## Vehicle Propulsion Systems Lecture 9 – Batteries

Modeling and Usage of Batteries

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## When I say batteries: What do you think of?

- Consumer products, replaceable. Zn Mn O<sub>2</sub> with NH<sub>4</sub> Cl electrolyte (Brunstensbatteri) → Alkaline Battery Zn Mn O<sub>2</sub> with KOH electrolyte. AA, AAA, Button cells (CR=Lithium LiMnO<sub>2</sub> 3.7V), (SR=Silver Oxide 1.55V), (LR=Alkaline 1.5 V)
- Consumer products, rechargeable.
   AA, AAA, Formfactors, NiCd (1.25V), NMH (1.2V), Lilon (4V) (1991).
- Lead Acid Batteries. Automotive Starter Batteries, UPS.
- Packs of cells.
   Lantern Cell (4.5 V=3x1.5V), Tesla model 3 pack



Batteries can contain poisonous metals, remember to recycle all your electronic devices properly!

## **Basic Battery Definitions**

## Definition of a Battery

A container consisting of one or more cells, in which chemical energy is converted into electricity and used as a source of power. History is associated with Volta's stack of Zinc and Copper disks separated by paper soaked in salt water.

Benjamin Franklin suggested, in 1748, the term battery for this invention, in the sense of a collection of things used together, like a battery of artillery.

- Cell A single Unit
- Block A number of cells in Parallel
- String A number of cells in Series
- Pack A collection of cells connected in series and/or parallel
- Battery A unit with a collection of cells ready for operation, Pack+BMS Battery Management System



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## More Battery Definitions



From Handbook of Batteries, Linden ed. (2008)



# Cell Form Factors



## Electro-Chemistry Background – Repetition

Electrolyte A substance that produces an electrically conducting solution when dissolved in a polar solvent, an example is table salt in water. The dissolved electrolyte separates into cations (+) and anions (-), which spreads uniformly in the solvent. Electrically, the solution is neutral.

Oxidizing reaction Is when a molecule loses an electron or increases its oxidation state of an atom or ion.

Reducing reaction Is when a molecule gains an electron or decreases its oxidation state of an atom or ion.

Redox reaction The global reaction where there are transfer of electrons between molecules.

Anode The electrode (in batteries) is where the oxidation reaction occurs. Electrons flow out.

Cathode The electrode (in batteries) is where the reduction reaction occurs. Electrons flow in.

Note that anode is - and cathode is + during discharge of a battery (normal usage). But when charging the battery they switch roles, so anode is + and cathode is -. In most texts this distinction is not made, instead the anode is always considered to be the - pole and the cathode the + pole.

## Turn our Attention to Secondary Batteries – Lead Acid as Initial Example





## Historical evolution of Secondary Batteries



## Historical Evolution of Lithium Ion Batteries



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## Some definitions that are important

- State of Charge (SOC) [%]
- Open Cirquit Voltage (OCV) [V]
- Internal resistance (IR) [mOhm]
- Depth of Discharge (DoD) [%]
- Cut-off voltage [V] (max & min for safe op.)
- C-rate how fast the battery is charged
  - 1C battery is fully charged in 1h
  - 2C battery is fully charged in 0.5h
  - 0.5C battery is fully charged in 2h
- Cycle 1 full discharge and full charge

## Some definitions that are important



#### Capacity vs C-Rate



- SOH is a figure of merit that reflects the general condition of a battery and its ability to deliver the specified performance compared with a fresh battery.
- It takes into account factors such as charge acceptance, internal resistance, capacity, voltage and self-discharge.
- It is a measure of the long term capability of the battery and gives an indication of the performance that can be expected from the battery.
- It indicates how much of the lifetime of the battery that has been consumed, and how much that remains.
- In an application the SOH is estimated by the battery management system (BMS).

## Outline

# Introduction Basic Definitions Evolution of Secondary Batteries Some Buzzwords The Nickel-Metal Hydride Battery Reactions in the anode and cathode Lithium Ion Batteries Future developments Monitoring and Control of Batteries What can happen (go wrong)? Battery Cell Modeling

## Nickel-Metal Hydride – NiMH

Cathode reaction	Anode reaction						
The reaction at the cathode reduces nickel oxyhodroxide to nickel hydroxide	The reaction at the anode oxidizes metal hydride (MH) to the metal alloy (M).						
$NiOOH + H_2O + e^-  ightarrow Ni(OH)_2 + OH^-$	$MH + OH^-  ightarrow M + H_2O + e^-$						
The energy release gives the voltage $E_0 = 0.52 \text{ V}$	The energy release gives the voltage $E_0 = 0.83 \text{ V}$						
The global redox reaction for the NiMH battery is							

 $MH + NiOOH \stackrel{dischg}{\rightleftharpoons}_{chg} M + Ni(OH)_2 \qquad E_0 = 1.35 \, \mathrm{V}$ 

The Hydroxyl Ion and Water pass through the electrolyte while the electron released at the anode goes through the electric circuit to the cathode.

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## Nickel-Metal Hydride – NiMH

#### Active Materials

- The active cathode material is Nickel Oxyhydroxide (NiOOH).
- While the active anode metal in NiMH-batteries is not a single metal, but an engineered alloy that contains a mixture of many metals.
- There are three basic types of alloys, that in their turn have internal variations.

<ul> <li>AB<sub>5</sub> (LaCePrNdNiCoMnAI)</li> </ul>	$La_{5.7}Ce_{8.0}Pr_{0.8}Nd_{2.3}Ni_{59.2}Co_{12.2}Mn_{6.8}AI_{5.2}$ $La_{10.5}Ce_{4.3}Pr_{0.5}Nd_{1.3}Ni_{60.1}Co_{12.7}Mn_{5.9}AI_{4.7}$
• $A_2B_7$ (LaCePrNdMgNiCoMnAlZr)	$\begin{array}{l} La_{4.8}Ce_{0.4}Pr_{9.1}Nd_{5.4}Mg_{1.7}Ni \ _{68.8}Co_{3.0}\ Mn_{0.2}\ Al_{5.5}\ Zr_{0.2} \\ Nd_{18.7}Mg_{2.5}Ni_{74.7}Co_{0.1}Al_{3.6}\ Zr_{0.2} \end{array}$
	$V_{18}Ti_{15}Zr_{18}Ni_{29}Cr_5Co_7Mn_8$ $V_5Ti_9Zr_{24}r_8Ni_{29}Cr_8Mn_4Sn_2$
• AB <sub>2</sub> (VTiZrNiCrCoMnAlSn)	$V_5 Ti_9 Zr_{26,2} Ni_{38} Cr_{3,5} Co_{1,5} Mn_{15,6} Al_{0,4} Sn_{0,8}$

## **Inactive Materials**

- The electrolyte in NiMH batteries of all types is routinely a mixture of about 30% potassium hydroxide (KOH) in water, providing high conductivity over a wide temperature range.
- It is most common for the electrolyte to have a lithium hydroxide additive at a concentration of about 17 g/L to promote improved charging efficiency at the nickel hydroxide electrode. This suppresses the oxygen evolution, which is the competing reaction to charge acceptance.
- It is also possible to substitute a portion of the KOH with NaOH. Where NaOH promotes high-temperature charging-efficiency, although this electrolyte can decrease cycle life through increased corrosion of the active MH materials.
- The electrolyte in the nickel-metal hydride batteries used in the Toyota Prius Hybrid, use a mixture of potassium hydroxide (KOH) and sodium hydroxide (NaOH).
- The separator is termed "permanently wettable polypropylene". This separator is a composite of polypropylene and polyethylene where the base composite fibers require special surface treatments to make them wettable to the electrolyte.

## Outline



## Lithium Ion Batteries – Components and Operating principles

- Anode and Cathode
   Store Lithium inside their structures
- Current Collectors
   Copper @ Anode,
   Aluminum @ Cathode
- Bonding interface materials
   e<sup>-</sup> conducting glue (Carbonite)
- Electrolyte Transports Li+
- Separator Keeps cathode and anode isolated Porous, electrolyte and ion transport
- SEI Solid Electrolyte Interphase



## Lithium Ion Batteries – Components and Operating principles





## **Chemical Reactions**

Cathode reaction (+)	Anode reaction(-)						
The reaction at the cathode reduces the Lithium Ion to Lithium when it enters the Metal oxide	The reaction at the anode oxidizes the Lithium to Lithium Ion when it leaves the Carbon Structure.						
$Li_{1-x}MO_2 + xLi^+ + xe^- \rightarrow LiMO_2$	$Li_y C  ightarrow C + y  Li^+ + y  e^-$						
M is a place holder for various Cathode transition metals. $E_0 \approx 4 \mbox{ V}$	The reaction consumes energy reducing the voltage $E_0 \approx -0.2 \ \text{V}$						
The global redox reaction for the Lithium Ion battery is							
$x/y Li_y C + Li_{1-x} MO_2 \stackrel{dischg}{\underset{chg}{\rightleftharpoons}} x/y C + Li MO_2 \qquad E_0 pprox = 3.7  { m V}$							

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## Lithium Ion Batteries – A Family of Cell Chemistries

- Lithium Iron Phosphate (LFP)
- Lithium Nickel Manganese Cobalt (NMC)
- Lithium Nickel Cobalt Aluminum (NCA)
- Lithium Manganese Oxide (LMO)
- Lithium Cobalt Oxide (LCO)
- Lithium Titanate (LTO)





Sodium Ion Batteries (Na-ion) are a possible alternative to Lithium Ion Batteries. They are not as energy dense, but they are cheaper, more abundant, and safer.

## Lithium Ion Batteries

## Key Processes in a Cell – Buzz words

- Intercalation Like diffusion, but the Lithium ions are inserted into the structure of the anode and cathode.
- SEI Solid-Electrolyte Interphase
- Dendrite growth
- Swelling during charging

## Lithium Ion Batteries

There are different options for materials in Lithium Ion Batteries. They are most often referred to using their Cathode material.



## Lithium Ion Batteries – Aging Mechanisms 1 (2)



## Lithium Ion Batteries – Aging Mechanisms 2 (2)



## Lithium Ion Batteries – Cell Voltage and Capacity Comparison



Battery Properties vary with Materials

Most variations are in cathode material

LTO and Graphite are most common where the latter gives higher voltage.

Outside the stability window the Electrolyte will start to oxidize and can become unstable with a high electric field.

# Lithium Ion Batteries – Power and Energy



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# Why is Lithium Attractive?

Periodic table, lightweight and electronegativity.

#### **Electronegativity of the Elements**

_																		
<b>H</b> 2.20		_																<sup>2</sup> He no data
<sup>3</sup> Li 0.98	<sup>⁴</sup> Be 1.57											Ę	5 B 2.04	6 2.55	<sup>7</sup> N 3.04	<sup>8</sup> 0 3.44	<sup>9</sup> F 3.98	Ne no data
<sup>11</sup> Na 0.93	<sup>12</sup> Mg 1.31											1	<sup>13</sup> Al 1.61	<sup>14</sup> Si 1.90	<sup>15</sup> P 2.19	<sup>16</sup> <b>S</b> 2.58	<sup>17</sup> Cl 3.16	<sup>18</sup> Ar no data
<sup>19</sup> K 0.82	20 Ca 1.00	<sup>21</sup> Sc 1.36	<sup>22</sup> <b>Ti</b> 1.54	<sup>23</sup> V 1.63	<sup>24</sup> <b>Cr</b> 1.66	<sup>25</sup> Mn 1.55	<sup>26</sup> Fe 1.83	<sup>27</sup> Co 1.88	<sup>28</sup> Ni 1.91	<sup>29</sup> Cu 1.90	I Z	n 55	<sup>31</sup> Ga 1.81	<sup>32</sup> Ge 2.01	<sup>33</sup> As 2.18	<sup>34</sup> <b>Se</b> 2.55	<sup>35</sup> <b>Br</b> 2.96	<sup>36</sup> Kr 3.00
<sup>37</sup> <b>Rb</b> 0.82	<sup>38</sup> <b>Sr</b> 0.95	<sup>39</sup> <b>Y</b> 1.22	<sup>40</sup> <b>Zr</b> 1.33	<sup>41</sup> <b>Nb</b> 1.6	42 <b>Mo</b> 2.16	<sup>43</sup> <b>TC</b> 1.9	<sup>44</sup> Ru 2.2	<sup>45</sup> Rh 2.28	<sup>46</sup> <b>Pd</b> 2.20	47 Ac 1.93	48 C	d 39	<sup>49</sup> <b>In</b> 1.78	<sup>50</sup> Sn 1.96	51 <b>Sb</b> 2.05	52 <b>Te</b> 2.1	<sup>53</sup>   2.66	<sup>54</sup> 2.6
55 Cs 0.79	56 Ba 0.89	57-71	<sup>72</sup> <b>Hf</b> 1.3	<sup>73</sup> Ta 1.5	<sup>74</sup> W 2.36	<sup>75</sup> <b>Re</b> 1.9	0s 2.2	<sup>77</sup> <b>lr</b> 2.2	<sup>78</sup> Pt 2.28	<sup>79</sup> 2.54	■ 80 ■ H	<b>g</b>	<sup>B1</sup> <b>TI</b> 1.62	<sup>82</sup> Pb 2.33	<sup>83</sup> <b>Bi</b> 2.02	<sup>84</sup> <b>Po</b> 2.0	85 At 2.2	<sup>86</sup> Rn no data
<sup>87</sup> Fr 0.7	** Ra 0.89	89-103	<sup>104</sup> <b>Rf</b> no data	Db no data	<sup>106</sup> Sg no data	<sup>107</sup> Bh no data	<sup>108</sup> HS no data	<sup>109</sup> Mt no data	Ds no dat		112 C	n lata r	Nh no data	<sup>114</sup> FI no data	MC no data	Lv no data	Ts no data	0g no data
Low																		
		57	.a C	e F		d P		m <sup>63</sup>		Gd	<sup>5</sup> Tb	66 Dy	y H	<b>0 E</b>	E <b>r T</b>	m 70	<b>/b</b>	-u
		89 A	10 1. NC 1 1 1	12 1. <b>h</b> F 1.3 1	<sup>13</sup> 1. <b>2</b> <sup>92</sup> 1. 5 1.3	<sup>14</sup> J 38 1. 1. 1. 1. 1. 1. 1. 1	15 1. <b>Ip <sup>94</sup></b> 36 1.	Pu <sup>95</sup> 28	1.2 96 1.3 96	<b>Cm</b>	<sup>7</sup> Bk 1.3	98 C1 1.3	5 1.2 f <sup>99</sup> f 1.	s F 3 100	m <sup>101</sup> .3	25 Id 102 .3	103 103 103 103	_ <b>r</b> data

## **Evolution of Li-Ion Batteries**

Cell generation	Cell chemistry specifications	
Generation V	- Li/O <sub>2</sub> (Lithium-air)	>2050??
Generation IV	<ul> <li>All solid-state with metallic lithium anode</li> <li>Conversion materials (primarily Li-S)</li> </ul>	~2025 - 2050
Generation IIIb	<ul> <li>Cathode: HE-NMC, HVS (high voltage spinel)</li> <li>Anode: Si / carbon</li> </ul>	~2020 - 2025
Generation IIIa	- Cathode: NMC 622 to NMC 811 - Anode: carbon (graphite) + 5-10% Si component	~2020 - 2025
Generation IIb	- Cathode: NMC 532 to NMC 622 - Anode: carbon (graphite)	7
Generation IIa	- Cathode: NMC 111 - Anode: carbon (graphite)	- Current
Generation I	- Cathode: LCO, LFP, NCA - Anode: carbon (graphite)	



YouTube on the title...

# Secondary Batteries

- What kills a battery?
- Control and monitoring of batteries
- What do we need to monitor?
- How can this be understood?

## Lithium Ion Batteries – Aging Mechanisms 3 (3)



## Li-Ion Battery Characteristics & Charging

- Charging Characteristics, Charging Efficiency
- Discharge Characteristics
- Internal Resistance
- Self-Discharge & Storage
- Cycle Life & Factors Affecting Cycle Life
- Effect of Temperature on Voltage, capacity, IR. Self-discharge. life
- State of Health

## Protection of Li-Ion Batteries- Shallow vs Deep Discharge

- Shallow Discharge
- Deep Discharge
- Shallow Discharge vs Deep discharge



## Outline



## Measurements - Step Responses on a Battery Pack



## Experiments: Steps in Current.

- Dynamic voltage response
- Not a pure resistance and integrator.
- Dynamic elements
- Time constants

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## Measurements - Step Responses



- Steps synchronized
- Steps enlarged

## **Battery Cell Modeling**

#### • Empirical Models — Physical Models



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## Another Classification that Stays Close to Control and Monitoring



## A Dive into the P2D (Doyle-Fuller-Newmann) Model

Describes the spatial state and evolution of:

- solid<sup>2</sup> electrolyte concentrations,
- Ion flows, and
- Potential.





## Examples of model packages with P2D and SPM model.

PyBAMM – Open Source models in Python. COMSOL Multiphysics – Battery Design Module.

- P2D
- SPM / SPMe
- 1D, 2D, 3D
- Thermal coupling
- Electrochemical coupling

- Mechanical coupling
- Multiphysics
- Battery pack design
- Battery pack thermal management
- Battery pack mechanical Design