## Designing a cell's electrochemistry

- Battery cell electrochemistry is designed to optimize a number of factors
- We desire high specific energy and/or energy density (energy per mass and/or energy per volume)
- We desire high specific power and/or power density
- We also desire low cost, long life, low toxicity, high recyclability, etc.
- Energy and power depend on overall maximum cell voltage and current, and ultimately all of these factors depend directly on the specific materials used in the electrodes and electrolyte





## Electrode potential

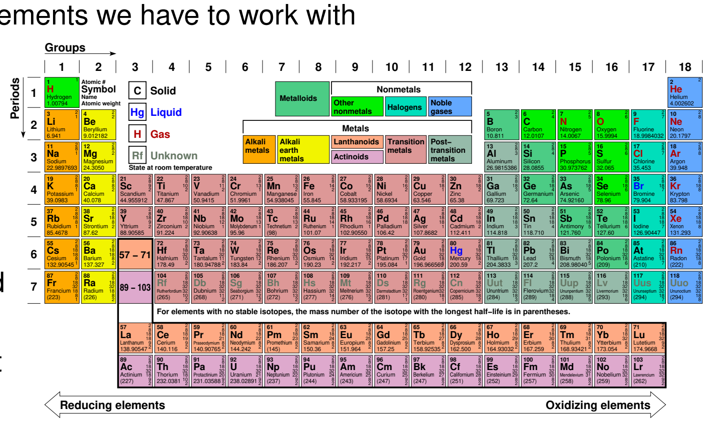
- The propensity of one material to gain or lose electrons in relation to another material is known as its electrode potential
- Compounds with negative electrode potential are used for negative electrodes, and those with positive electrode potential for positive electrodes
- The larger the difference between the electrode potentials of the two electrodes, the greater the voltage of the cell and the greater the amount of energy that can be produced by the cell
- Can this be tuned arbitrarily? No! All we have to work with are the elements available in nature





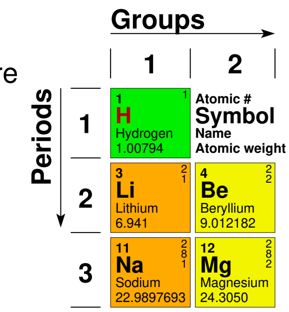
## This is what we have to work with

- Periodic table shows the elements we have to work with
- Relative reducing and oxidizing capabilities of the elements indicated by arrow below table
- Strong reducing elements grouped on left, strong oxidizing elements grouped on right
- Need elements from far left and far right sides of table



## Understanding each periodic-table entry

- The number at the top left of each box in the table is atomic number of the element (number of protons in atom's nucleus)
- The element's symbol is listed under its atomic number
  - Symbols are color coded in this periodic table to indicate whether element is solid, liquid, or gas at room temperature
- Full element name is listed under element's symbol
- Finally, mean atomic weight is listed under element name (where atomic weight of proton or neutron equals 1 g mol$^{-1}$)
- List of numbers in top right of box indicate number of electrons in each electron shell (each shell corresponds to possible set of electron energy levels)

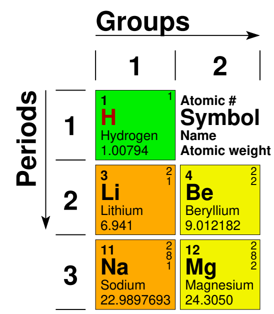







## Organization of the periodic table

- The background color of each box indicates whether element is a metal or nonmetal (if so, what kind), or a metalloid
- The rows of the table are called periods
  - All elements in any period have the same number of electron shells
  - Period number equals number of electron shells
- The columns of the table are called groups
  - All elements in any group (generally) have the same number of valence electrons in their outer valence shell (but, transition metals are a little strange)

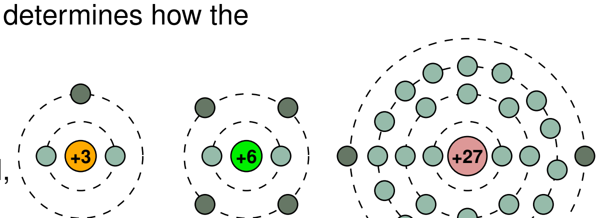







## Why number of valence electrons is important

- Elements within each individual group (column) have same number of valence electrons (except transition metals)
- Since number of valence electrons determines how the element reacts with others, those 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




Lithium: 1 valence electron

Carbon: 4 valence electrons

Cobalt: 2 valence electrons

## Valence

- The most reactive elements are at the left and right of table
  - Alkali metals, group 1, have only one valence electron
  - Halogens, group 17, are short only one valence electron
- Atoms having one or two valence electrons more than a closed shell are highly reactive because the extra electrons are easily removed to form positive ions
  - Reducing agents in left columns have surplus of valence-shell electrons, which they donate in a redox reaction, becoming oxidized
- Atoms having 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, or to share electrons and form covalent bonds
  - Oxidizing agents in right columns have a deficit of valence-shell electrons and accept electrons in a redox reaction, becoming reduced





## Electrochemical series

- 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)
- The difference in electrical potential energy before and after a reaction can be measured as a voltage difference
- The electrochemical series is a list or table of metallic elements or ions arranged according to their electrode half-reaction potentials
- (A short example table to the right)

Strengths of oxidizing and reducing agents

| Reduction half-reaction | Potential $E^0$ (V) |
|---|---|
| $Li^+_{(aq)} + e^- \Rightarrow Li_{(s)}$ | $-3.04$ |
| $Na^+_{(aq)} + e^- \Rightarrow Na_{(s)}$ | $-2.71$ |
| $Zn^{2+}_{(aq)} + 2e^- \Rightarrow Zn_{(s)}$ | $-0.76$ |
| $2H^+ + 2e^- \Rightarrow H_2$ | 0.00 |
| $Cu^{2+}_{(aq)} + 2e^- \Rightarrow Cu(s)$ | 0.34 |
| $F_{2(g)} + 2e^- \Rightarrow 2F^-_{(aq)}$ | 2.87 |





## Electrochemical series (cont)

- The values for the table entries are reduction potentials:
- Lithium at the top of the list has the most negative number, indicating that it is the strongest reducing agent
- Fluorine is the strongest oxidizing agent, having the largest positive value for standard 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)

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## Summary

- For high specific energy and power, we desire light elements (near the top of the periodic table)
- For high voltage, we want strong oxidizing and reducing agents paired together, having an excess and a deficiency of valence electrons (near left and right sides of the periodic table)
- Other considerations include: availability of an electrolyte to support the half-cell reactions, low cost, long life, low toxicity, high recyclability, etc.