

# ***Battery Boot Camp***

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## **1.1: Introduction to the course**

- This course is all about how electrochemical (battery) cells work, as fundamental preparatory understanding for how to use them optimally in an application.
- The three main foci of the course are:
  1. Modeling: Defining mathematical descriptions of cell dynamics;
  2. Simulation: Using computer tools to predict performance; and
  3. Identification: Fitting a model to cell data obtained via lab tests.
- This chapter of notes very quickly covers a lot of background re. battery terminology, function, and general application.<sup>1</sup>
- Later chapters will cover much more depth in some mathematical understanding of how cells work, and details in particular areas.

## **Preliminaries**

- Cells are the smallest individual electrochemical unit, and deliver a voltage that depends on the cell chemistry.
  - There are primary (single use) and secondary (rechargeable) cells.

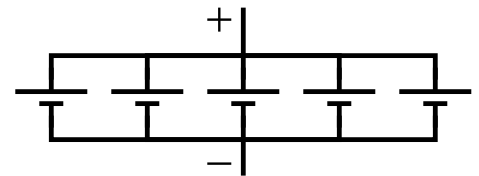
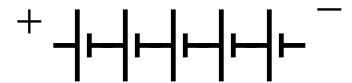
<sup>1</sup> Much of the content of this chapter of notes is adapted from the excellent web site: <http://www.mpoweruk.com/>, and is used within the guidelines posted on the site.

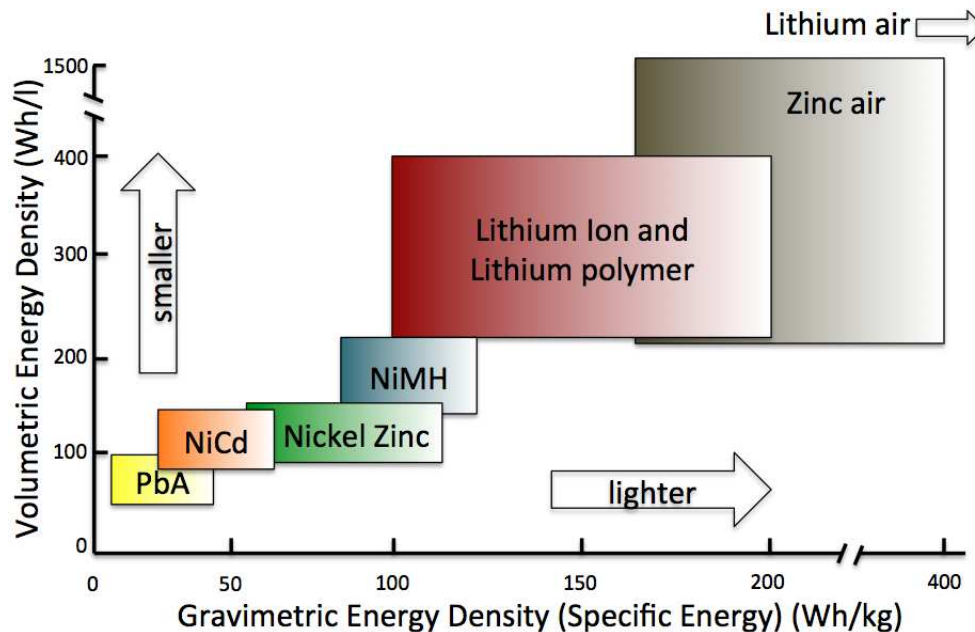
- A cell is different from a battery, but many people (incl. me at times) use the term “battery” to describe any electrochemical energy source, even if it is a single cell, and this can lead to confusion.
- Batteries and battery packs are made up from groups of cells.
  - Sometimes these are packaged in a single physical unit, as in 12 V lead-acid batteries, which comprise six 2 V cells in series, or in many high-capacity lithium-ion batteries, where a number of cells are wired in parallel in a single package.
  - Other times, the connections are external to the cells.
- We use schematic symbols to represent cells and batteries in a circuit diagram.

$\begin{array}{c} | \\ \hline | \end{array}$   
Cell

$\begin{array}{c} | \\ \hline | \end{array}$   
Battery
- Cell (nominal) voltage depends on the combination of active chemicals used in the cell.
  - For many nickel-based cells (*e.g.*, NiCad, NiMH), this is 1.2 V.
  - For many lithium-based cells, this is over 3 V.
- Cell (nominal) capacity specifies the quantity of charge, in ampere hours (Ah), that the battery is rated to hold.
- The C rate is a relative measure of cell current. It is the constant-current charge or discharge rate that the cell can sustain for one hour.
  - A 20 Ah cell should be able to deliver 20 A (“1C”) for 1 h or 2 A (“C/10”) for about 10 h (but, the relationship is not strictly linear).
  - If the cell is discharged at a 10C rate, it will be completely discharged in about six minutes.

- A cell stores energy in electrochemical form, which it can later release to do work.
  - The total energy storage capacity of a cell is roughly its nominal voltage multiplied by its nominal capacity (Wh or kWh).
- The energy release rate is the cell's instantaneous power (W or kW).
- When cells are connected in series, the battery voltage is the sum of the individual cell voltages, but the capacity is the same for the chain since the same current passes through all of the cells.
  - A battery constructed from five 3 V, 20 Ah cells in series will have a voltage of 15 V, a capacity of 20 Ah, and energy capacity of 300 Wh.
- When cells are connected in parallel, the battery voltage is equal to the cells' voltage, but the capacity is the sum of the cells' capacities, since the battery current is the sum of all the cell currents.
  - The battery will have a voltage of 3 V, a capacity of 100 Ah, and energy capacity of 300 Wh.
- Specific energy and energy density are measures of the maximum amount of stored energy per unit weight or volume (respectively).

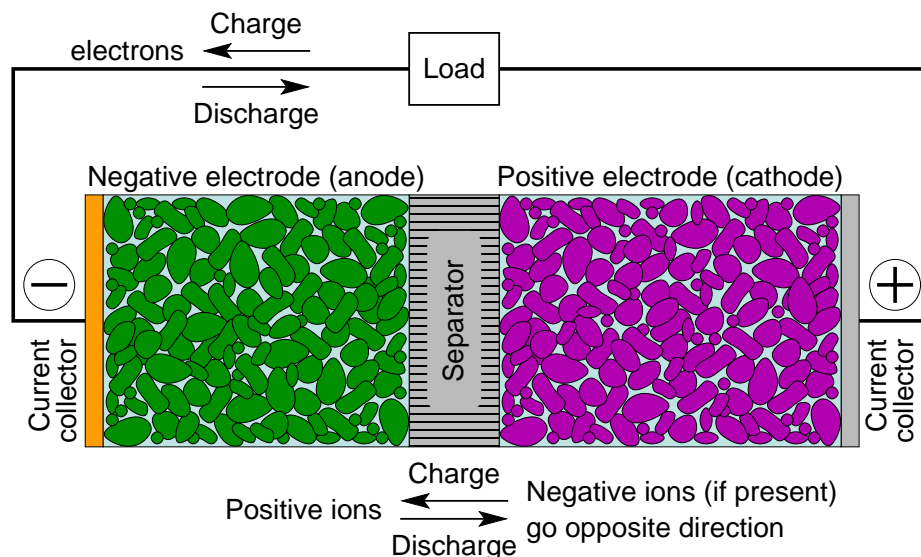




- For a given weight, a higher specific energy cell chemistry will store more energy, and for a given storage capacity, a higher specific energy cell will be lighter.
- For a given volume, a higher energy density cell chemistry will store more energy, and for a given storage capacity, a higher energy density cell will be smaller.
- In general, higher energy densities and specific energies are obtained by using more reactive chemicals.
- The downside is that more reactive chemicals tend to be unstable and may require special safety precautions.
- The quality of the active materials used in cell construction matters. Impurities limit cell performance that can be achieved.
- Cells from different manufacturers with similar cell chemistries and similar construction may yield different performance.

## 1.2: How electrochemical cells work

- Each cell comprises at least three, and sometimes four components:



- The negative electrode: Often a metal or an alloy or hydrogen.
  - During discharge, gives up electrons to external circuit, is oxidized (OIL: “Oxidation is Loss (of electrons)”).
  - During charge, accepts electrons from external circuit, is reduced (RIG: “Reduction is Gain (of electrons)”).
  - During discharge, it is the anode.<sup>2</sup>
- The positive electrode: Often a metallic oxide, sulfide, or oxygen.
  - During discharge, accepts electrons from circuit, is reduced.
  - During charge, gives up electrons to external circuit, is oxidized.
  - During discharge, it is the cathode.<sup>3</sup>
- The electrolyte (the ionic conductor) provides the medium for internal ion charge transfer between the electrodes.
  - The electrolyte is typically a solvent containing dissolved chemicals—the salt—providing ionic conductivity.

<sup>2</sup> Technically, during charge it is the cathode, but most people still call it the anode.

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- ◆ It must be an electronic insulator to avoid self discharge.
- ◆ Cations are ions with net positive charge: during discharge they move through the electrolyte toward the positive electrode.
- ◆ Anions are ions with net negative charge: during discharge they move through the electrolyte toward the negative electrode.
- ◆ Cells using aqueous (containing water) electrolytes are limited to less than 2 V because the oxygen and hydrogen in water dissociate in the presence of higher voltages.
- ◆ Lithium batteries use non-aqueous electrolytes as their overall voltages are above 2 V.
- The separator electrically isolates the positive and negative electrodes to avoid self discharge of the cell.
- The table shows components for common electrochemical cells:

Electrochemistry	Negative electrode	Positive electrode	Electrolyte	Nominal voltage
Lead acid	Pb	PbO <sub>2</sub>	H <sub>2</sub> SO <sub>4</sub>	2.1 V
Dry cell	Zn	MnO <sub>2</sub>	ZnCl <sub>2</sub>	1.6 V
Alkaline	Zn	MnO <sub>2</sub>	KOH	1.5 V
Nickel cadmium	Cd	NiOOH	KOH	1.35 V
Nickel zinc	Zn	NiOOH	KOH	1.73 V
Zinc air	Zn	O <sub>2</sub>	KOH	1.65 V

### The discharge process

- Electrochemical potential energy at the negative electrode favors a chemical process that would release electrons into the external circuit and positively charged ions into the electrolyte.

- Also, electrochemical potential at the positive electrode favors a chemical process that would accept both electrons from the external circuit and positively charged ions from the electrolyte.
- The resulting electrical pressure or potential difference between the terminals is called the cell voltage or electromotive force (EMF).
- Cell performs work when an external circuit is completed, converting stored chemical potential energy into electrical energy on demand.

### The charge process

- In primary cells, this electrochemical reaction is not reversible.
  - During discharge, the chemical compounds are permanently changed and electrical energy is released until the original compounds are completely exhausted.
  - Primary cells can be used only once.
- In secondary cells, this electrochemical reaction is reversible.
  - The original chemical compounds can be reconstituted by the application of an electrical potential between the electrodes, injecting energy into the cell.
  - Such cells can be discharged and recharged many times.
- During charge, cations move from positive to negative electrode through electrolyte; electrons move from positive to negative electrode through external circuit.
- The energy “pumped” into the cell transforms the active chemicals back to their original state.

## 1.3: Choice of active chemicals

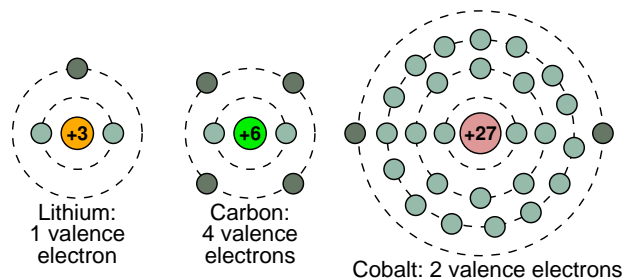
- The voltage and current generated by a cell is directly related to the types of materials used in the electrodes and electrolyte.
- The propensity of a metal or compound to gain or lose electrons in relation to another material is known as its electrode potential.
- Compounds with negative electrode potential are used for negative electrodes, and those with positive electrode potential for positive electrodes.
- The larger the difference between the electrode potentials of the two electrodes, the greater the EMF of the cell and the greater the amount of energy that can be produced by the cell.

Groups		Periodic Table of the Elements																																																
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18																															
Periods	1	<div>1</div> <div>H</div> <div>Hydrogen</div> <div>1.00794</div>	<div>Atomic #</div> <div>Symbol</div> <div>Name</div> <div>Atomic weight</div>	<div>C</div> <div>Solid</div>					<div>Metalloids</div>		<div>Nonmetals</div>									<div>2</div> <div>He</div> <div>Helium</div> <div>4.002602</div>																														
	2	<div>3</div> <div>Li</div> <div>Lithium</div> <div>6.941</div>	<div>4</div> <div>Be</div> <div>Beryllium</div> <div>9.012182</div>	<div>Hg</div> <div>Liquid</div>						<div>Other nonmetals</div>	<div>Halogens</div>	<div>Noble gases</div>								<div>5</div> <div>B</div> <div>Boron</div> <div>10.811</div>	<div>6</div> <div>C</div> <div>Carbon</div> <div>12.0107</div>	<div>7</div> <div>N</div> <div>Nitrogen</div> <div>14.0067</div>	<div>8</div> <div>O</div> <div>Oxygen</div> <div>15.9994</div>	<div>9</div> <div>F</div> <div>Fluorine</div> <div>18.9984032</div>	<div>10</div> <div>Ne</div> <div>Neon</div> <div>20.1797</div>																									
	3	<div>11</div> <div>Na</div> <div>Sodium</div> <div>22.9897693</div>	<div>12</div> <div>Mg</div> <div>Magnesium</div> <div>24.3050</div>	<div>H</div> <div>Gas</div>											<div>13</div> <div>Al</div> <div>Aluminum</div> <div>26.9815386</div>	<div>14</div> <div>Si</div> <div>Silicon</div> <div>28.0855</div>	<div>15</div> <div>P</div> <div>Phosphorus</div> <div>30.973762</div>	<div>16</div> <div>S</div> <div>Sulfur</div> <div>32.065</div>	<div>17</div> <div>Cl</div> <div>Chlorine</div> <div>35.453</div>	<div>18</div> <div>Ar</div> <div>Argon</div> <div>39.948</div>																														
	4	<div>19</div> <div>K</div> <div>Potassium</div> <div>39.0983</div>	<div>20</div> <div>Ca</div> <div>Calcium</div> <div>40.078</div>	<div>Rf</div> <div>Unknown</div>	<div>State at room temperature</div>	<div>21</div> <div>Sc</div> <div>Scandium</div> <div>44.955912</div>	<div>22</div> <div>Ti</div> <div>Titanium</div> <div>47.867</div>	<div>23</div> <div>V</div> <div>Vanadium</div> <div>50.9415</div>	<div>24</div> <div>Cr</div> <div>Chromium</div> <div>51.9961</div>	<div>25</div> <div>Mn</div> <div>Manganese</div> <div>54.938045</div>	<div>26</div> <div>Fe</div> <div>Iron</div> <div>55.845</div>	<div>27</div> <div>Co</div> <div>Cobalt</div> <div>58.933195</div>	<div>28</div> <div>Ni</div> <div>Nickel</div> <div>58.6934</div>	<div>29</div> <div>Cu</div> <div>Copper</div> <div>63.546</div>	<div>30</div> <div>Zn</div> <div>Zinc</div> <div>65.38</div>	<div>31</div> <div>Ga</div> <div>Gallium</div> <div>69.723</div>	<div>32</div> <div>Ge</div> <div>Germanium</div> <div>72.64</div>	<div>33</div> <div>As</div> <div>Arsenic</div> <div>74.92160</div>	<div>34</div> <div>Se</div> <div>Selenium</div> <div>78.96</div>	<div>35</div> <div>Br</div> <div>Bromine</div> <div>79.904</div>	<div>36</div> <div>Kr</div> <div>Krypton</div> <div>83.798</div>																													
	5	<div>37</div> <div>Rb</div> <div>Rubidium</div> <div>85.4678</div>	<div>38</div> <div>Sr</div> <div>Strontium</div> <div>87.62</div>			<div>41</div> <div>Nb</div> <div>Niobium</div> <div>92.90638</div>	<div>42</div> <div>Mo</div> <div>Molybdenum</div> <div>95.96</div>	<div>43</div> <div>Tc</div> <div>Technetium</div> <div>(98)</div>	<div>44</div> <div>Ru</div> <div>Ruthenium</div> <div>101.07</div>	<div>45</div> <div>Rh</div> <div>Rhodium</div> <div>102.90550</div>	<div>46</div> <div>Pd</div> <div>Palladium</div> <div>106.42</div>	<div>47</div> <div>Ag</div> <div>Silver</div> <div>107.8682</div>	<div>48</div> <div>Cd</div> <div>Cadmium</div> <div>112.411</div>	<div>49</div> <div>In</div> <div>Indium</div> <div>114.818</div>	<div>50</div> <div>Sn</div> <div>Tin</div> <div>118.710</div>	<div>51</div> <div>Sb</div> <div>Antimony</div> <div>121.760</div>	<div>52</div> <div>Te</div> <div>Tellurium</div> <div>127.60</div>	<div>53</div> <div>I</div> <div>Iodine</div> <div>126.90447</div>	<div>54</div> <div>Xe</div> <div>Xenon</div> <div>131.293</div>																															
	6	<div>55</div> <div>Cs</div> <div>Cesium</div> <div>132.90545</div>	<div>56</div> <div>Ba</div> <div>Barium</div> <div>137.327</div>	<div>57 – 71</div>		<div>72</div> <div>Hf</div> <div>Hafnium</div> <div>178.49</div>	<div>73</div> <div>Ta</div> <div>Tantalum</div> <div>180.94788</div>	<div>74</div> <div>W</div> <div>Tungsten</div> <div>183.84</div>	<div>75</div> <div>Re</div> <div>Rhenium</div> <div>186.207</div>	<div>76</div> <div>Os</div> <div>Osmium</div> <div>190.23</div>	<div>77</div> <div>Ir</div> <div>Iridium</div> <div>192.217</div>	<div>78</div> <div>Pt</div> <div>Platinum</div> <div>195.084</div>	<div>79</div> <div>Au</div> <div>Gold</div> <div>196.966569</div>	<div>80</div> <div>Hg</div> <div>Mercury</div> <div>200.59</div>	<div>81</div> <div>Tl</div> <div>Thallium</div> <div>204.3833</div>	<div>82</div> <div>Pb</div> <div>Lead</div> <div>207.2</div>	<div>83</div> <div>Bi</div> <div>Bismuth</div> <div>208.98040</div>	<div>84</div> <div>Po</div> <div>Polonium</div> <div>(209)</div>	<div>85</div> <div>At</div> <div>Astatine</div> <div>(210)</div>	<div>86</div> <div>Rn</div> <div>Radon</div> <div>(222)</div>																														
	7	<div>87</div> <div>Fr</div> <div>Francium</div> <div>(223)</div>	<div>88</div> <div>Ra</div> <div>Radium</div> <div>(226)</div>	<div>89 – 103</div>		<div>104</div> <div>Rf</div> <div>Rutherfordium</div> <div>(261)</div>	<div>105</div> <div>Db</div> <div>Dubnium</div> <div>(268)</div>	<div>106</div> <div>Sg</div> <div>Seaborgium</div> <div>(271)</div>	<div>107</div> <div>Bh</div> <div>Bohrium</div> <div>(272)</div>	<div>108</div> <div>Hs</div> <div>Hassium</div> <div>(277)</div>	<div>109</div> <div>Mt</div> <div>Meitnerium</div> <div>(276)</div>	<div>110</div> <div>Ds</div> <div>Darmstadtium</div> <div>(281)</div>	<div>111</div> <div>Rg</div> <div>Roentgenium</div> <div>(280)</div>	<div>112</div> <div>Cn</div> <div>Copernicium</div> <div>(285)</div>	<div>113</div> <div>Uut</div> <div>Ununtrium</div> <div>(284)</div>	<div>114</div> <div>Fl</div> <div>Flerovium</div> <div>(289)</div>	<div>115</div> <div>Uup</div> <div>Ununpentium</div> <div>(288)</div>	<div>116</div> <div>Lv</div> <div>Livermorium</div> <div>(293)</div>	<div>117</div> <div>Uus</div> <div>Ununseptium</div> <div>(294)</div>	<div>118</div> <div>Uuo</div> <div>Ununoctium</div> <div>(294)</div>																														
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Reducing elements										Oxidizing elements																																								

- The relative reducing and oxidizing capabilities of the elements are indicated by the arrow below the periodic table above.



- The number contained in each box in the table is the atomic number of the element (the number of protons in the nucleus of each atom).
- The strong reducing elements are grouped to the left, while the strong oxidizing elements are grouped to the right.
- Elements within each individual group (generally) have the same number of valence electrons in their outer valence shell (but, transition metals are a little strange).
- Because the number of valence electrons determines how the atom reacts chemically with other atoms, elements within a particular group tend to have similar chemical properties.
- When the outer electron shell is full, as in the noble gases, there are no “free” electrons available to take part in chemical reactions.
  - Hence the noble gases are chemically non-reactive or inert.
- The most reactive elements are found at the left and right of the table.
  - Alkaline metals, group 1, have only one valence electron, and
  - Halogens, group 17, are short only one valence electron.
- All the elements in any one period have the same number of electron shells or orbits which corresponds to the number of possible energy levels of the electrons in the atom. The period number corresponds to the number of electron shells.
- Atoms with one or two valence electrons more than a closed shell are highly reactive because the extra electrons are easily removed to form positive ions (oxidation).



- Reducing agents have surplus of valence-shell electrons, which they donate in a redox reaction, becoming oxidized.
- Atoms with one or two valence electrons fewer than a closed shell are also highly reactive because of a tendency either to gain the missing electrons and form negative ions (reduction), or to share electrons and form covalent bonds.
  - Oxidizing agents have a deficit of valence-shell electrons and accept electrons in a redox reaction, becoming reduced.
- The lowest energy for a species is when its valence shell is filled: these atoms tend to be chemically inert.
- The atom's energy level is changed by gaining or losing electrons, and it is this energy that is released as electrical energy during discharge, or absorbed during charge (of a secondary battery).

### Electrochemical series

- The electrochemical series is a list or table of metallic elements or ions arranged according to their electrode potentials.

Strengths of Oxidizing and Reducing Agents	
Cathode (Reduction) Half-Reaction	Standard Potential $E^0$ (volts)
$\text{Li}^+_{(\text{aq})} + \text{e}^- \Rightarrow \text{Li}_{(\text{s})}$	-3.04
$\text{K}^+_{(\text{aq})} + \text{e}^- \Rightarrow \text{K}_{(\text{s})}$	-2.92
$\text{Ca}^{2+}_{(\text{aq})} + 2\text{e}^- \Rightarrow \text{Ca}_{(\text{s})}$	-2.76
$\text{Na}^+_{(\text{aq})} + \text{e}^- \Rightarrow \text{Na}_{(\text{s})}$	-2.71
$\text{Zn}^{2+}_{(\text{aq})} + 2\text{e}^- \Rightarrow \text{Zn}_{(\text{s})}$	-0.76
$2\text{H}^+ + 2\text{e}^- \Rightarrow \text{H}_2$	0.00
$\text{Cu}^{2+}_{(\text{aq})} + 2\text{e}^- \Rightarrow \text{Cu}_{(\text{s})}$	0.34
$\text{O}^{3+}_{(\text{g})} + 2\text{H}^+_{(\text{aq})} + 2\text{e}^- \Rightarrow \text{O}_{2(\text{g})} + \text{H}_2\text{O}_{(\text{l})}$	2.07
$\text{F}_{2(\text{g})} + 2\text{e}^- \Rightarrow 2\text{F}^-_{(\text{aq})}$	2.87

- A sample from the table of standard potentials shows the extremes.
- The order shows the tendency of one metal to reduce the ions of any other metal below it in the series.
- The values for the table entries are reduction potentials, so lithium at the top of the list has the most negative number, indicating that it is the strongest reducing agent. The strongest oxidizing agent is fluorine with the largest positive number for standard electrode potential.
- If we were to create a cell combining the top and bottom reactions, the cell voltage would be 5.91 V (but so far we cannot, since there is no known electrolyte that will withstand that voltage without decomposing).

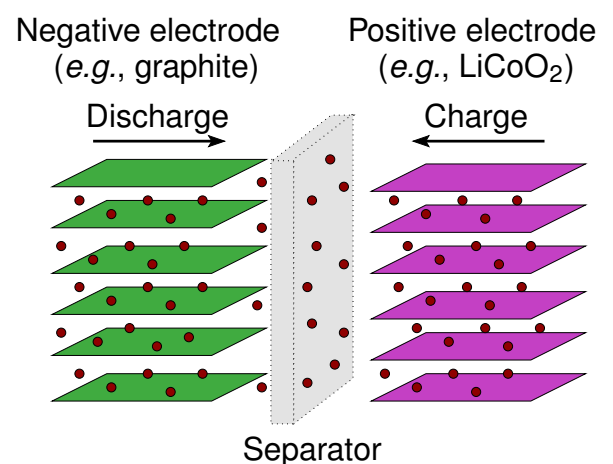
### **Alternative chemical reactions**

- More recently new cell chemistries have been developed using alternative chemical reactions to the traditional redox scheme.
- Metal hydride cell chemistry depends on the ability of some metals to absorb large quantities of hydrogen (like a sponge).
- These metallic alloys, termed hydrides, can provide a storage sink for hydrogen that can reversibly react in battery cell chemistry.
- Such metals or alloys are used for the negative electrodes. The positive electrode is nickel hydroxide as in NiCd batteries.
- The electrolyte, which is also a hydrogen-absorbent aqueous solution such as potassium hydroxide, takes no part in the reaction but serves to transport the hydrogen between the electrodes.
- As we will see, lithium-ion cells work in a similar way.

## **1.4: Lithium-ion cell preview**

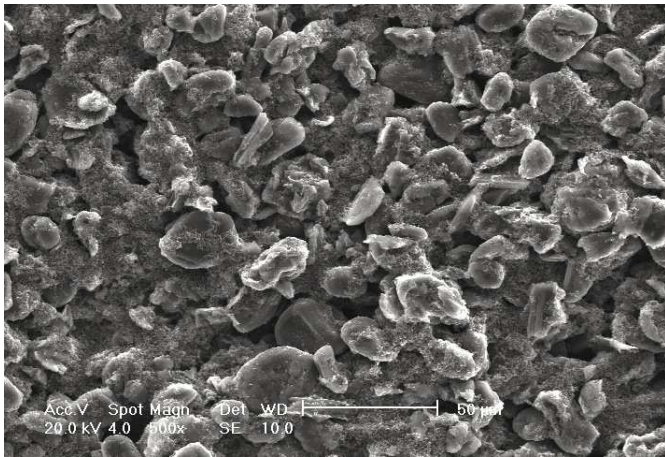
- This course focuses on lithium-ion cells, which have some advantages (although much that we cover is general, and could be applied to other chemistries):
  - They have higher energy density than most secondary cells.
  - They also operate at higher voltages than other rechargeable cells, typically about 3.7 V for lithium-ion vs. 1.2 V for NiMH or NiCd.
    - ◆ This means a single cell can often be used rather than multiple NiMH or NiCd cells.
  - Lithium-ion batteries also have a lower self-discharge rate than other types of rechargeable cells.
    - ◆ NiMH and NiCd cells can lose anywhere from 1–5 % of their charge per day, even if they are not installed in a device.
    - ◆ Lithium-ion cells will retain most of their charge even after months of storage.
- Some disadvantages of lithium-ion cells compared with others:
  - Lithium-ion batteries are more expensive than similar capacity NiMH or NiCd batteries.
    - ◆ Li-ion batteries usually include special circuitry to protect the battery from damage due to overcharging or undercharging.
    - ◆ They are more complex to manufacture, and are manufactured in much smaller numbers than NiMH or NiCd batteries.
    - ◆ Li-ion batteries are becoming less expensive and over time we should see their price decrease significantly.

- Lithium ion cells are not available in standard cells sizes (AA, C and D) like NiMH and NiCd cells.<sup>4</sup>
- Lithium-ion batteries also require sophisticated chargers that can carefully monitor the charge process.
  - ◆ And because of their different shapes and sizes, each type of Li-ion battery requires a charger designed to accommodate it.
  - ◆ This means lithium ion battery chargers are more expensive and more difficult to find than NiMH and NiCd battery chargers.
- Lithium-ion cells work differently from the electrochemical cells we looked at earlier in this chapter: Rather than a redox reaction, they depend on an “intercalation” mechanism.
- This involves the insertion of lithium ions into the crystalline lattice of the host electrode without changing its crystal structure.
- These electrodes have two key properties:
  - Open crystal structures, which allow the the insertion or extraction of lithium ions in the vacant spaces,
  - The ability to accept compensating electrons at the same time.
- Lithium is stored in the electrodes much like water is stored in a sponge.
- Li is stored in the electrodes, and  $\text{Li}^+$  moves through the electrolyte.
- $\text{Li}^+$  enters an electrode, becoming Li when an electron is available.

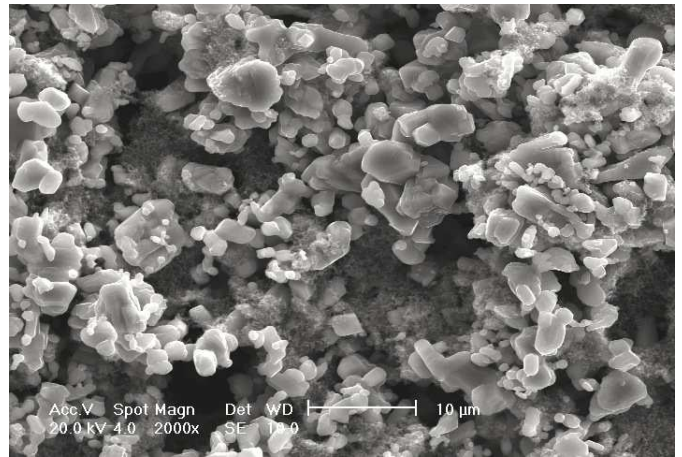


<sup>4</sup> Note that the Energizer “e<sup>2</sup> Lithium” is not a lithium-ion cell. It is a standard non-rechargeable 1.5 V galvanic cell with lithium/iron-disulfide ( $\text{Li}/\text{FeS}_2$ ) chemistry.

- Conversely, Li exits an electrode and becomes  $\text{Li}^+$  when it can give up an electron.
  - Within the electrode, the lithium atom's electron is loosely shared with neighboring atoms.
  - The lithium is not tightly bonded in one place and is actually quite free to move around.
  - Lithium enters the surface of the electrode particles, but diffuses inward to equalize the concentration of lithium in the electrode.
- During discharge, lithium ions are dissociated from the negative electrode and migrate across the electrolyte and are inserted into the crystal structure of the positive electrode.
- Simultaneously, compensating electrons traverse the external circuit and are accepted by the positive electrode to balance the reaction.
- The process is completely reversible. Thus the lithium ions pass back and forth between the electrodes during charging and discharging.
  - The intercalation mechanism is much gentler than an electrochemical reaction, so lithium-ion cells have much longer lives than other secondary cells.
- It is critical to understand that the electrodes are not homogeneous blocks, but rather millions of small particles.
- This increases the surface area where reactions may occur, decreasing cell resistance, and enhancing power delivery capability.

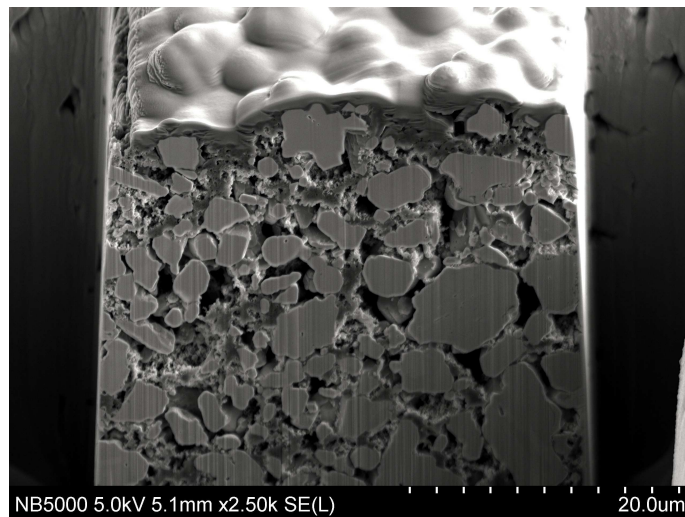


Mesophase carbonaceous spheres (graphite)



Lithium manganese oxide

- A cross-sectional slice of electrode material looks like:



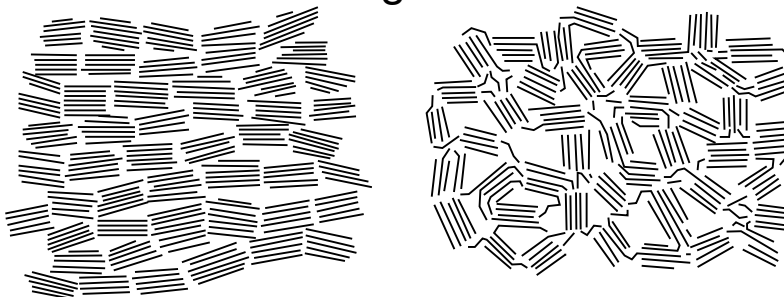
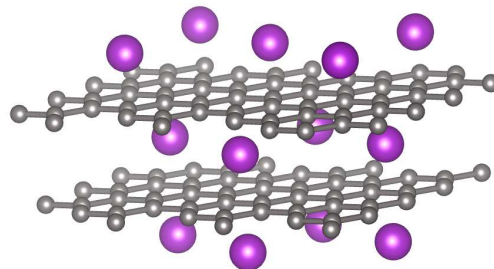
- Mixed in with the primary electrode materials are binders (to glue things together) and conductive additives (to enhance electron conduction, which is otherwise poor in positive electrode materials).
  - These are not “active” portions of the cell, so are not often mentioned, but are always present.



## 1.5: Lithium-ion cell makeup

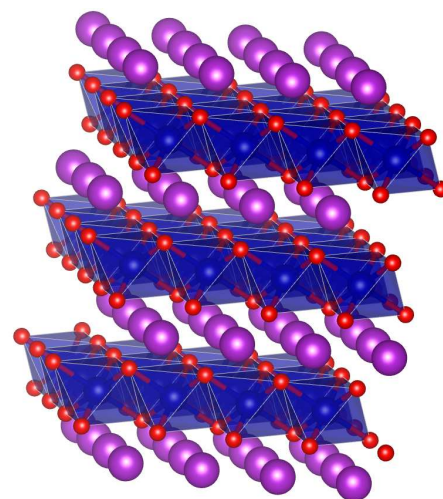
### Negative electrodes

- Presently, all commercial Li-ion cells use some form of graphite ( $C_6$ ) for the negative electrode material.
- Graphite has graphene layers of  $C_6$  structures that are tightly bonded.
- These layers are loosely stacked.
- Lithium can intercalate between them.
- Negative electrodes use natural or synthetic graphite (which have somewhat different layering properties), or natural “hard” or disordered carbons, which have many small pockets of graphene layers, arranged in random configurations.



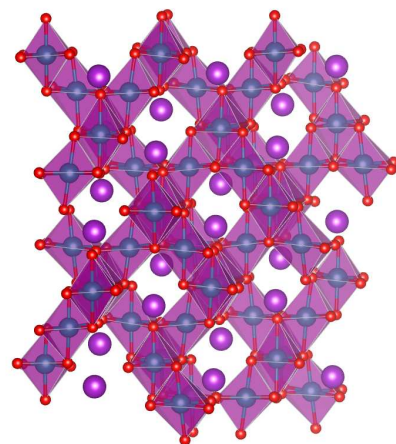
### Positive electrodes

- There is much more variability in the choice for positive electrodes.
- In 1980, John B. Goodenough discovered that  $Li_xCoO_2$  (LCO) was a viable material for lithium intercalation.
- LCO has layers, somewhat like graphite, so it is often called a “layered cathode.”

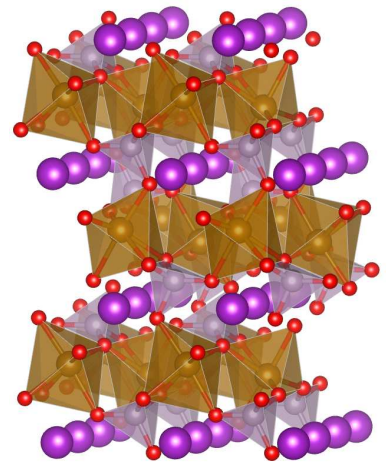




- The  $\text{LiO}_6$  octahedra are shown as lighter, the  $\text{CoO}_6$  as darker in the figure. Lithium intercalates between the darker layers.
- This LCO material is commonly used in portable electronics cells, but suffers some problems when trying to scale up:
  - Cobalt is rare, toxic, and expensive;
  - Only about half the theoretic capacity is useable (“x” can use only about half of its range of 0 to 1), else the cell ages rapidly.
- Nickel can be substituted for cobalt, resulting in higher energy density (higher voltages at same capacity), but is not very thermally stable. Aluminum, chromium, and manganese can be substituted as well, resulting in somewhat different properties.
- NCM (a.k.a. NMC) is a blend of nickel, cobalt, and manganese, which retains the layered structure, and has properties from all three constituent metals. NCA is a blend of nickel, cobalt, and aluminum, which has also been commercialized (Saft).
- In 1983, Goodenough and Thackeray proposed  $\text{Li}_x\text{Mn}_2\text{O}_4$  (LMO) as an alternate intercalation material: Mn sits in the octahedral sites, Li in the tetrahedral.
- This material has a cubic “spinel” structure. It allows 3D diffusion (vs. 2D for layered and 1D for olivine).
- The value of “x” typically varies between 0 and 1, but can go as high as 2 (LMO is unstable in acidic conditions when “x” is greater than 1).

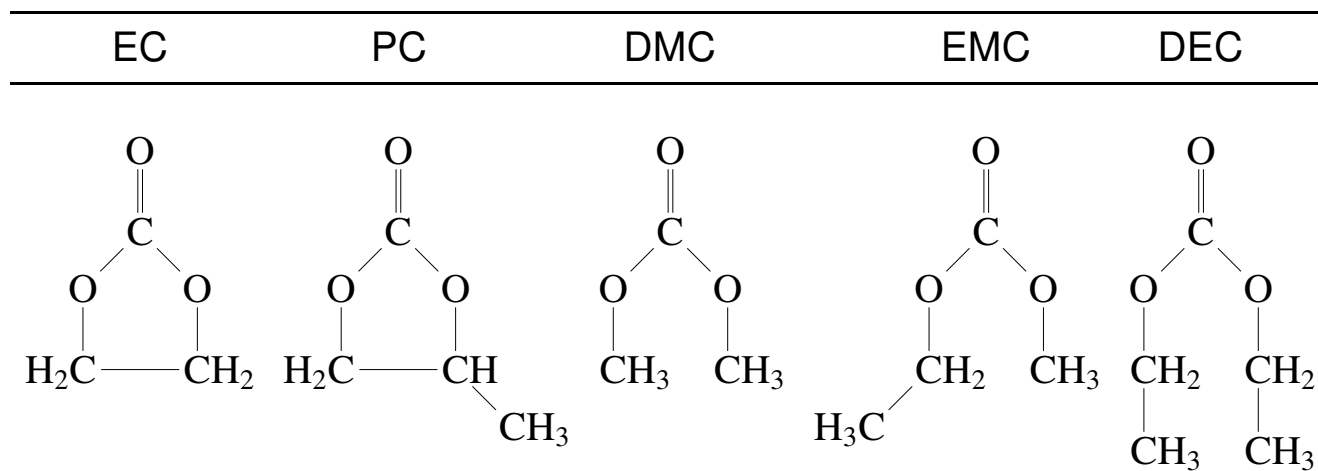


- The LMO positive-electrode material is cheaper and safer than LCO, but can have short lifetime due to the manganese dissolving into the electrolyte under some conditions.
- Additives can be added to help prevent this, but this “art” is presently the realm of black magic and trade secrets.
- In 1997, Goodenough proposed olivine style phosphates as a third major category of positive-electrode material.
- $\text{Li}_x\text{FePO}_4$  (LFP) is the most common in this family.
- This material is low cost, and low toxicity, but also low energy density.
- 1D structure tends to have high resistance.
- There are other candidate materials, mostly mixtures of the above.



### Electrolyte: Salt and solvent

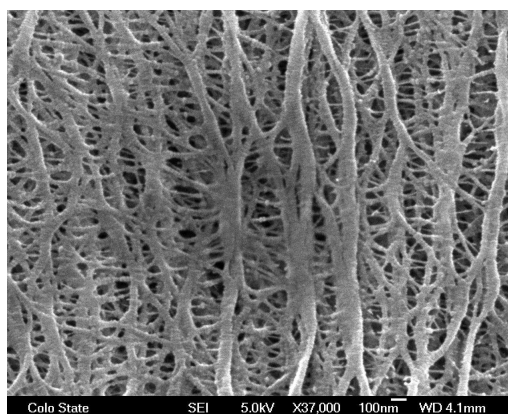
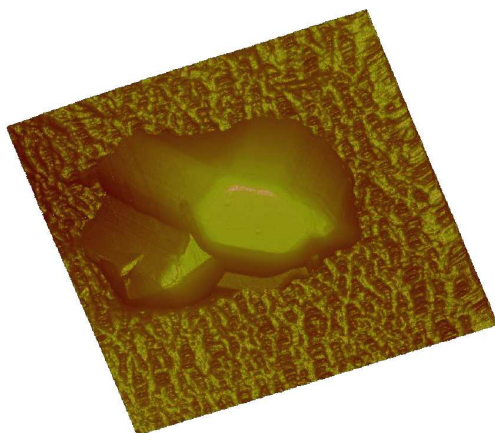
- The electrolyte is the media that conducts ions between electrodes.
- It comprises a salt, acid, or base dissolved in a solvent.
- Since lithium reacts violently with water, the electrolyte is composed of non-aqueous organic solvents plus a lithium salt and acts purely as a conducting medium, not taking part in the chemical reaction.
- The most commonly used salt is  $\text{LiPF}_6$ , but some other candidates include  $\text{LiBF}_4$ ,  $\text{LiClO}_4$ , and others.
- Solvents include ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), diethyl carbonate (DEC).



- The solvent does not participate in the chemical processes of the cell, so we typically ignore it in our models (different solvents have different properties re. aging, low-temperature performance, etc.)
- So, we often talk about the salt as the electrolyte, even though the electrolyte also includes the solvent.

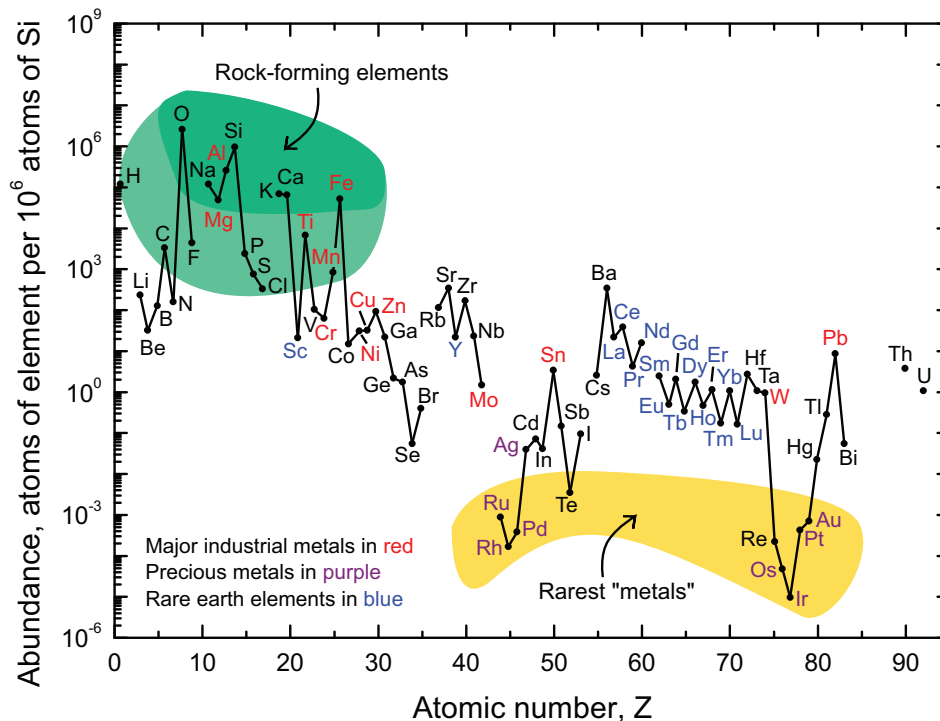
### Separator

- The separator is a permeable membrane with holes large enough to let lithium ions pass through unimpeded, but small enough that the negative- and positive-electrode particles do not touch (which would short-circuit the cell).
- It is also an electronic insulator.



## 1.6: Availability of lithium

- Are we about to replace the present oil shortage with a future lithium shortage? The chart below shows the relative abundance of chemical elements in the earth's crust.



- Lithium is between 20 and 100 times more abundant in terms of the number of atoms than lead and nickel. The reason it is less common is that lithium, being much more reactive than either metal, is not usually found in its free state, but combined with other elements.
- Cadmium and mercury—whose use is now deprecated because of their toxicity—are 1,000 times less common than lithium.
- The lithium content in a lithium-ion battery is actually quite small. Consider a lithium cobalt oxide (*i.e.*, positive electrode =  $\text{LiCoO}_2$ ) cell:
  - Lithium content in  $\text{LiCoO}_2$  is only 7 % by weight.

- $\text{LiCoO}_2$  itself makes up between 25 % and 33 % of the cell weight, so that the lithium content of the electrode in the cell amounts to about 2 % of the weight of the cell.
  - In addition the electrolyte, which accounts for about 10 % of the cell weight, also contains smaller amounts of dissolved lithium.
  - Overall, the total lithium content in a high energy cell is typically less than 3 % by weight.
- 
- Lithium-ion batteries used in EVs and HEVs weigh about  $7 \text{ kg kWh}^{-1}$ , and so that the lithium content will be about  $0.2 \text{ kg kWh}^{-1}$ .
  - A typical EV passenger vehicle may use batteries with capacities between 30 kWh and 50 kWh so that the lithium content will be about 6 kg to 10 kg per EV battery.
  - The capacity of HEV batteries is typically less than 10 % of the capacity of an EV battery and the weight of lithium used is correspondingly 10 % or less of EV battery weight.
  - Thus 1 million EVs would consume less than 10,000 tons of lithium (without recycling) and 1 million HEVs would consume no more than 1,000 tons .
  - Considering the available supply of lithium (over 200 billion tons, including from seawater) there is more than enough lithium available to satisfy the world demand for high energy automotive batteries.

## 1.7: Manufacturing (1): Making the electrodes

- An idea of how cells are made can aid understanding how they work.
- Cells are manufactured in different form factors.
  - Cylindrical cells are... err... cylindrical (round “jelly roll”).
  - Prismatic cells are... prismatic (flat “jelly roll”)
  - Pouch cells are also flat, but comprise stacked plates.



Cylindrical cells



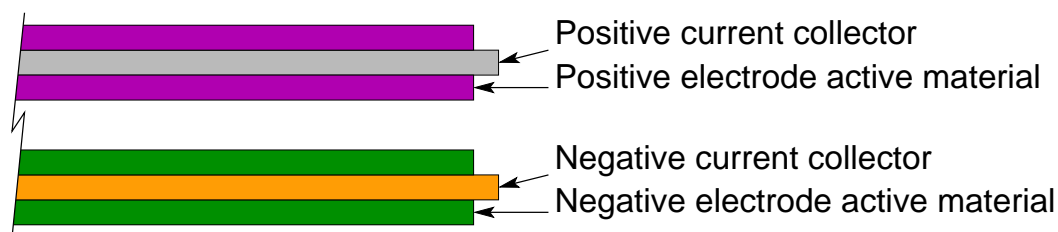
Prismatic cells



Pouch cells

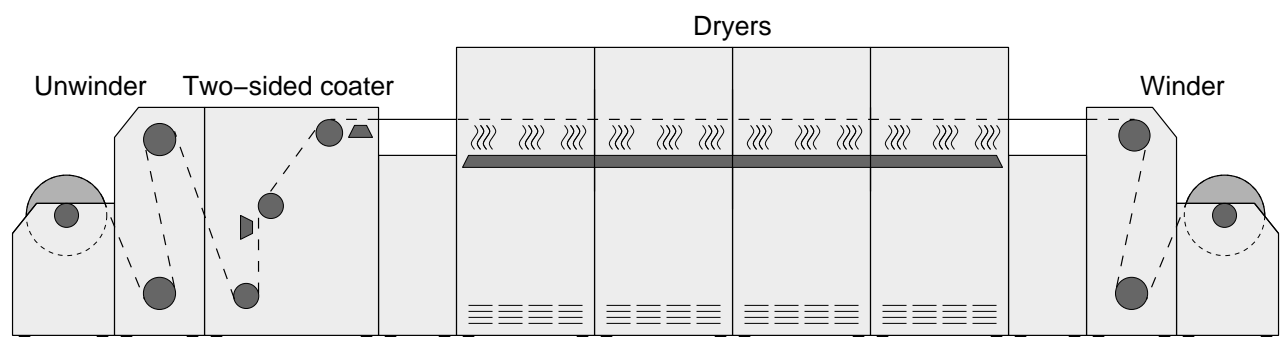
### Electrode coating

- Electrodes in lithium-ion cells are of similar form and are made by similar processes on similar or identical equipment.
- The active electrode materials are coated on both sides of metallic foils which act as the current collectors conducting the current in to and out of the cell.



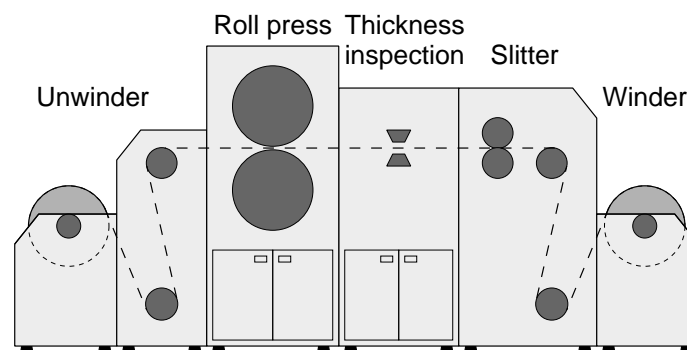
- The negative-electrode material is a form of carbon (usually a form of graphite), and the positive-electrode is a lithium metal oxide.

- Both materials are delivered to the factory in the form of black powder; to the untrained eye they are nearly indistinguishable.
  - Since contamination between the negative- and positive-electrode materials will ruin the cell, great care must be taken to prevent them from coming into contact with each other. So, negative and positive electrodes are usually processed in different rooms.
  - Particles must be small in order to achieve the large electrode material effective surface area needed for high-current cells.
  - Particle shape is also important. Smooth spherical shapes with rounded edges are desirable since sharp edges are susceptible to higher electrical stress and decomposition of the negative-electrode passivating SEI layer, which can lead to very large heat generation and possible thermal runaway when the cells are in use.
- The metal electrode foils are delivered on large reels, typically about 0.5 m wide, with copper for the negative-electrode current collector and aluminum for the positive-electrode current collector.
- These reels are mounted directly on the coating machines where the foil is unreeled as it is fed into the machine through precision rollers.





- The first stage is to mix the electrode materials with a conductive binder to form a slurry that is spread on the surface of the foil as it passes into the machine.
- A knife edge is located just above the foil and the thickness of the electrode coating is controlled by adjusting the gap between the knife edge and the foil.
  - The thickness is chosen so that the energy storage per unit area of negative and positive electrodes are matched.
- From the coater, the coated foil is fed directly into a long drying oven to bake the electrode material onto the foil.
- As the coated foil exits the oven it is re-reeled.
- The coated foils are subsequently fed into a calendaring (*i.e.*, pressing) and slitting machine.

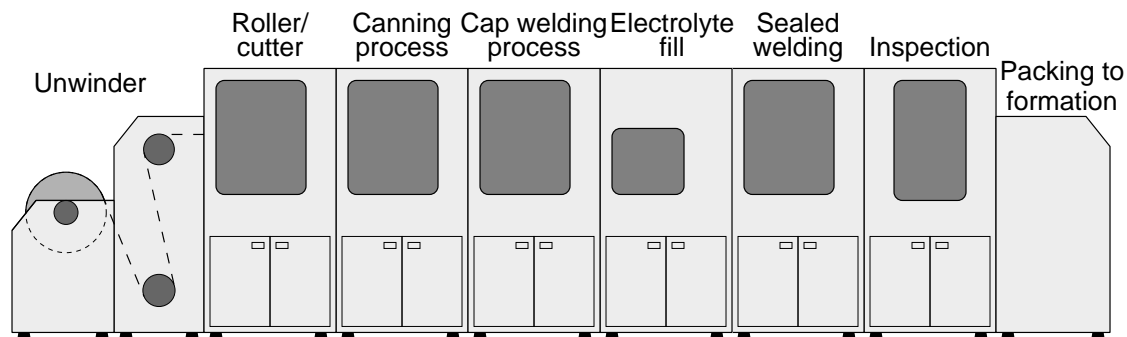


- Calendaring is done to compress the electrode active material, compacting the spaces between particles, pressing out porosity.
- Slitting cuts the foil into narrower strips of the desired width.
- Later they are cut to length. Any burrs on the edges of the foil strips could give rise to internal short circuits in the cells so the slitting machine must be very precisely manufactured and maintained.

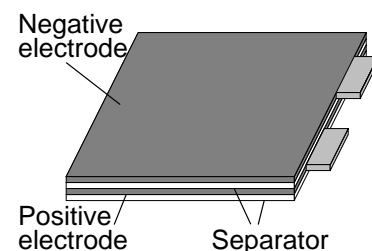


## 1.8: Manufacturing (2): Assembling the cell

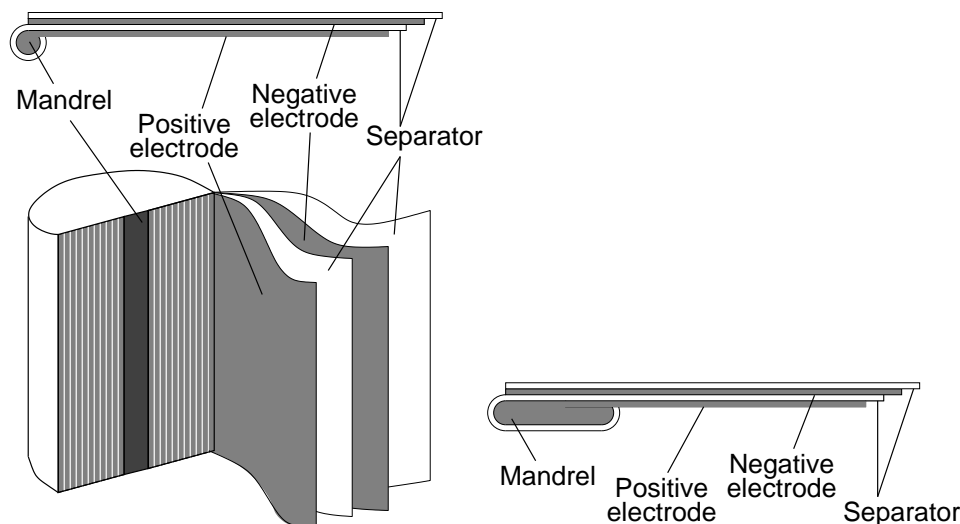
- Cell assembly comprises building the electrode sub assembly, packaging and welding, filling with electrolyte, sealing and welding, and inspection.



- The first stage in the assembly process is to build the electrode sub-assembly in which the separator is sandwiched between the negative and positive electrodes.
- Two basic electrode structures are used, depending on the type of cell casing to be used:
  - A stacked structure for use in pouch cells, and
  - A spiral wound structure for use in cylindrical/prismatic cells.
- Pouch/prismatic cells are often used for high capacity battery applications to optimize the use of space.
- Pouch designs use a stacked electrode structure in which the negative- and positive-electrode foils are cut into individual electrode plates which are stacked alternately and kept apart by the separator.



- The separator may be cut to the same size as the electrodes but more likely it is applied in a long strip wound in a zig-zag fashion between alternate electrodes in the stack.
- All negative-electrode tabs are welded in parallel and to the cell's negative terminal; all positive-electrode tabs are welded in parallel and to the cell's positive terminal.
- For cylindrical cells the negative- and positive-electrode foils are cut into two long strips which are wound on a cylindrical mandrel, together with the separator which keeps them apart, to form a jelly roll.



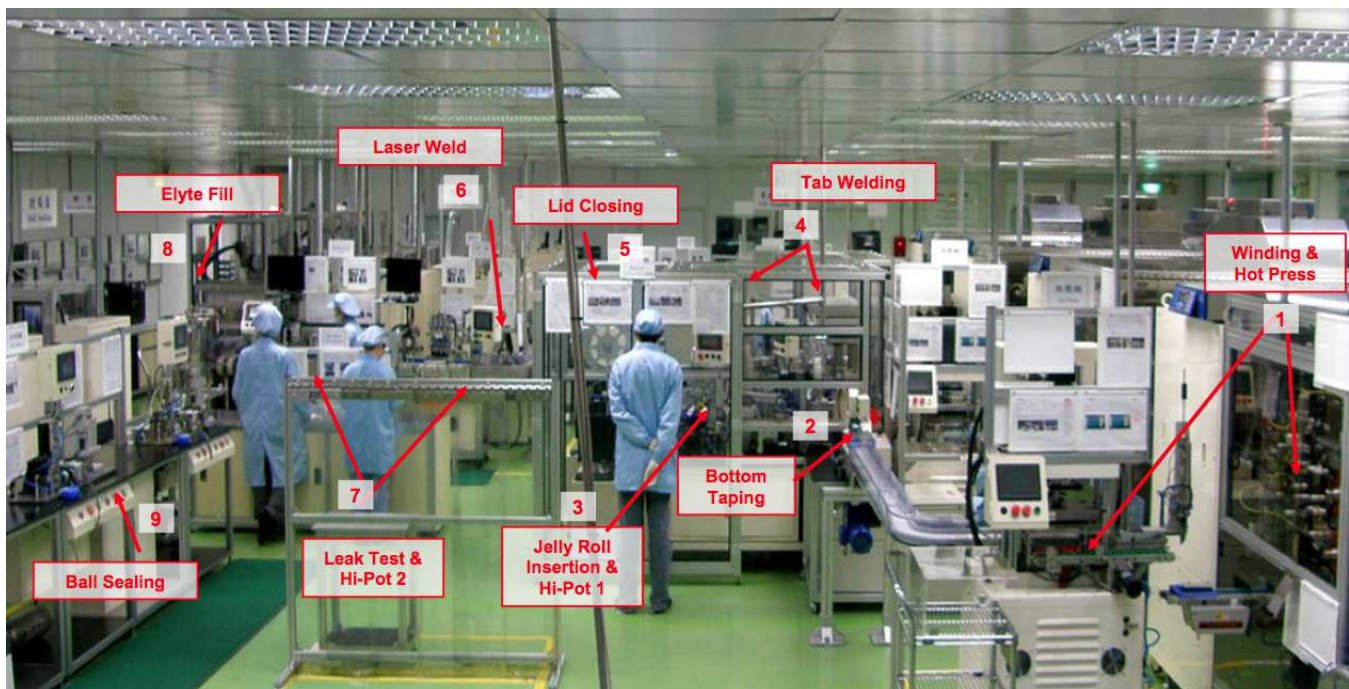
- Most prismatic cells are constructed similarly, by winding electrodes on a flat mandrel.
- A single tab connects each electrode to its corresponding terminal, although high power cells may have multiple tabs welded along the edges of the electrode strip to carry the higher currents.
- The next stage is to connect the electrode structure to the terminals and any safety devices, and to insert this sub-assembly into the can.

- The can is then sealed via laser welding or heating, depending on the case material, leaving an opening for injecting the electrolyte.
- The following stage is to fill the cell with the electrolyte and seal it.
- This must be done in a dry room as electrolyte reacts with water.
  - Moisture will cause the electrolyte to decompose with the emission of toxic gases.
  - Lithium hexafluoride ( $\text{LiPF}_6$ ) for instance, one of the most commonly used electrolyte materials, reacts with water forming toxic hydrofluoric acid (HF).
- Afterwards the cell is given an identification with a label or by printing a batch or serial number on the case.

### Formation

- Once the cell assembly is complete the cell must be put through at least one precisely controlled charge / discharge cycle to activate the working materials, transforming them into their usable form.
- Instead of the normal constant current/constant voltage charging curve, the charging process begins with a low voltage which builds up gradually. This is called the formation process.
- For most lithium chemistries this involves creating the SEI (solid electrolyte interphase) on the negative electrode. This is a passivating layer which is essential for moderating the charging process under normal use.
- During formation, data on the cell performance, such as capacity and impedance, are gathered and recorded for quality analysis.

- The spread of the performance measurements gives an indication of whether the process is under control.
- Although not the prime purpose of formation, the process allows a significant percentage of early life cell failures due to manufacturing defects, the so-called “infant mortalities,” to occur in the manufacturer’s plant rather than in the customers’ products.
- Tight tolerances and strict process controls are essential throughout the manufacturing process.
  - Contamination, physical damage and burrs on the electrodes are particularly dangerous since they can cause penetration of the separator giving rise to internal short circuits in the cell and there are no protection methods which can prevent or control this.
- Cleanliness is essential to prevent contamination and cells are normally manufactured in clean room conditions with controlled access to the assembly facilities often via air showers.



## **1.9: Failure modes**

- This course focuses on the operation of ideal cells, but with the ultimate direction leading toward controls: to be able to effect optimal battery controls, an understanding of the cell failure modes is essential.
- Failures occur because of: cell design faults, poorly controlled manufacturing processes, aging, uncontrolled operations, and abuse.
  - Battery controls can't do too much about the first two (too late!), but can do something about the others.

### Aging

- Cell performance gradually deteriorates with time due to unwanted chemical reactions and physical changes to the active chemicals.
- Process is generally irreversible, and eventually results in cell failure.
- The following are some examples of causes:
  - *Corrosion* (undesired chemical reaction with environment) consumes some of the active chemicals in the cell leading to increased impedance and capacity loss
  - *Chemical loss through evaporation*. Gaseous products resulting from over-charging are lost to atmosphere causing capacity loss.
  - *Crystal formation*: Electrode particles evolve as larger crystals are formed. This reduces the effective surface area of the electrodes and hence their current carrying and energy storage capacity.
  - *Dendritic growth*: Formation of treelike structures on electrodes, which can ultimately pierce separator and cause short circuit.

- *Passivation*: Growth of a resistive layer that builds up on the electrodes, impeding the chemical action of the cell.
  - *Shorted cells*: Cells that were marginally acceptable when new may have contained latent defects that become apparent only as the aging process takes its toll: poor cell construction, contamination, burrs on metal parts leading to a short circuit.
  - *Electrode or electrolyte cracking*: Some solid electrolyte cells such as lithium polymer can fail because of cracking of the electrolyte.
- These causes lead to undesirable effects:
- *Increased internal impedance*: The cell internal impedance tends to increase with age (e.g., as the larger crystals form, reducing the effective surface area of the electrodes).
  - *Reduced capacity*: This is another consequence of cell aging and crystal growth. It is sometimes recoverable through reconditioning the cell by subjecting the cell to one or more deep discharges.
  - *Increased self discharge*: The changing crystal structure of the active chemicals as noted above can cause the electrodes to swell increasing the pressure on the separator and, as a consequence, increasing the self-discharge rate of the cell.
- Aging processes are generally accelerated by elevated temperatures.

### Uncontrolled operating conditions and abuse

- Good batteries are not immune to failure, which can be provoked by the way they are used or abused. “Bad things” include:
- Unsuitable charging profile and/or overcharging,

- High ambient or storage temperatures; lack of cooling.
- Most of these conditions result in overheating of the cell, which is what ultimately kills it.
- Physical abuse is also a “bad thing”:
  - This may include dropping, crushing, penetrating, impact, immersion in fluids, freezing or contact with fire, any of which could occur to an automotive battery for instance.
- It is generally accepted that the battery may not survive all these trials, however the battery should not itself cause an increased hazard or safety problem in these circumstances.
- There are several possible failure modes associated with the complete breakdown of the cell, but it is rarely possible to predict which one will occur. It depends very much on the circumstances.
  - *Open circuit*: This is a failsafe mode for the cell but maybe not for the application. Once the current path is cut and the battery is isolated, the possibility of further damage to the battery is limited. This may not suit the user however. If one cell of a multi-cell battery goes open circuit then the whole battery will be out of commission.
  - *Short circuit*: If one cell of a battery chain fails because of a short circuit, the rest of the cells may be slightly overloaded but the battery will continue to provide power to its load. This may be important in emergency situations.
    - ◆ Short circuits may be external to the cell or internal within the cell. The battery management system (BMS) should be able to

protect the cell from external shorts but there's not much the BMS can do to protect the cell from an internal short circuit.

- ◆ Within the cell there are different degrees of failure.
  - ✦ Hard Short: Solid connection between electrodes causes extremely high current flow and complete discharge, resulting in permanent damage to the cell.
  - ✦ Soft Short: Small localized contact between electrodes. Possibly self correcting due to melting of the small regions in contact caused by the high current flow which in turn interrupts the current path as in a fuse.
- Explosion and/or fire: The rate at which a chemical action proceeds tends to double for every 10 °C increase in temperature. If the heat generated by these reactions cannot be removed as quickly as it is generated, this can lead to a further increase in temperature and set up a self-sustaining uncontrolled positive feedback known as thermal runaway. This can lead to fire/explosion, and must be avoided at all cost.

## **Where from here?**

- Until now, many of the ideas that have been introduced apply equally well to cells of any chemistry.
- From now on, we focus on lithium-ion cells in particular.
- We begin by looking at equivalent-circuit models of cells.
- We then explore physics-based modeling, from microscale, through continuum scale, to full reduced-order cell-scale models.