Advanced Secondary Batteries And Their Applications for Hybrid and Electric Vehicles

Su-Chee Simon Wang
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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)**

<table>
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<tr>
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Less stable

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

\[ \begin{align*}
2H^+ + 2e^- & \rightarrow H_2 \\
Cu^{2+} + 2e^- & \rightarrow Cu
\end{align*} \]
Calculate Cell Voltage
(Open circuit)

Positive electrode: Cu
Negative electrode: Zn

Cell open circuit voltage $E_{oc} = E^+_c - E^-_o$

- $E^+_c = 0.34$ V
- $E^-_o = -0.76$ V

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

*Current: extrinsic*
### Table

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Calculate Cell Voltage (Open Circuit)

- Hydrogen Fuel Cells (with hydrogen and oxygen electrodes)
  \[ \text{O}_2 + 4\text{H}^+ + 4e \leftrightarrow 2\text{H}_2\text{O} \quad 1.23 \text{ V} \]
  \[ \text{H}^+ + e \leftrightarrow 1/2\text{H}_2 \quad 0.00 \text{ V} \]
  \[ E_{oc} = 1.23 - 0 = \quad 1.23 \text{ V} \]

- Lithium Fluorine Battery
  \[ \text{F}_2 + 2e \leftrightarrow 2\text{F}^- \quad 2.87 \text{ V} \]
  \[ \text{Li}^+ + e \leftrightarrow \text{Li} \quad -3.01 \text{ V} \]
  \[ E_{oc} = 2.87 - (-3.01) = \quad 5.88 \text{ V} \]
# How to Make High Voltage Batteries

## Strong reducing agents

<table>
<thead>
<tr>
<th>Period</th>
<th>Element</th>
<th>Symbol</th>
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<th>Mass Number</th>
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<td>H</td>
<td>1</td>
<td>1.0079</td>
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<tr>
<td>2</td>
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<td>Li</td>
<td>3</td>
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<td>11</td>
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<td>19</td>
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<td>Rb</td>
<td>Rb</td>
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<tr>
<td>55</td>
<td>Cs</td>
<td>Cs</td>
<td>55</td>
<td>132.91</td>
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<tr>
<td>87</td>
<td>Fr</td>
<td>Fr</td>
<td>87</td>
<td>(223)</td>
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## Strong oxidants

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<tr>
<td>13</td>
<td>Al</td>
<td>Al</td>
<td>13</td>
<td>26.982</td>
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<tr>
<td>17</td>
<td>Cl</td>
<td>Cl</td>
<td>17</td>
<td>35.453</td>
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<td>18</td>
<td>Ar</td>
<td>Ar</td>
<td>18</td>
<td>39.948</td>
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</tbody>
</table>

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* Lanthanide series
  - La: 138.91
  - Ce: 140.12
  - Pr: 140.91
  - Nd: 144.24
  - Pm: 145
  - Sm: 150.36
  - Eu: 151.96
  - Gd: 157.25
  - Tb: 158.93
  - Dy: 162.50
  - Ho: 164.93

# Actinide series
  - Ac: 227
  - Th: 232.04
  - Pa: 231.04
  - U: 238.03
  - Np: 237
  - Pu: 244
  - Am: 243
  - Cm: 247
  - Bk: 247
  - Cf: 251
  - Es: 252
  - Fm: 257
  - Md: 258
  - No: 259
  - 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
    \[ \text{Zn}^{2+} + 2e^- \rightarrow \text{Zn} \]
  - Positive electrode is the anode
    \[ \text{Cu} \rightarrow \text{Cu}^{2+} + 2e^- \]

- **During discharge**
  - Positive electrode is the cathode
    \[ \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} \]
  - Negative electrode is the anode
    \[ \text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \]
**Power Energy and Charge**

- **Power = Voltage * Current**
  - $1 \text{ W (watt)} = 1 \text{ V (volt)} \times 1 \text{ A (ampere)}$
  - $1 \text{ kW} = 1000 \text{ W}$

- **Energy = Power * Time**
  - $1 \text{ Wh (watt-hour)} = 1 \text{ W} \times 1 \text{ h (hour)}$
  - $1 \text{ kWh} = 1000 \text{ Wh}$
  - $1 \text{ Wh} = 3600 \text{ J (joules)}$

- **Charge = Current * Time**
  - $1 \text{ Ah} = 1 \text{ A} \times 1 \text{ h}$
  - $1 \text{ kAh} = 1000 \text{ Ah}$
  - $1 \text{ Ah} = 3600 \text{ C (coulombs)}$
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
    • 1.5 V (3 Ah)
  – Lead acid SLI battery
    • 12 V (50 Ah)
  – Prius battery
    • 202 V (6.5 Ah)
  – Lithium ion battery (laptop)
    • 10 V (5 Ah)

• **Gasoline (tank)**
  – 600 kWh
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 ($I_{\text{ch}}$) and discharge ($I_{\text{dis}}$)

- $E_{\text{ch}}$
- overpotential: $\eta_{\text{ch}}$
- $E_{\text{oc}}$
- $E_{\text{dis}}$
- overpotential: $\eta_{\text{dis}}$

Voltage vs. Time

0  SOC (%)  100  0  DOD (%)  100
Charge and Discharge Curves

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

![Constant current charge ($I_{ch}$) and discharge ($I_{dis}$) graph](image)
Battery Component Resistance Distribution

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

<table>
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<tr>
<th>Component</th>
<th>Resistance</th>
<th>Percentage</th>
</tr>
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<tbody>
<tr>
<td>terminals</td>
<td>0.1 mohm</td>
<td>0.8 %</td>
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<tr>
<td>tabs</td>
<td>0.6 mohm</td>
<td>4.7 %</td>
</tr>
<tr>
<td>KOH/separators</td>
<td>3 mohm</td>
<td>23.6 %</td>
</tr>
<tr>
<td>positive electrode</td>
<td>1.5 mohm</td>
<td>11.8 %</td>
</tr>
<tr>
<td>positive substrate</td>
<td>2.5 mohm</td>
<td>19.7 %</td>
</tr>
<tr>
<td>negative electrode</td>
<td>2 mohm</td>
<td>15.7 %</td>
</tr>
<tr>
<td>negative substrate</td>
<td>3 mohm</td>
<td>23.6 %</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>12.7 mohm</strong></td>
<td><strong>100 %</strong></td>
</tr>
</tbody>
</table>
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

- $\Delta G$: Free energy change from reactants to products during discharge (J/mole) $\rightarrow$ negative value
  
  $\Delta G = - nF E_{oc}$ ($nF E_{oc}$: electric work) $\leftrightarrow$ Max.
  
  - $n$: Number of moles of electron transferred
  - $F$: Faraday’s constant (96500 C/mole)
  - $E_{oc}$: Open circuit cell voltage

- Theoretical Specific energy
  
  $nF E_{oc}$ / total weight of reactants
Theoretical Specific Energy
(Lithium Ion Battery)

- Lithium ion battery half cell reactions
  
  (+) $\text{CoO}_2 + \text{Li}^+ + e \leftrightarrow \text{LiCoO}_2 \quad n = 1$
  
  $E^o = 1 \text{ V}$

  (-) $\text{Li}^+ + \text{C}_6 + e \leftrightarrow \text{LiC}_6$
  
  $E^o \sim -3 \text{ V}$

- Overall reaction during discharge
  
  $\text{CoO}_2 + \text{LiC}_6 \rightarrow \text{LiCoO}_2 + \text{C}_6$
  
  $E_{oc} = E^+ - E^- = 1 - (-3) = 4 \text{ V}$

  $E_{oc} = 4 \text{ V}$
Theoretical Specific Energy
(Lithium Ion Battery)

• Free energy change ($\Delta G$) during discharge
  \[ \Delta G = -nFE_{oc} = -1 \times 96500 \times 4 = -386000 \text{ J} \]
  \[ = -386 \text{ kJ} = -107.2 \text{ Wh/mole} \]

• Total weight of reactants
  \[ \text{CoO}_2 + \text{LiC}_6 \rightarrow \text{LiCoO}_2 + \text{C}_6 \]
  \[ \text{CoO}_2 \rightarrow 91 \text{ grams} \]
  \[ \text{LiC}_6 \rightarrow 7 + 12 \times 6 = 79 \text{ grams} \]
  Total weight \( \rightarrow 170 \text{ grams (0.17 kg)/mole} \)

• Theoretical specific energy
  \[ 107.2 \text{ Wh/0.17 kg} = 630.6 \text{ Wh/kg} \]

• Theoretical energy density
  \[ 107.2 \text{ Wh/0.055 L} = 1949 \text{ Wh/L} \]
Practical Specific Energy

- Practical specific energy of a battery is significantly lower than the theoretical value (~30%) $\Rightarrow \sim 190 \text{ Wh/kg}$ for lithium battery (USABC target for EV $> 150 \text{ Wh/kg}$)

  - Lower discharge voltage ($E_{\text{dis}} < E_{\text{oc}}$)
    - Voltage losses (broader resistance)
  - Extra material weight
    - Current collectors
    - Terminals
    - Battery case
    - Separators

Theoretical specific energy $= nF E_{\text{oc}} / \text{total weight of reactants} = 630.6 \text{ Wh/kg}$
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 \( E_{\text{dis}} < E_{\text{oc}} \)
    - Activation polarization losses
    - Ohmic losses
    - Concentration polarization losses
  - Extra material weight
    - Current collectors
    - Terminals
    - Battery case
    - Separators
Kinetics in Batteries

- Source of voltage losses (broad resistance)
  - Electrode activation polarization losses ($\eta_a$)
    - Butler-Volmer equation
      - Depends on electrode reactions
  - Ohmic losses ($\eta_\Omega$)
    - Ohm’s law (Ohmic resistance)
      - Electronic resistance (electrode current collector, tabs. and terminals)
      - Ionic resistance (electrolyte and separator)
      - Temperature effects
  - Concentration polarization losses ($\eta_c$)
    - Nernst equation
      - Depends on diffusion in electrolyte and solid state
Charge and Discharge Curves

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

- Charge
- Overcharge
- Discharge

$E_{ch}$

Overpotential: $\eta_{ch}$

$\eta_{dis} = \eta_a + \eta_\Omega + \eta_c$

$E_{dis}$

$E_{oc}$

$\eta^{+}$

$\eta^{-}$

SOC (%): 0 to 100

DOD (%): 0 to 100

Time vs. Voltage Diagram

- Voltage scale
- Time scale

+ (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)

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

- Current density \( i \) (electrochemical reaction at electrode/electrolyte interface) is a function of:
  - \( \eta_a \): Activation polarization loss
  - \( i_0 \): Exchange current density
  - \( \alpha \): The symmetry factor
  - \( F \): Faraday’s constant
  - \( R \): Molar gas constant
  - \( T \): Temperature
Effect of Rate on Discharge

Rate Dependence of Discharge Curves for 12-EV-85 Modules
discharge voltage vs. discharge capacity

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

Higher current \( \Rightarrow \) higher \( \eta \)

Concentration polarization losses

C/8 Rate

2-C Rate

Capacity (Ah)

Voltage (V)

- 10A
- 20A
- 40A
- 80A
- 160A
Concentration Polarization Losses (Nernst Equation)

• During discharge
  – Reaction at the positive electrode:
    \[ \text{Cu}^{+2} + 2e^- \rightarrow \text{Cu} \]
  – Reaction at the negative electrode:
    \[ \text{Zn} \rightarrow \text{Zn}^{+2} + 2e^- \]
  – Cell reaction:
    \[ \text{Zn} + \text{Cu}^{+2} \rightarrow \text{Cu} + \text{Zn}^{+2} \]

• Nernst equation

\[
E_{oc, real} = E_{oc, table} + \frac{RT}{nF} \ln \left( \frac{A^a}{B^b} \right)
\]

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

\[
E_{oc, real} = E_{oc, table} + \frac{RT}{nF} \ln \left( \frac{\text{Cu}^{+2}}{\text{Zn}^{+2}} \right)
\]

(If \( \text{Zn}^{+2} = \text{Cu}^{+2} = 1M \))
Total Voltage Losses

- $E_{oc} - E_{dis} = \text{Total voltage losses (} \eta_{dis}, \text{ extrinsic)} = \text{Activation losses (} \eta_a) + \text{Ohmic losses (} \eta_\Omega) + \text{Concentration losses (} \eta_c)$
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

Block Parameters: 200 volts, 6.5 Ah Ni-MH battery

- Battery type: Lead-Acid
- Nominal Voltage (V): 12
- Rated Capacity (Ah): 32
- Initial State-Of-Charge (%): 100

- EO = 12.645, R = 0.009375, K = 0.33, A = 0.66, B = 117.1875

Graph showing voltage over time:

- Voltage ranges from 14 to 9
- Time (hours) ranges from 0 to 2

Diagram of a battery model showing components such as voltage, current, and state-of-charge.
Experimental Results
V.S. MATLAB Model

Marine Lead Acid Battery (12V, 32 Ah)

- C/2 Test
- 1C Test
- 2C Test
- C/2 Model
- 1 C Model
- 2 C 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
  - PbO₂
- Negative electrodes
  - Pb
- Current collectors
  - Lead (or alloy) grids
- Separators
  - Porous or glass mat
- Electrolyte
  - 5M H₂SO₄ aqueous solution
Theoretical Specific Energy

- Lead acid battery half cell reactions
  \[ \text{PbO}_2 + \text{SO}_4^{2-} + 4 \text{H}^+ + 2 \text{e} \leftrightarrow \text{PbSO}_4 + 2 \text{H}_2\text{O} \]
  \[ E^\circ = 1.69 \text{ V} \]

  \[ \text{PbSO}_4 + 2 \text{e} \leftrightarrow \text{Pb} + \text{SO}_4^{2-} \]
  \[ E^\circ = -0.36 \text{ V} \]

- Overall reaction during discharge
  \[ \text{PbO}_2 + \text{Pb} + 2\text{H}_2\text{SO}_4 \rightarrow 2 \text{PbSO}_4 + 2 \text{H}_2\text{O} \]
  \[ V_{oc} = V_+ - V_- = 1.69 - (-0.36) = 2.05 \text{ V} \]
Theoretical Specific Energy

- Free energy change ($\Delta G$) during discharge
  \[ \Delta G = -nFE = -2 \times 96500 \times 2.05 = -395700 \text{ J} \]
  \[ = -395.7 \text{ kJ} = -109.9 \text{ Wh/mole} \]

- Total weight of reactants
  \[ \text{PbO}_2 + \text{Pb} + 2\text{H}_2\text{SO}_4 \rightarrow 2 \text{ PbSO}_4 + 2 \text{ H}_2\text{O} \]
  \[ \text{PbO}_2 \rightarrow 239 \text{ grams} \]
  \[ \text{Pb} \rightarrow 207 \text{ grams} \]
  \[ 2\text{H}_2\text{SO}_4 \rightarrow 98 \times 2 = 196 \text{ grams} \]
  \[ \text{Total weight} \rightarrow 642 \text{ grams (0.642 kg)/mole} \]

- Theoretical specific energy
  \[ 109.9 \text{ Wh/0.642 kg} = \textbf{171 Wh/kg} \]

- Theoretical energy density
  \[ 109.9 \text{ Wh/0.1 L} = 1099 \text{ Wh/L} \]
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:
  - \(2 \text{ PbSO}_4 + 2 \text{ H}_2\text{O} \rightarrow \text{PbO}_2 + \text{Pb} + \text{H}_2\text{SO}_4\) (2.05 V)
  - Competing reaction: \(2\text{H}_2\text{O} \rightarrow \text{O}_2 + 2\text{H}_2\) (1.23 V)
Electrolyte ($\text{H}_2\text{SO}_4$) Concentration

- Overall reaction during charge
  
  $$2 \text{PbSO}_4 + 2 \text{H}_2\text{O} \rightarrow \text{PbO}_2 + \text{Pb} + \text{H}_2\text{SO}_4$$
  
  The concentration of sulfuric acid increases to 5 M

- Overall reaction during discharge
  
  $$\text{PbO}_2 + \text{Pb} + \text{H}_2\text{SO}_4 \rightarrow 2 \text{PbSO}_4 + 2 \text{H}_2\text{O}$$
  
  The concentration of sulfuric acid decreases
Cell Capacity Under Different Discharge Rates

- 4.59 Ah
- 5.10 Ah
- 5.6 Ah
- 6.00 Ah
Failure Mode

- Positive electrode
  - Lead grid corrosion
    \[
    \text{PbO}_2 + \text{Pb} + \text{H}_2\text{SO}_4 \rightarrow 2 \text{PbSO}_4 + 2 \text{H}_2\text{O}
    \]
  - 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
• Equilibrium and kinetics
• Various secondary batteries
  ▪ Lead acid batteries
  ▸ Nickel metal hydride batteries
  ▪ Lithium ion batteries
• Applications
  ▪ Electric vehicles
  ▪ Hybrid electric vehicles
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 $\text{AB}_5$ or $\text{MmNi}_{3.55}\text{Co}_{0.75}\text{Al}_{0.2}\text{Mn}_{0.5}$ 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
  \[
  \text{NiOOH} + \text{H}_2\text{O} + e \leftrightarrow \text{Ni(OH)}_2 + \text{OH}^- \\
  E^o = 0.45 \text{ V}
  \]
  \[
  \text{M} + \text{H}_2\text{O} + e \leftrightarrow \text{MH} + \text{OH}^- \\
  E^o = -0.83 \text{ V}
  \]

- Overall reaction during discharge
  \[
  \text{NiOOH} + \text{MH} \rightarrow \text{Ni(OH)}_2 + \text{M} \\
  E_{oc} = E_+ - E_- = 0.45 - (-0.83) = 1.28 \text{ V}
  \]
Theoretical Specific Energy

• Free energy change ($\Delta G$) during discharge
  
  \[ \Delta G = -nFE = -1 \times 96500 \times 1.28 = -123520 \text{ J} \]
  
  \[ = -123.5 \text{ kJ} = -34.3 \text{ Wh/mole} \]

• Total weight of reactants
  
  NiOOH + MH $\rightarrow$ Ni(OH)$_2$ + M
  
  NiOOH $\rightarrow$ 92 grams
  
  MH $\rightarrow$ 70 grams
  
  Total weight $\rightarrow$ 162 grams (0.162 kg)/mole

• Theoretical specific energy
  
  \[ 34.3 \text{ Wh}/0.162 \text{ kg} = \textbf{212 Wh/kg} \]

• Theoretical energy density
  
  \[ 34.3 \text{ Wh}/0.02 \text{ L} = 1715 \text{ Wh/L} \]
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)

![Flat discharge voltage curve](image)

- C/8 rate
- 3HR (1.59A) 4.6 Ah
- 5HR (1.02A) 5.1 Ah
- 10HR (560mA) 5.6 Ah
- 20HR (300mA) 6 Ah
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
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 \((\text{LiMO}_2, \text{M} = \text{cobalt, nickel, manganese, aluminum, or combination of two to three metals})\), spinel lithium manganese oxide \((\text{LiMn}_2\text{O}_4)\), and lithium iron phosphate \((\text{LiFePO}_4)\) on aluminum current collector

• Negative electrodes
  – **Carbon** or **graphite** on copper current collector

• Separators
  – Celgard microporous, polyethylene, or ceramic separators

• Electrolyte
  – \(\text{LiPF}_6\) dissolved in ethylene carbonate \((\text{EC})\)
    • Solvent with high dielectric constant \((89.6 \text{ at } 40\,^\circ\text{C})\)
    • Lithium salt with high conductivity
    • 0.005 S/cm as compared to 0.5 S/cm for aqueous electrolyte
Carbon Negative Electrode

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

Lithium ion battery 18650
- 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
  \[ \text{CoO}_2 + \text{Li}^+ + e \leftrightarrow \text{LiCoO}_2 \]
  \[ E^o = 1 \text{ V} \]
  \[ \text{Li}^+ + \text{C}_6 + e \leftrightarrow \text{LiC}_6 \]
  \[ E^o \sim -3 \text{ V} \]

- Overall reaction during discharge
  \[ \text{CoO}_2 + \text{LiC}_6 \rightarrow \text{LiCoO}_2 + \text{C}_6 \]
  \[ E_{oc} = E_+ - E_- = 1 - (-3.01) = 4 \text{ V} \]
Theoretical Specific Energy

- Free energy change ($\Delta G$) during discharge
  \[ \Delta G = -nFE = -1 \times 96500 \times 4 = -386000 \text{ J} \]
  \[ = -386 \text{ kJ} = -107.2 \text{ Wh/mole} \]

- Total weight of reactants
  \[
  \text{CoO}_2 + \text{LiC}_6 \rightarrow \text{LiCoO}_2 + \text{C}_6
  \]
  \[
  \text{CoO}_2 \rightarrow 91 \text{ grams}
  \]
  \[
  \text{LiC}_6 \rightarrow 79 \text{ grams}
  \]
  Total weight \( \rightarrow \) 170 grams (0.17 kg)/mole

- Theoretical specific energy
  \[
  107.2 \text{ Wh}/0.17 \text{ kg} = \textbf{630.6 Wh/kg}
  \]

- Theoretical energy density
  \[
  107.2 \text{ Wh}/0.055 \text{ L} = 1949 \text{ Wh/L}
  \]
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

![Graph showing voltage and current for lithium batteries with aqueous electrolyte.]

- Water decomposition voltage: 1.23 V
- Lithium ion battery: ~4 V
- H₂ evolution: -3.2 V
- O₂ evolution: 1.8 V
Charge

- Overall reaction during charge

\[ \text{LiCoO}_2 + \text{C}_6 \rightarrow \text{CoO}_2 + \text{LiC}_6 \]

Lithium metal deposition could still happen during rapid charge when

**Temp < 5°C**
Overcharge

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

\[
\text{LiCoO}_2 + C_6 \rightarrow \text{CoO}_2 + \text{LiC}_6 \text{ (theoretical)}
\]

\[
\text{LiCoO}_2 + C_6 \rightarrow \text{Li}_{1-x}\text{CoO}_2 + \text{Li}_x\text{C}_6 \text{ (actual)}
\]
Discharge

• Overall reaction during discharge

\[ \text{CoO}_2 + \text{LiC}_6 \rightarrow \text{LiCoO}_2 + \text{C}_6 \]
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 °C

- **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.

---

Capacity determined by the positive electrode.
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).

\[
\text{Li}^+ + \text{C}_6 + \text{e} \leftrightarrow \text{LiC}_6
\]
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

\[ \text{Li} + \text{EC} \rightarrow \text{thicker SEI} \]
(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)

<table>
<thead>
<tr>
<th>Structure</th>
<th>Material</th>
<th>$E_{oc}$</th>
<th>Capacity</th>
<th>Safety</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layered oxides (2D)</td>
<td>LiCoO$_2$</td>
<td>3.6 to 3.7</td>
<td>151 Ah/kg</td>
<td>Acceptable</td>
<td>Low</td>
</tr>
<tr>
<td></td>
<td>Li(Co-Ni)O$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>LiCo$<em>{1/3}$Ni$</em>{1/3}$Mn$_{1/3}$O$_2$ (L-333)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spinel (3D)</td>
<td>LiMn$_2$O$_4$</td>
<td>3.7</td>
<td>119 Ah/kg</td>
<td>good</td>
<td></td>
</tr>
<tr>
<td>Olivine (1D)</td>
<td>LiFePO$_4$</td>
<td>3.4</td>
<td>161 Ah/kg</td>
<td>best</td>
<td></td>
</tr>
</tbody>
</table>

- 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)

<table>
<thead>
<tr>
<th>Battery Types</th>
<th>Capacity (Ah)</th>
<th>Nominal Voltage (V)</th>
<th>Weight (kg)</th>
<th>Practical Specific Energy (Wh/kg)</th>
<th>Operating Thermal Ambient (Discharging) °C</th>
<th>L x B x H (mm)</th>
<th>Volume L (m³)</th>
<th>Energy Density (KWh/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA40FM</td>
<td>40</td>
<td>5.2</td>
<td>1.6</td>
<td>80.0</td>
<td>-20 ~ 55</td>
<td>129 x 50 x 150</td>
<td>9.7 x 10⁻⁴</td>
<td>152</td>
</tr>
<tr>
<td>CA50FM</td>
<td>50</td>
<td>5.2</td>
<td>1.8</td>
<td>83.9</td>
<td>-20 ~ 55</td>
<td>127 x 42 x 116</td>
<td>11 x 10⁻⁴</td>
<td>145.5</td>
</tr>
<tr>
<td>CA100FM</td>
<td>100</td>
<td>5.2</td>
<td>3.8</td>
<td>83.9</td>
<td>-20 ~ 55</td>
<td>264 x 64 x 185</td>
<td>25 x 10⁻⁴</td>
<td>114.5</td>
</tr>
<tr>
<td>CA160FM</td>
<td>160</td>
<td>5.2</td>
<td>5.5</td>
<td>90.5</td>
<td>-20 ~ 55</td>
<td>261 x 72.5 x 280</td>
<td>26.5 x 10⁻⁴</td>
<td>156.5</td>
</tr>
<tr>
<td>CA400FM</td>
<td>400</td>
<td>5.2</td>
<td>15.7</td>
<td>93.4</td>
<td>-20 ~ 55</td>
<td>451 x 72 x 285</td>
<td>85.5 x 10⁻⁴</td>
<td>156.0</td>
</tr>
</tbody>
</table>
New Development
(Negative Electrode)

• Spinel negative electrode (Altair)
  – Lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$)
  
    • Advantages
    – At lower voltage (~ 2.5 V) lithium is thermodynamically stable in electrolyte \( \implies \) no SEI
    – Rapid charge and discharge
    – Extremely long cycle life ($> 20,000$)
  
    • Disadvantages
    – Lower voltage (2.5 V)
    – Low electronic conductivity (additives)

A supercapacitor!
Battery V.S. Supercapacitor

Gasoline
Battery V.S. Supercapacitor

Supercapacitors VS. Lithium Batteries

- Commercial supercaps
- Nickel-Carbon supercap
- Graphene-Based supercap
- CALB iron phosphate battery
- Altair (国轩) titanate battery

Specific power (kW/kg)

Specific energy (Wh/kg)
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

Tesla
Chinese Electric Vehicles

Build Your Dreams (BYD)
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

<table>
<thead>
<tr>
<th>Parameter (Units) of fully burdened system</th>
<th>Minimum Goals for Long Term Commercialization</th>
<th>Long Term Goal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power Density (W/L)</td>
<td>460</td>
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<td>Specific Power – Discharge, 80% DOD/30 sec (W/kg)</td>
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<td>Specific Power – Regen, 20% DOD/10 sec W/kg</td>
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<td>Energy Density – C/3 Discharge Rate (Wh/L)</td>
<td>230</td>
<td>300</td>
</tr>
<tr>
<td>Specific Energy – C/3 Discharge Rate (Wh/kg)</td>
<td>150</td>
<td>200</td>
</tr>
<tr>
<td>Specific Power/Specific Energy Ratio</td>
<td>2:1</td>
<td>2:1</td>
</tr>
<tr>
<td>Total Pack Size (kWh)</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Life (Years)</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Cycle Life – 80% DOD (Cycles)</td>
<td>1,000</td>
<td>1,000</td>
</tr>
<tr>
<td>Power &amp; Capacity Degradation (% of rated spec)</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Selling Price – 25,000 units @ 40 kWh ($/kWh)</td>
<td>&lt;150</td>
<td>100</td>
</tr>
<tr>
<td>Operating Environment (°C)</td>
<td>-40 to +50</td>
<td>-40 to +85</td>
</tr>
<tr>
<td>Normal Recharge Time</td>
<td>6 hours (4 hours Desired)</td>
<td>3 to 6 hours</td>
</tr>
<tr>
<td>High Rate Charge</td>
<td>20-70% SOC in &lt;30 minutes @ 150W/kg (&lt;20min @ 270W/kg Desired)</td>
<td>40-80% SOC in 15 minutes</td>
</tr>
<tr>
<td>Continuous discharge in 1 hour - No Failure (% of rated energy capacity)</td>
<td>75</td>
<td>75</td>
</tr>
</tbody>
</table>
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

1 tab

2 tabs

terminal

1 tab

2 tabs

terminal

terminal

+ - + - + - + -

+ - - - - - - -

+ - - - - - - -

+ - - - - - - -

+ - - - - - - -

+ - - - - - - -

+ - - - - - - -

+ - - - - - - -
Specific Energy VS Power

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

High Specific Energy (Range)
- 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

\[ F = mgC_r + \frac{1}{2}\rho C_D A v^2 + ma + mg\sin(\theta) \]

- \( C_r \): coefficient of rolling resistance
- \( C_D \): Coefficient of air drag
- \( \rho \): Density of air
- \( A \): Cross section of the vehicle
- \( \theta \): Slope of the road

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

Power \( P = F \times v \) (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
  \[ \text{Range (km)} = \left( \frac{\epsilon}{e} \right) \times F_b \]
  \( \epsilon \): 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
  \( \epsilon = 150 \) Wh/kg (lithium ion battery)
  \( F_b = \frac{250}{1500} = 0.167 \)
  \( \text{Range} = (150 / 0.11) \times 0.167 = \sim 220 \text{ km} \)
  \( (150 \text{ Wh/kg} \times 250 \text{ kg} = 37.5 \text{ kWh}) \)
**Battery Design for EV (Example)**

- Specific weighted consumption

<table>
<thead>
<tr>
<th>“e”</th>
<th>CONDITIONS</th>
</tr>
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<tbody>
<tr>
<td>0.06</td>
<td>Well designed, low acceleration rail vehicles, and level conditions</td>
</tr>
<tr>
<td>0.07</td>
<td>GM prototype impact with superior aerodynamics but impractical features</td>
</tr>
<tr>
<td>0.09</td>
<td>Stop, start, low acceleration, slow speed bus on level roads, good weather, stops every 300 m</td>
</tr>
<tr>
<td>0.11</td>
<td>For a normal car with all-season tires, generally flat terrain</td>
</tr>
<tr>
<td>0.15</td>
<td>Smooth freeway driving, good weather, level terrain</td>
</tr>
<tr>
<td>0.20</td>
<td>Hilly terrain</td>
</tr>
</tbody>
</table>
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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• Applications
  ■ Electric vehicles
  ➢ Hybrid electric vehicles
# Introduction

- **Hybrid electric vehicle types**

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<tr>
<th>Types</th>
<th>Main Attributes</th>
<th>Battery</th>
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</thead>
<tbody>
<tr>
<td>Micro-1</td>
<td>Stop, power for idle loads, crank ICE</td>
<td>VRLA</td>
</tr>
<tr>
<td>Micro-2</td>
<td>Micro-1 plus regenerative braking</td>
<td>VRLA</td>
</tr>
<tr>
<td>Mild-1</td>
<td>Micro-2 plus lunch assist</td>
<td>VRLA</td>
</tr>
<tr>
<td>Mild-2</td>
<td>Mild-1 plus limited power assist</td>
<td>VRLA, NiMH</td>
</tr>
<tr>
<td>Moderate</td>
<td>Mild-2 plus full power assist</td>
<td>NiMH</td>
</tr>
<tr>
<td>Strong</td>
<td>Moderate plus extended power assist (limited electric drive)</td>
<td>NiMH</td>
</tr>
<tr>
<td>Plug-in HEV</td>
<td>Strong plus extended electric drive</td>
<td>NiMH, Li-ion</td>
</tr>
</tbody>
</table>

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