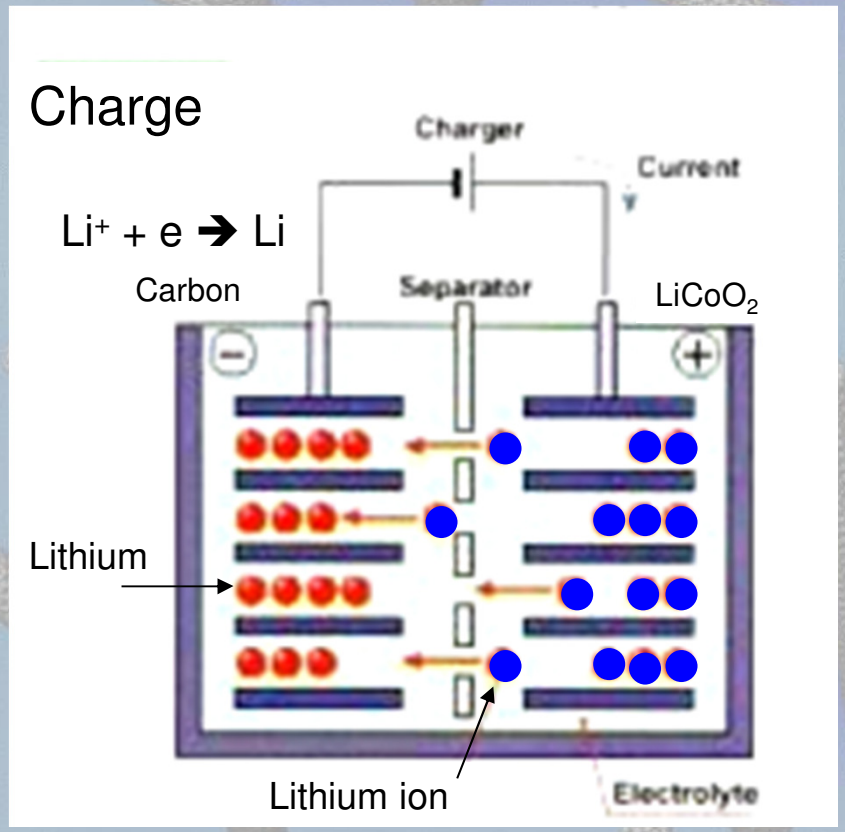
- Lithium batteries cannot use aqueous electrolyte

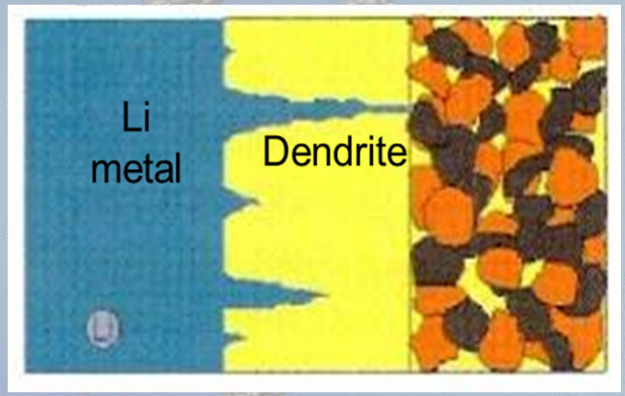


Charge

- Overall reaction during charge

$LiCoO_2 + C_6 \rightarrow CoO_2 + LiC_6$



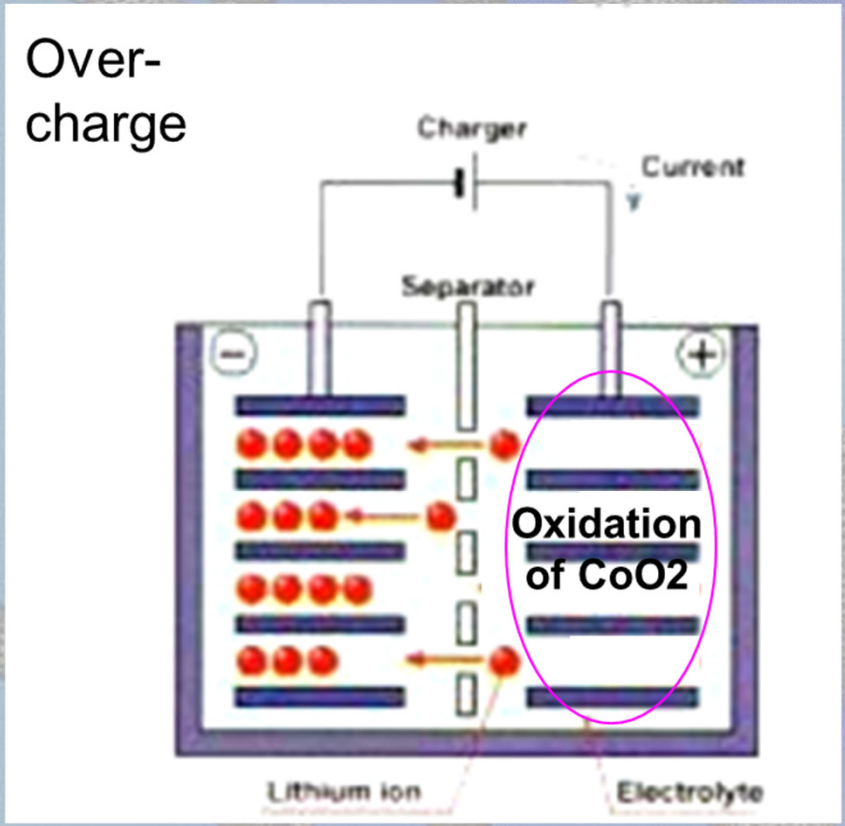


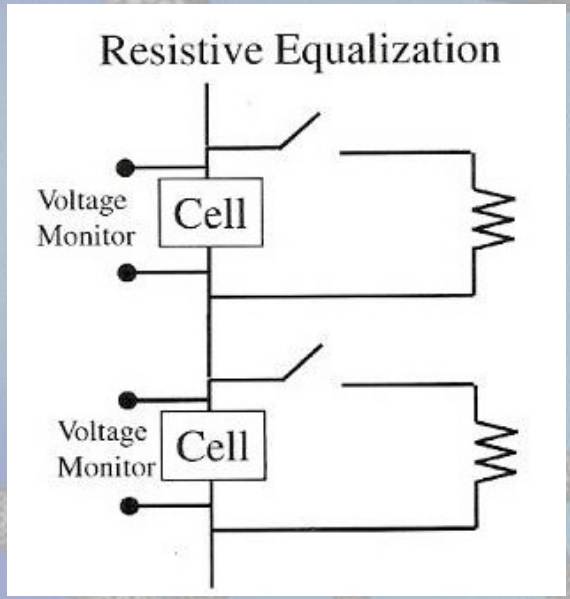
Lithium metal deposition could still happen during rapid charge when

Temp < 5°C

Overcharge

- Positive electrode is oxidized and oxygen released (exothermic reaction)





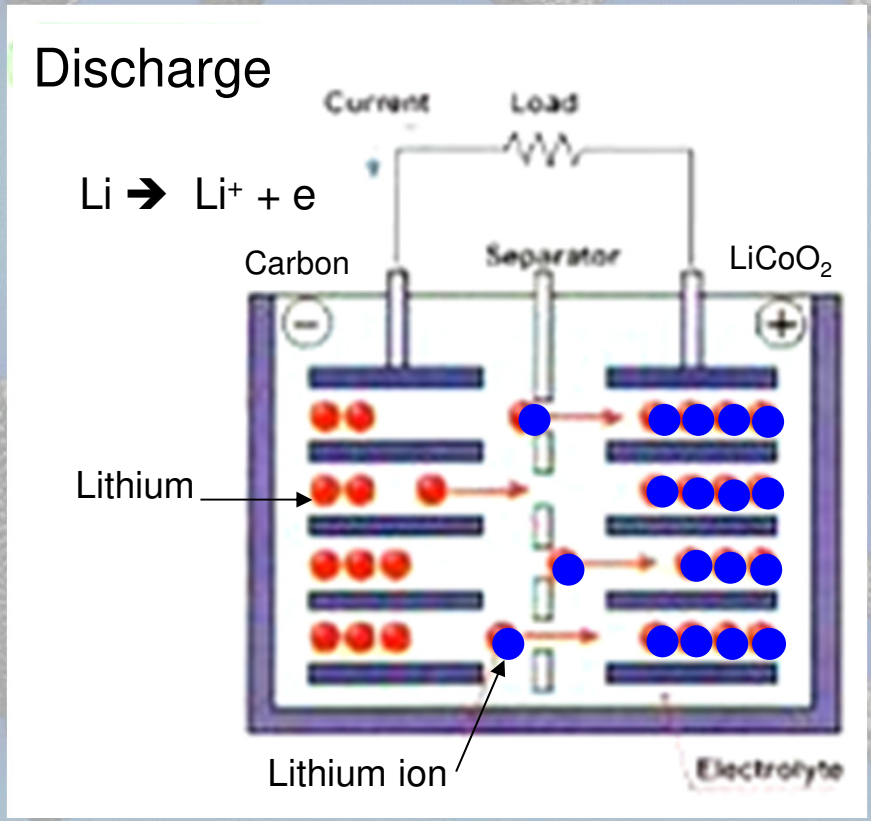
$LiCoO_2 + C_6 \rightarrow CoO_2 + LiC_6$ (theoretical)

$LiCoO_2 + C_6 \rightarrow Li_{1-x}CoO_2 + Li_xC_6$ (actual)

Discharge

- Overall reaction during discharge

$CoO_2 + LiC_6 \rightarrow LiCoO_2 + C_6$

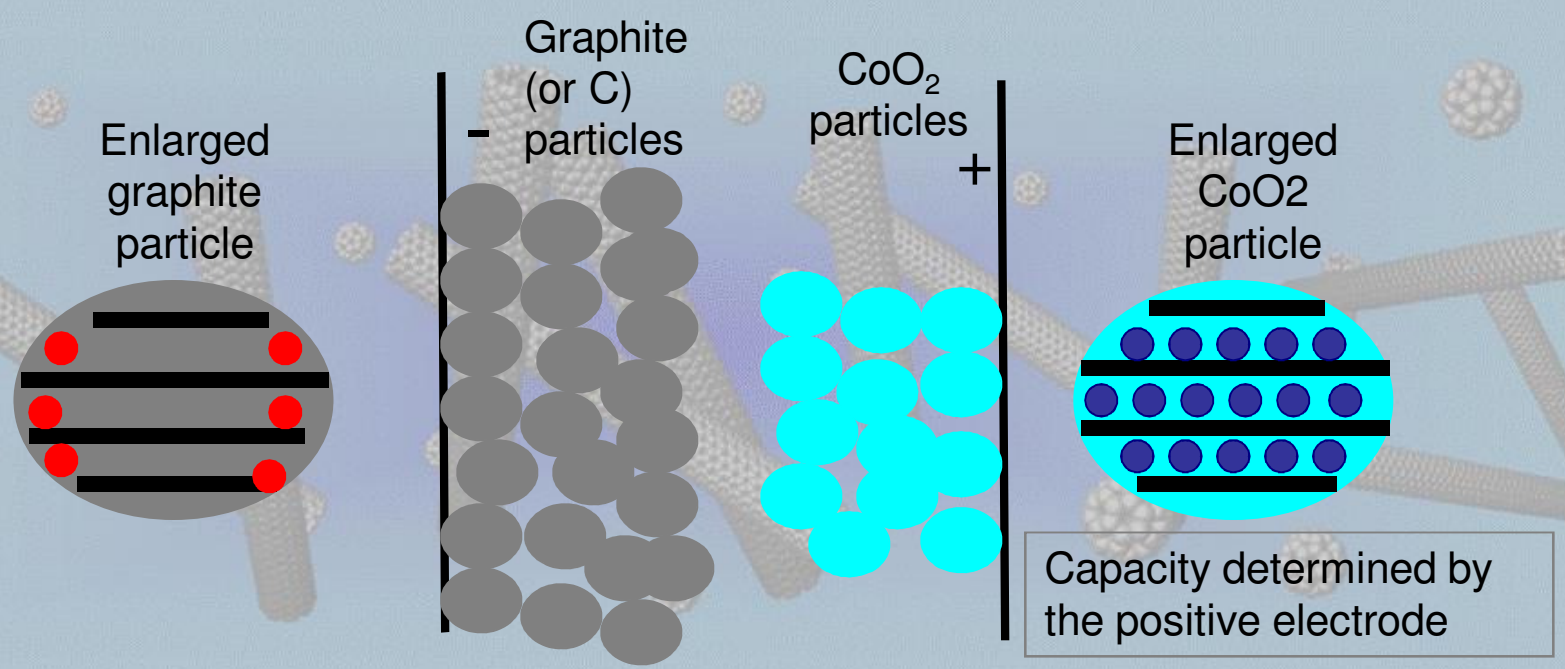


Thermal Runaway

- Overcharge
  - Exothermic reaction of oxidized positive electrode material with electrolyte
- High ambient temperature
  - **SEI** (solid electrolyte interphase) decomposition at temperature 90 to 120 ℃
- Short circuit
  - Internal
  - External
- High charge or discharge current

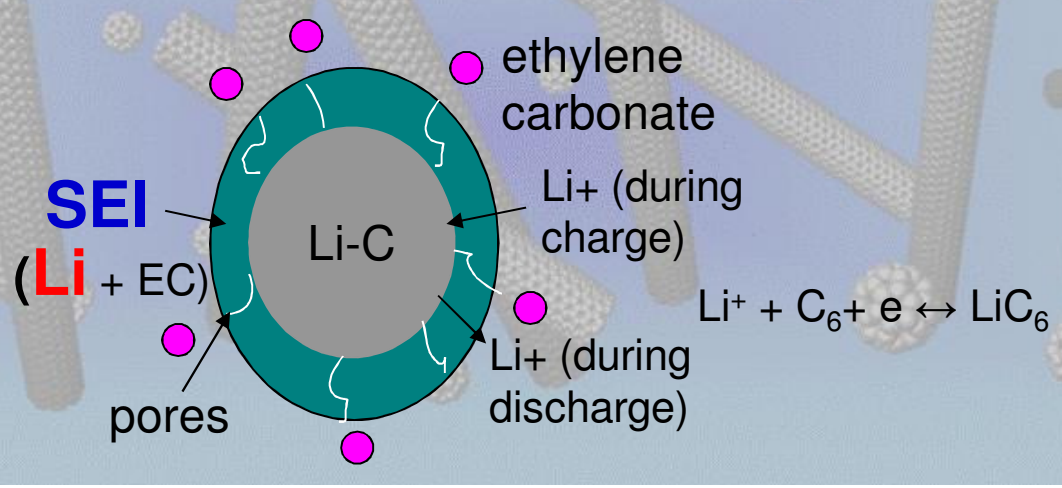
Formation of SEI

- Lithium ion battery is assembled inside a dry room (does not need a dry box w/inert atmosphere) with lithium ions impregnated in the positive electrode (the smaller electrode)
- During the first charge, lithium ions are transferred from the positive to the negative electrode and form lithium metal



Formation of SEI

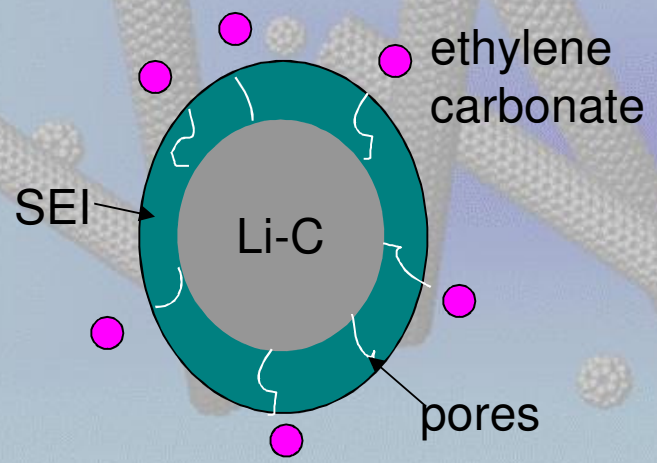
- The electrolyte, ethylene carbonate (**EC**), is **not thermodynamically stable** with lithium metal
- SEI is formed on carbon or graphite particles during the first charge (Li active material wasted)
- SEI properties
  - SEI has porous structure (more porous if SEI formation steps are not optimized) ↓
  - SEI is ionic conductor (electronic insulator) ↑



$Li^+ + C_6 + e \leftrightarrow LiC_6$

Thickening of SEI (Failure Mode)

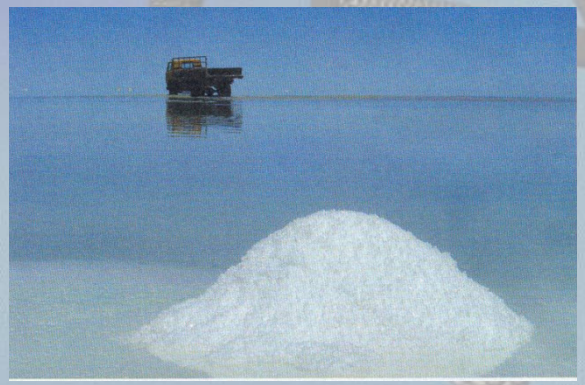
- Charge discharge cycles
  - Volume changes in the carbon or graphite particles crack SEI and expose fresh Li to electrolyte (EC)
- Storage (calendar life)
  - Ethylene carbonate (EC) diffuse through SEI (pores) and react with Li inside SEI



Li + EC ➔ thicker SEI (capacity loss & high impedance➔ rate capability loss)

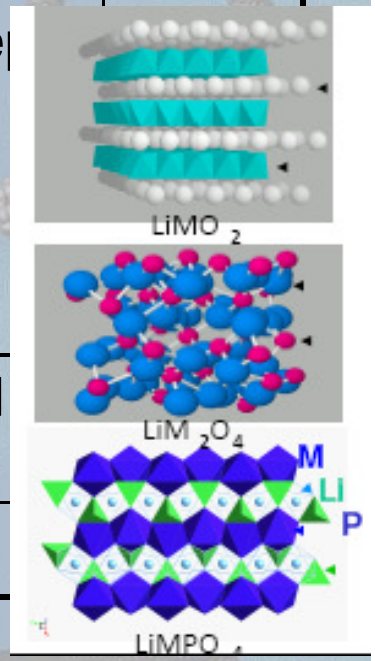
Advantages and Disadvantages

- Advantages
  - Very high energy and power
  - Excellent charge retention
- Disadvantages
  - Safety concerns
  - High cost (control systems)
  - Lithium deposition during charge at low temperature
  - Short calendar life



New Development
(Positive Electrode)

Structure	Material	E_{oc}	Capacity	Safety	Cost
Layered oxides (2D)	$LiCoO_2$ $Li(Co\text{-}Ni)O_2$ $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ (L-333)	3.6 to 3.7	151 Ah/kg	Acceptable	
Spinel (3D)	$LiMn_2O_4$	3.7	119 Ah/kg	good	
Olivine (1D)	$LiFePO_4$	3.4	161 Ah/kg	best	



- Spinel is more proven than olivine except a high temperature
- Spinel has relatively lower capacity (119 vs.150 or 160 Ah/kg for other materials) and solubility problems
- Olivine has very low conductivity

New Lithium Iron Phosphate Cells (CALB, Thunder Sky, GBS)

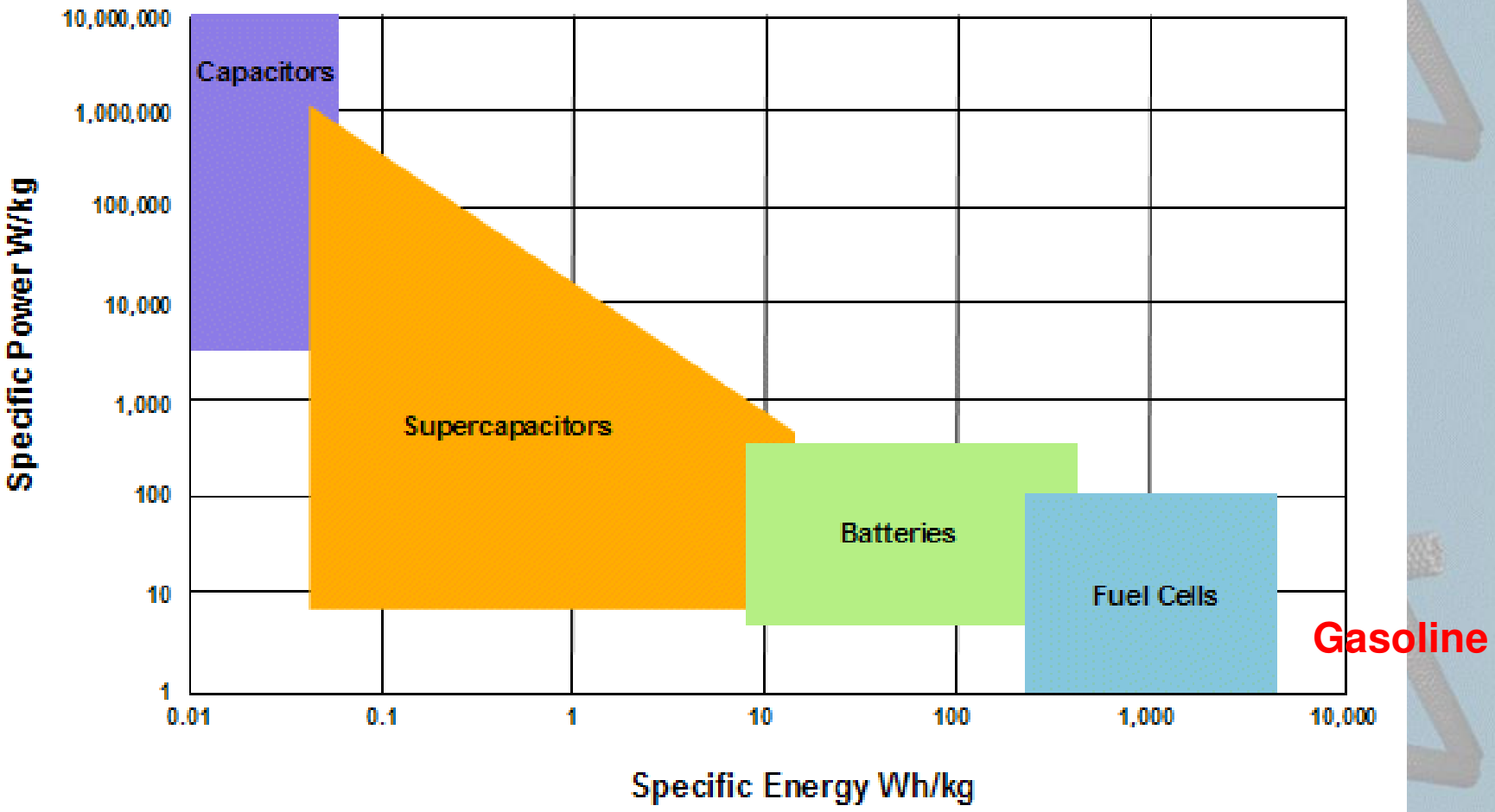
CA Series Lithium Battery (http://en.calb.cn/)								
Battery Types	Capacity (Ah)	Nominal Voltage (V)	Weight (Kg)	Practical Specific Energy (Wh/kg)	Operating Thermal Ambient (Discharging) °C	L x B x H (mm)	Volume L (m^3)	Energy Density (KWh/m^3)
CA40FI	40	3.2	1.6	80.0	−20 ~ 55	129 x 50 x 150	9.7×10^{-4}	132
CA50FI	50	3.2	1.8	88.9	−20 ~ 55	227 x 42 x 116	11×10^{-4}	145.5
CA100FI	100	3.2	3.6	88.9	−20 ~ 55	264 x 64 x 166	28×10^{-4}	114.3
CA180FI	180	3.2	5.8	99.3	−20 ~ 55	181 x 72.5 x 280	36.8×10^{-4}	156.5
CA400FI	400	3.2	13.7	93.4	−20 ~ 55	451 x 72 x 288	93.5×10^{-4}	136.9

New Development
(Negative Electrode)

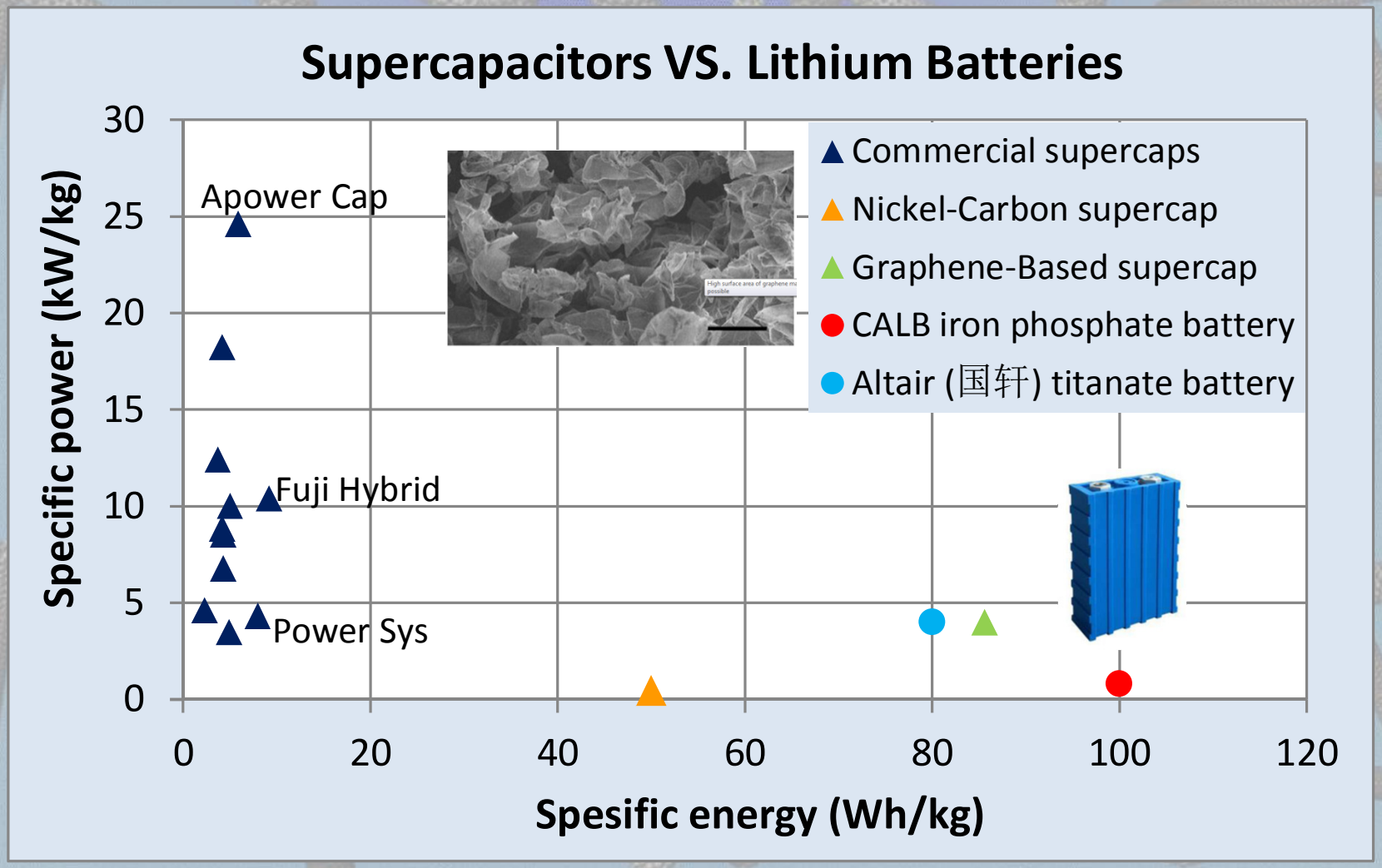
- Spinel negative electrode (Altair)
  - Lithium titanate ($Li_4Ti_5O_{12}$)
    - Advantages
      - At lower voltage (~ 2.5 V) lithium is thermodynamically stable in electrolyte ➔ **no SEI**
      - Rapid charge and discharge
      - Extremely long cycle life **(> 20,000**)
    - Disadvantages
      - Lower voltage (2.5 V)
      - Low electronic coductivity (additives)

A supercapacitor!

Battery V.S. Supercapacitor



Battery V.S. Supercapacitor



Summary (Three Batteries)

- Lead acid battery
  - Low energy, < 40 Wh/kg
  - Moderate power, > 200 W/kg
  - Short life (deep discharge cycle), ~ 400 EV cycles
  - Low cost, ~ $150/kWh
- Nickel metal hydride battery
  - Moderate energy, < 100 Wh/kg
  - High power, > 1000W/kg
  - Long life, ~ 2000 EV cycles
  - High cost, ~ $1000/kWh (cell)
- Lithium ion battery
  - High energy, < 200Wh/kg
  - High power, > 1000W/kg
  - Long life, ~ 2000 EV cycles
  - High cost, ~ $ 400/kWh (control system)

Outline

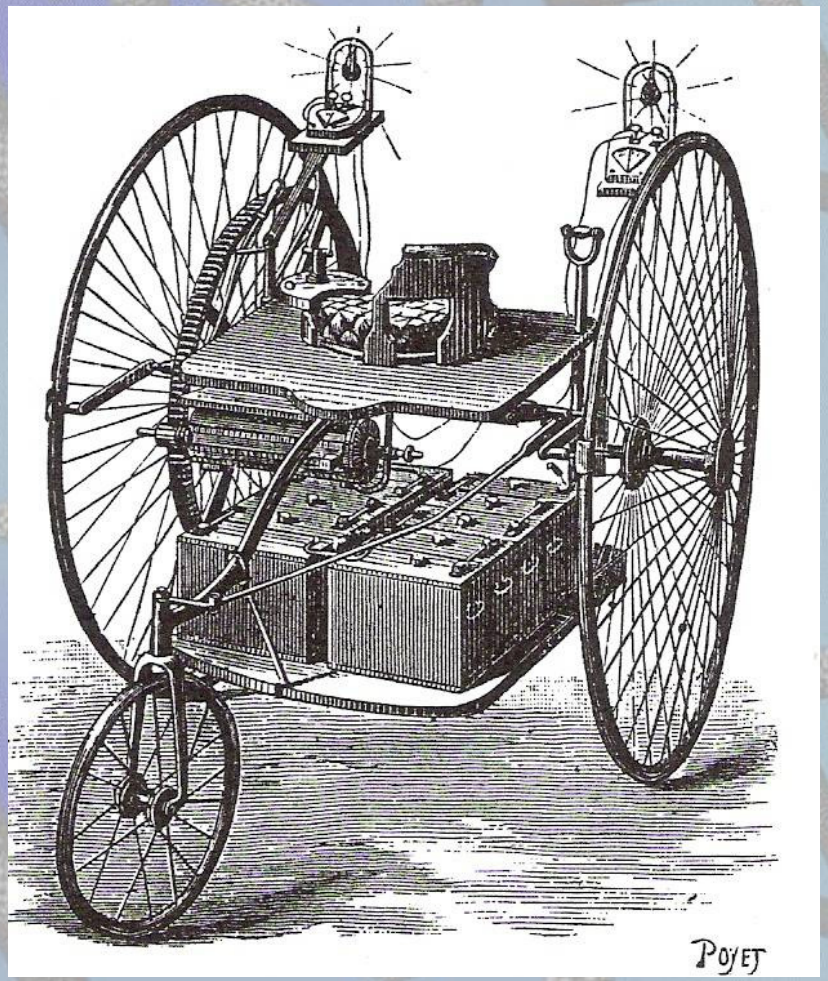
- Introduction to batteries
- Equilibrium and kinetics
- Various secondary batteries
  - Lead acid batteries
  - Nickel metal hydride batteries
  - Lithium ion batteries
- Applications
  - Electric vehicles
  - Hybrid electric vehicles

Electric Vehicles

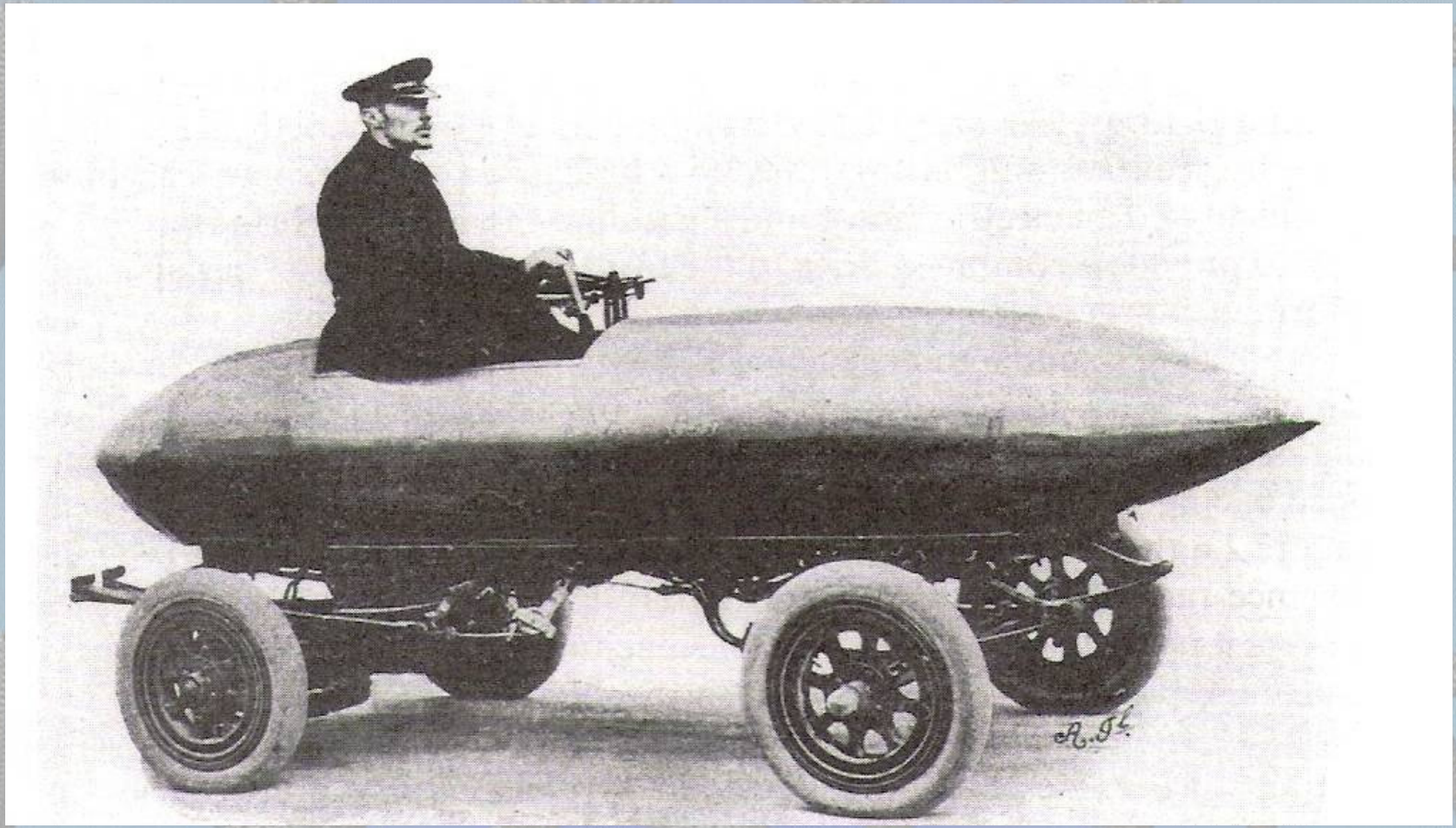
- History of electric vehicles
  - Electric motor demonstrated in 1832
  - Planté invented lead acid batteries in 1860
  - Electric vehicles were more popular than vehicles with internal combustion engines early 20th century (from 1900 to 1912)
    - 30,000 electric vehicles in US
    - 200,000 electric vehicle worldwide
  - The invention of battery powered starter (1911) wiped out electric vehicles after 1920

Early Electric Vehicle

- Ayrton & Perry EV (1882)
  - Ten lead acid battery cells (200 pounds)
  - Peak power output ➔ 400 Watts
  - Range ➔ 10 ~ 25 miles
  - Speed ➔ 10 mph



Electric Vehicle Speed Record



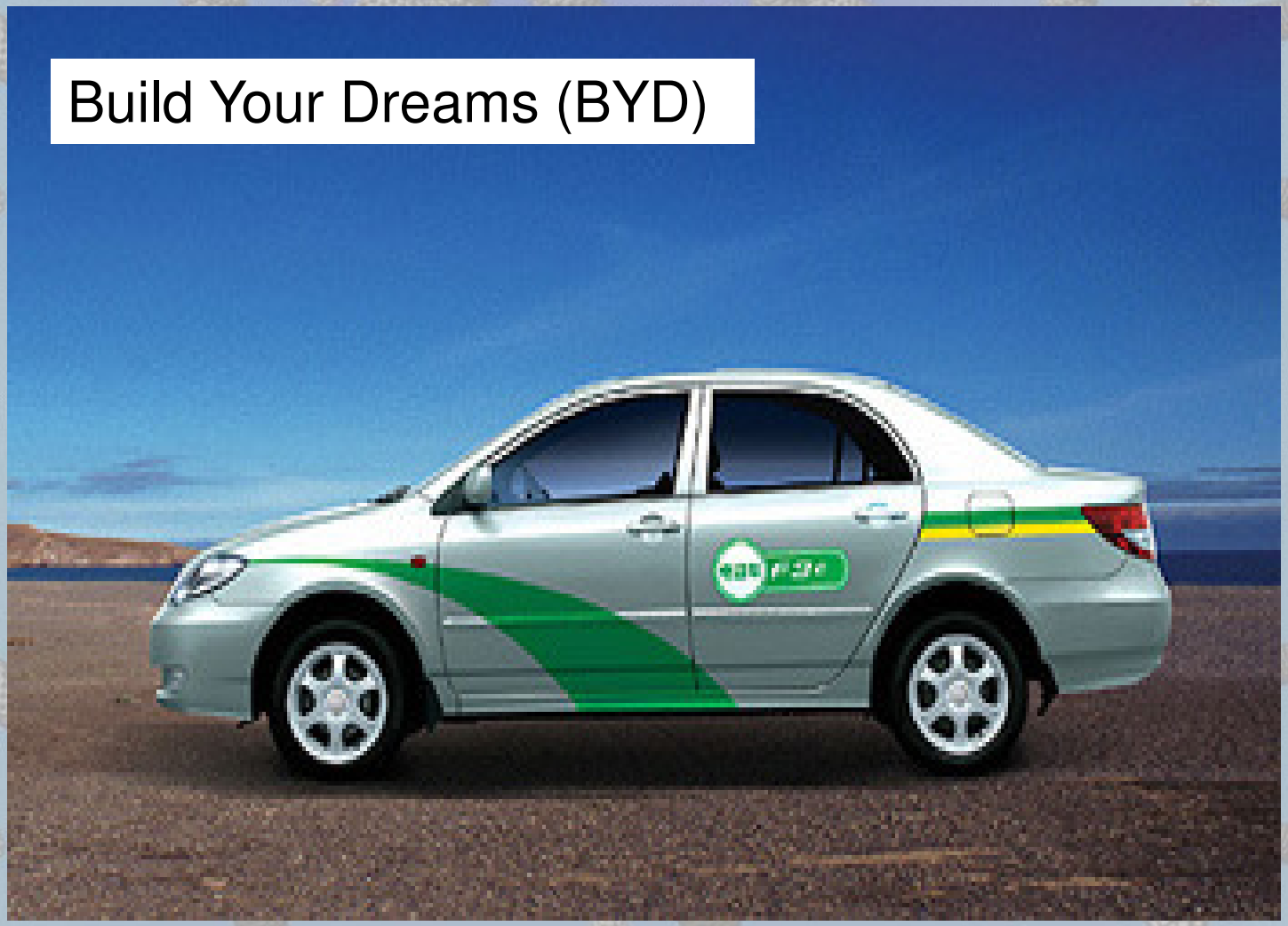
Jenatzy electric race car sets world speed record at 61 mph (1899-1902)

Electric Vehicles

- Renewed interests on electric vehicles
  - Uncertainties on the supply of petroleum based fuels
  - High price of petroleum based fuels
  - Improved technologies on batteries
- Global opportunities
  - More opportunities in countries such as China and India
    - Less or no crude oil reserves compared to the US
    - More city driving
    - Shorter range requirements

Renewal of Electric Vehicles

Chinese Electric Vehicles



GM Chevy Volt

Years in development: 4

Battery range: 40 miles

Supplemented by onboard gas generator

Passengers: 4

Price: $40000

Nissan Leaf

Years in development: 4

Battery range: 100 miles (100% electric, 0 emissions)

Passengers: 4

Price: $32780

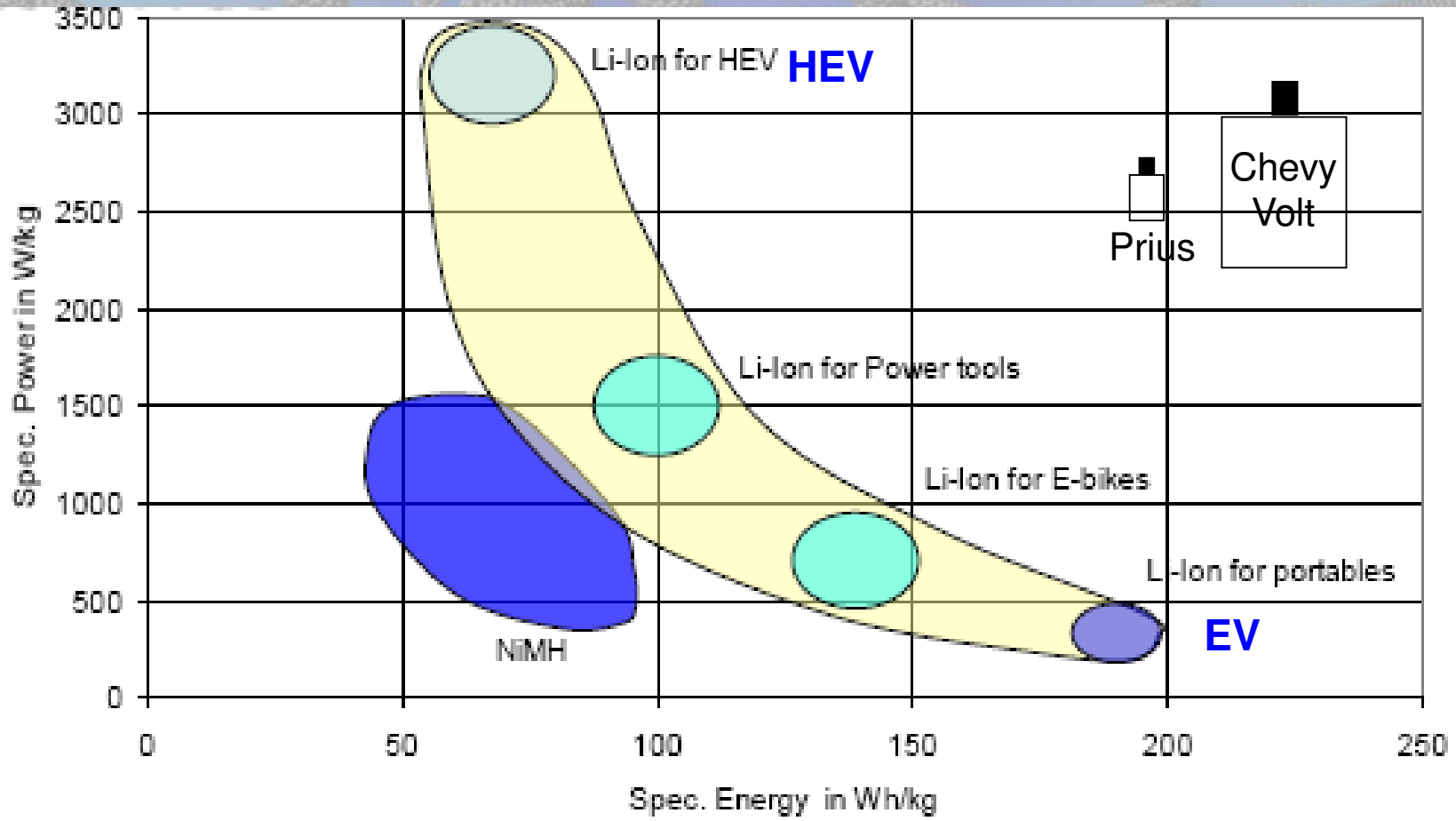
Chinese Concept Electric Vehicles

Indian Electric Vehicles

USABC Goals for EV Batteries

Parameter(Units) of fully burdened system	Minimum Goals for Long Term Commercialization	Long Term Goal
Power Density(W/L)	460	600
Specific Power – Discharge, 80% DOD/30 sec(W/kg)	300	400
Specific Power - Regen, 20% DOD/10 secW/kg	150	200
Energy Density - C/3 Discharge Rate(Wh/L)	230	300
Specific Energy - C/3 Discharge Rate(Wh/kg)	150	200
Specific Power/Specific Energy Ratio	2:1	2:1
Total Pack Size(kWh)	40	40
Life(Years)	10	10
Cycle Life - 80% DOD (Cycles)	1,000	1,000
Power & Capacity Degradation(% of rated spec)	20	20
Selling Price - 25,000 units @ 40 kWh($/kWh)	<150	100
Operating Environment(°C)	-40 to +50 20% Performance Loss (10% Desired)	-40 to +85
Normal Recharge Time	6 hours (4 hours Desired)	3 to 6 hours
High Rate Charge	20-70% SOC in <30 minutes @ 150W/kg (<20min @ 270W/kg Desired)	40-80% SOC in15 minutes
Continuous discharge in 1 hour - No Failure(% of rated energy capacity)	75	75

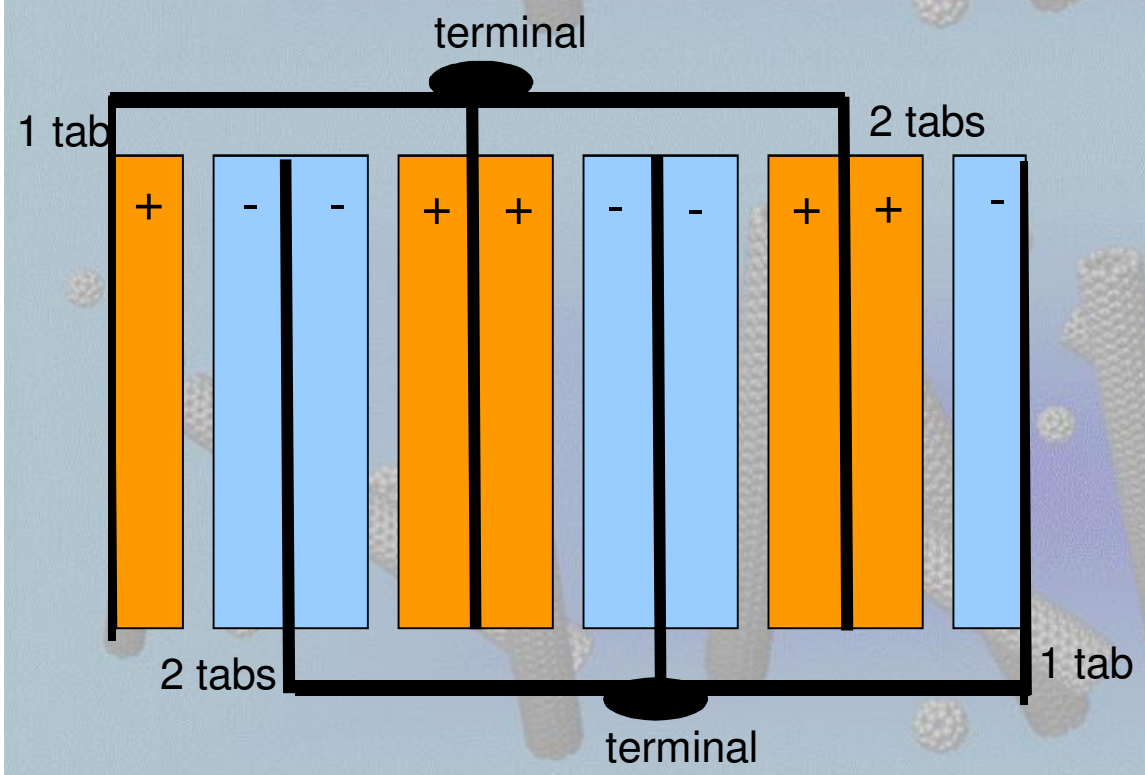
Specific Energy VS Power for Different Batteries



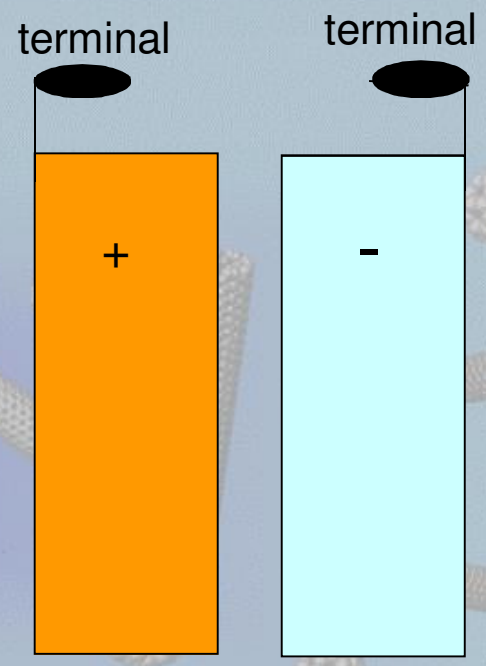
maximum discharge current high energy type: typical: 2C rate
maximum discharge current high power type: typical: 10 – 40 C rate

Specific Energy VS Power
(with the same capacity)

High Specific Power Cell

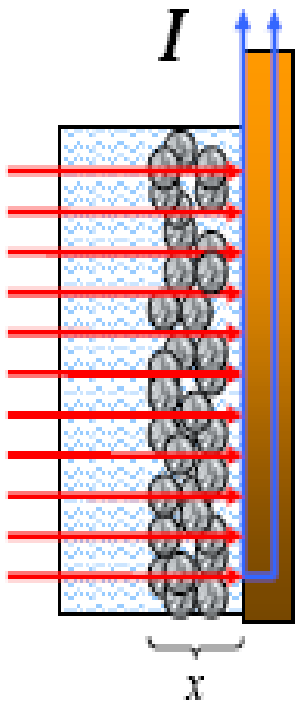


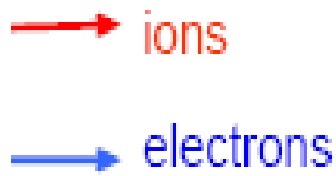
High Specific Energy Cell



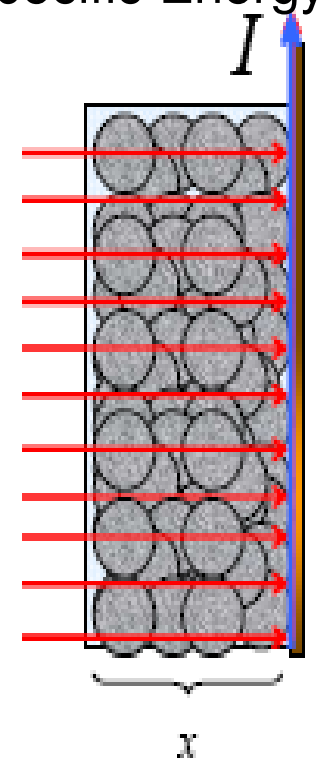
Specific Energy VS Power

High Specific Power





High Specific Energy (**Range**)



- Bias power at the cost of energy
- Smaller particles, lower density
- Thinner electrodes
- Thicker current collectors (minimize IR)

- **Bias energy at the cost of power**
- **Larger particles, higher density**
- **Thicker electrodes**
- **Thinner current collectors (more active material)**

Battery Design for EV (Example)

- Method I: Estimate force required to move the vehicle

  $$F = mg*C_r + \frac{1}{2}\rho C_D A v^2 + ma + mg*\sin(\theta)$$

  C_r: coefficient of rolling resistance

  C_D: Coefficient of air drag

  ρ: Density of air

  A: Cross section of the vehicle

  θ: Slope of the road

- Calculate power and energy required to drive the vehicle for 200 km

  Power P = F * v (velocity)

  Energy = $\int P\, dt$

  (integration from time t = 0 to T for driving 200 km)

  Total energy (Wh) required for the battery pack to drive 200 km

Battery Design for EV (Example)

- Use the empirical equation

  Range (km) = (Є/e) * F_b

  Є: Usable battery specific energy (Wh/kg)

  e: Specific weight consumption (Wh/(kg*km))

  (e = 0.11 for a normal car driving on flat terrain)

  F_b: Battery fraction

- For the battery pack

  Є = 150 Wh/kg (lithium ion battery)

  F_b = 250 / 1500 = 0.167

  Range = (150 / 0.11) * 0.167 = ~ **220 km**

  (150 Wh/kg * 250 kg = **37.5 kWh**)

Battery Design for EV (Example)

- Specific weighted consumption

"e"	CONDITIONS
0.06	Well designed, low acceleration rail vehicles, and level conditions
0.07	GM prototype impact with superior aerodynamics but impractical features
0.09	Stop, start, low acceleration, slow speed bus on level roads, good weather, stops every 300 m
0.11	For a normal car with all-season tires, generally flat terrain
0.15	Smooth freeway driving, good weather, level terrain
0.20	Hilly terrain

Battery Design for EV (summary)

- Energy: ~ 40 kWh for 200 km range
- Power (acceleration): ~ 100 kW , 250kg (400 W/kg)
- Power (regenerative braking): ~ 40 kW (160 W/kg)
  - The efficiency of city driving is higher than that of highway driving
- Weight: battery fraction F_b = 0.167 (less than 1/3 vehicle weight)
- Life: 10 years and 100,000 miles
- Cost: competitive with internal combustion drive train

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Power Density(W/L)	460	600
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Introduction

- Hybrid electric vehicle types

Types	Main Attributes	Battery
Micro-1	Stop, power for idle loads, crank ICE	VRLA
Micro-2	Micro-1 plus regenerative braking	VRLA
Mild-1	Micro-2 plus lunch assist	VRLA
Mild-2	Mild-1 plus limited power assist	VRLA, **NiMH**
Moderate	Mild-2 plus full power assist	**NiMH**
Strong	Moderate plus extended power assist (limited electric drive)	**NiMH**
Plug-in HEV	Strong plus extended electric drive	**NiMH, Li-ion**

VRLA: Valve regulated lead acid battery NIMH: Nickel metal hydride battery

Battery Design with Higher Power Output

- Thinner electrodes and separators
- More electrodes in parallel
- Shorter aspect ratio
- Thicker and heavier current collectors
- Conductive additives mixed with active materials in electrodes