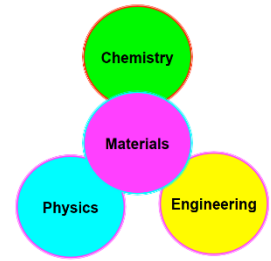


## 1. Materials Chemistry

Materials chemistry is the application of chemistry to the design, synthesis, characterization and understanding and utilization of materials with potentially useful physical properties. It is the understanding and control of functional condensed matter from a chemical perspective. If you are good at controlling the material, you are good at controlling the technology developed from or associated with it.



## 2. Nanomaterials

Nanomaterials are materials that are in the dimensions of nanometers ( $10^{-9}$  m). Typically, nanomaterials are 1 to 100 nm in overall dimensions. Depending on the degree of the dimension, the nanomaterial will fall under a specific category, as shown by the table below, along with their approximate size.

Dim.	Material Category	Size
0D	Quantum Dots	1 – 100 nm Diameter
1D	Nanowires and Nanotubes	1 – 100 nm Diameter
2D	Flakes / Arrays / Surfaces / Films	Several $\text{nm}^2$ to $\mu\text{m}^2$ Thickness 1 – 100 nm
3D	Gels	Several nm in all 3 dimensions

**Nanotechnology:** The creation and exploitation of materials with structural features in between those of atoms and bulk material.

Properties in nanoscale are different from that of in bulk, i.e. gold nanoparticles are powerful catalysts but gold in bulk form is unreactive.

Nanomaterial as a technology has existed from a long time. They have been used in swords, glass windows in cathedrals, etc. The key benefits of nanomaterials are that they are lightweight due to their density, as well as having more surface area. Having more surface area allows them to participate in reactions more easily.

*“If you are good at controlling the material, you are good at controlling the technology”*

**Richard Feynman:** 1959, credited with development of nanomaterials. *“There’s plenty of room at the bottom”. “What would happen if we could arrange the atoms one by one the way we want them?”*

**Q:** How many 10nm nanocubes are required to produce the same surface area as a one cubic meter cube? How much volume do they occupy?

**A:** The surface area of a cubic meter is  $6 \text{ m}^2$ . The surface of this single nanocube is  $600 \text{ nm}^2$ .

$$N_{\text{nc}} = \frac{6 \text{ m}^2}{600 \text{ nm}^2} = 10^{16}$$

The volume occupied by this number of nanocubes is:

$$V_{\text{nc}} = 10^{16} \times (10 \text{ nm})^3 = 0.01 \text{ cm}^3 = 10^{-8} \text{ m}^3$$

Thus, to have the same surface area as a  $1 \text{ m}^3$  cube, we only require  $10^{-8} \text{ m}^3$  with  $10^{16}$  nanocubes.

Smaller materials have a higher surface area to volume ratio. In bulk materials, most atoms or molecules are contained within the volume of the material. In nanomaterials, the proportion of surface atoms increases dramatically as diameter is increased. As the size of the nanomaterials increases, the melting temperature also increases, but approaches a certain temperature.

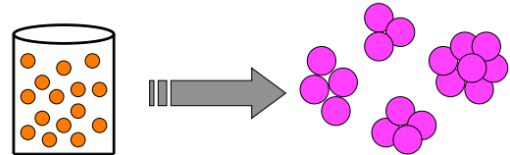
### 3. Nanomaterial Synthesis

There are multiple ways to synthesize nanomaterials depending on size:

Scale (approx.)	Synthetic methods
0.1 – 10 nm	Covalent synthesis
< 1 – 100 nm	Self-assembly techniques
100 nm – 1 $\mu\text{m}$	Processing, modifications

Within each synthetic method however, there are two approaches: Bottom-Up and Top-Down.

**Bottom-Up:** Assembling the nanomaterial from Nano-building blocks or atom/molecular building. *i.e. chemical vapor deposition, chemical synthesis, sol-gel, hydrothermal synthesis*

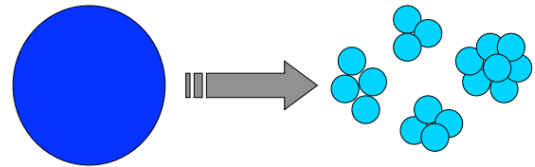


**Chemical Vapor Deposition:** Solid material is deposited from a vapor by a chemical reaction on or near a normally heated substrate surface, with the resulting solid material being in the form of a thin film, powder or a single crystal.

**Sol-gel:** The chemical transformation of a liquid (sol) into a gel state with subsequent post-treatment and transition into a solid oxide material. The 'sol' is the colloidal solution made of solid particles few hundred nm in diameter, suspended in liquid phase. The gel is a solid macromolecule immersed in a solvent. Final product has high purity and uniform nanostructure, and it is achievable at low temperatures

**Solvothermal:** Reactants are dissolved in water (hydrothermal) or another solvent inside a closed container, which is then heated above the boiling point of the solvent using an oven. Carbon nanotubes are formed this way.

**Top-Down:** The Top-Down approach synthesizing the nanomaterial by sculpting it from a bulk material, and other similar physical methods. *i.e. ball milling, sonication, lithography, exfoliation*



**Exfoliation:** Scotch tape method. Take the bulk material and attach an adhesive tape and tear off layers from the bulk material. *Graphene is made using this method from 3D Graphite.*

**Ball Milling:** Place the bulk material inside a container with small stainless-steel balls and oscillate the container until desired nanomaterial structures are created.

**Sonication:** Application of sound energy to agitate particles inside a container. The agitation by sound energy causes nanomaterials to separate from the bulk material.

**Lithography:** Stamping a template; Coat, Protect, Expose, Etch and repeat. A wafer is coated with a photoresist layer and is exposed to UV light or some other form of wavelength. The light causes a photochemical reaction in the photoresist layer which breaks down the polymer chains. The wafer is then rinsed in a developing solution to produce multiple patterned layers of different materials.

**Electron Beam Lithography:** The pattern is written in a polymer film with a beam of electrons. Diffraction effects are greatly reduced, and the final resolution is higher, but it is an expensive process.

**X-Ray Lithography:** uses X-rays instead of light waves to reduce diffraction effects, but the radiation damages most of the materials used for masks and lenses.

#### 4. Characterization Techniques

When looking at nanomaterials in an experimental/lab setting, there are multiple ways to characterize them based on dimensions, surface features, shapes, etc. There are several different ways of characterizing nanomaterials (as shown in the table below), but the following 5 are the most common.

**X-Ray Diffraction:** Determines atomic composition characteristics, i.e. crystal structure, crystal size.

**Raman Spectroscopy:** Laser-based microscope device used to determine composition of a nanomaterial.

**Atomic Force Microscopy:** Measures the force between a probe and the sample material. Useful to determine thickness, particle size, shape and surface structure.

**Scanning Electron Microscopy:** Scans the surface of the material with a focused beam of electrons. Determines Surface Topology, particle shape, and assembly of the structure.

**Transmission Electron Microscope:** A beam of electrons is passed through the specimen to determine crystallinity, particle size and shape.

Technique	Properties characterized
X-ray diffraction (XRD)	Crystal structure, crystallite size
UV-Vis-NIR spectroscopy	Light absorption and scattering
Photoluminescence spectroscopy	Light emission
Chemisorption, physisorption	Surface area, pore size
Small angle X-ray scattering (SAXS)	Characteristic distances of partially ordered nanomaterials
Scanning electron microscopy (SEM)	Particle shape and assembly of structure
Transmission electron microscopy (TEM)	Particle size, shape and crystallinity
Energy dispersive X-ray analysis (EDX)	Chemical composition
Atomic force microscopy (AFM)	Particle size, shape and surface structure
Scanning tunneling microscopy (STM)	Particle size, shape and work function
X-ray photoelectron spectroscopy (XPS)	Valence state, chemical composition
Ultraviolet photoelectron spectroscopy (UPS)	Electron valence band
X-ray emission spectroscopy (XES)	Electron band gap
Extended X-ray absorption fine structure (EXAFS)	Chemical composition, bonding environment
Near-edge X-ray absorption fine structure (NEXAFS)	Chemical composition

## 5. Batteries

Batteries are another application of nanomaterials. There are 4 main components of a cell, regardless of its type: the 2 electrodes Anode and Cathode, Electrolyte and Separator.

**Anode:** Negative electrode of a cell associated with oxidative chemical reactions that release electrons into the external circuit.

**Cathode:** Positive electrode of a cell associated with reductive chemical reactions that gain electrons from the external circuit. *This is also the most expensive component in a battery because of being created with Cobalt.*

**Electrolyte:** Material providing pure ionic conductivity between the anode and the cathode of a cell.

**Separator:** Physical barrier between the anode and the cathode incorporated into most cell designs to prevent electrical shorting. It can be a gelled electrolyte, microporous plastic film, or other porous inert materials filled with electrolyte. They must be permeable to ions and inert in the battery environment.

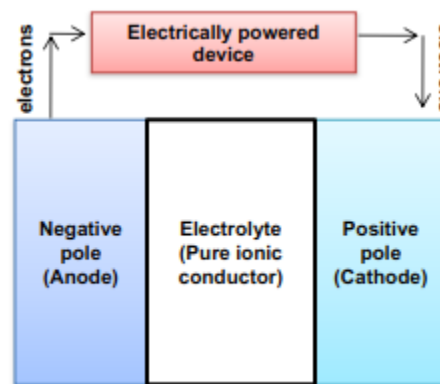
Cells operate by undergoing reduction-oxidation (Redox) reactions. In the cell, electrons leave the anode and flow through the wire to the cathode. As the electrons leave the anode, the cations formed as a result dissolve into the electrolyte solution in the anode compartment. As the electrons reach the cathode, cations in the cathode are attracted to the now negative cathode. The electrons are taken by the cations and the natural metal is deposited on the cathode.

**Electromotive Force (emf):** The potential difference between the anode and the cathode. It is also called the cell potential and is designated  $E_{\text{cell}}$ . The unit of measurements is Volts (V). This potential difference for many combinations of electrodes have been measured and tabulated, as shown in the table below.

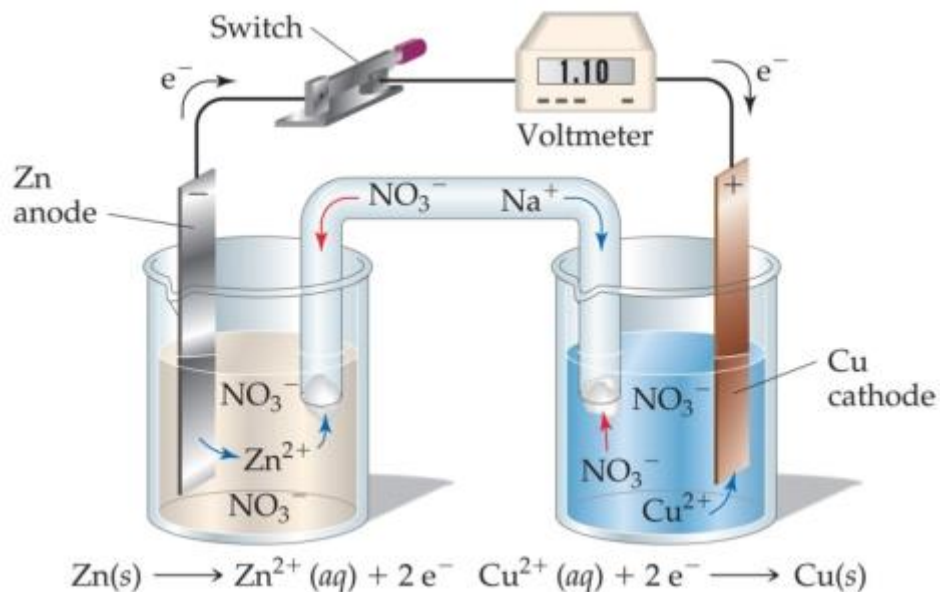
Potential (V)	Reduction Half-Reaction
+2.87	$\text{F}_2(\text{g}) + 2 \text{e}^- \longrightarrow 2 \text{F}^-(\text{aq})$
+1.51	$\text{MnO}_4^-(\text{aq}) + 8 \text{H}^+(\text{aq}) + 5 \text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 4 \text{H}_2\text{O}(\text{l})$
+1.36	$\text{Cl}_2(\text{g}) + 2 \text{e}^- \longrightarrow 2 \text{Cl}^-(\text{aq})$
+1.33	$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14 \text{H}^+(\text{aq}) + 6 \text{e}^- \longrightarrow 2 \text{Cr}^{3+}(\text{aq}) + 7 \text{H}_2\text{O}(\text{l})$
+1.23	$\text{O}_2(\text{g}) + 4 \text{H}^+(\text{aq}) + 4 \text{e}^- \longrightarrow 2 \text{H}_2\text{O}(\text{l})$
+1.06	$\text{Br}_2(\text{l}) + 2 \text{e}^- \longrightarrow 2 \text{Br}^-(\text{aq})$
+0.96	$\text{NO}_3^-(\text{aq}) + 4 \text{H}^+(\text{aq}) + 3 \text{e}^- \longrightarrow \text{NO}(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$
+0.80	$\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag}(\text{s})$
+0.77	$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \longrightarrow \text{Fe}^{2+}(\text{aq})$
+0.68	$\text{O}_2(\text{g}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{H}_2\text{O}_2(\text{aq})$
+0.59	$\text{MnO}_4^-(\text{aq}) + 2 \text{H}_2\text{O}(\text{l}) + 3 \text{e}^- \longrightarrow \text{MnO}_2(\text{s}) + 4 \text{OH}^-(\text{aq})$
+0.54	$\text{I}_2(\text{s}) + 2 \text{e}^- \longrightarrow 2 \text{I}^-(\text{aq})$
+0.40	$\text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + 4 \text{e}^- \longrightarrow 4 \text{OH}^-(\text{aq})$
+0.34	$\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Cu}(\text{s})$
0 [defined]	$2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{H}_2(\text{g})$
-0.28	$\text{Ni}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Ni}(\text{s})$
-0.44	$\text{Fe}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Fe}(\text{s})$
-0.76	$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Zn}(\text{s})$
-0.83	$2 \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \longrightarrow \text{H}_2(\text{g}) + 2 \text{OH}^-(\text{aq})$
-1.66	$\text{Al}^{3+}(\text{aq}) + 3 \text{e}^- \longrightarrow \text{Al}(\text{s})$
-2.71	$\text{Na}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Na}(\text{s})$
-3.05	$\text{Li}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Li}(\text{s})$

The maximum possible cell potential between electrodes is determined by taking the absolute value of the EMF value.

As shown by this table, Lithium ion cells have the highest cell potential. Therefore, it is very common to be used in almost all applications that require a rechargeable battery.



**Q:** Calculate the cell potential at standard conditions of a cell composed of a Zinc anode and a Copper cathode, as shown by the figure. The potential for the oxidation reaction is -0.76 V and the potential for the reduction reaction is +0.34 V.



**A:**

The cell potential at standard conditions can be found through this equation:

$$E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ}(\text{cathode}) - E_{\text{red}}^{\circ}(\text{anode})$$

For oxidation in the cell  $E_{\text{red}}^{\circ} = -0.76\text{V}$

For Reduction in the cell  $E_{\text{red}}^{\circ} = +0.34\text{V}$

$$E_{\text{cell}}^{\circ} = +0.34\text{V} - (-0.76\text{V})$$

$$E_{\text{cell}}^{\circ} = 1.10\text{ V}$$

Thus, the standard cell potential for the given cell is 1.10 V.

There are many types of batteries. They can be separated into Primary and Secondary batteries:

Primary (Disposable) Batteries	Secondary (Rechargeable) Batteries
<ul style="list-style-type: none"> <li>• Zinc carbon (flashlights, toys)</li> <li>• Heavy duty zinc chloride (radios, recorders)</li> <li>• Alkaline (all of the above)</li> <li>• Lithium (photoflash)</li> <li>• Silver, mercury oxide (hearing aid, watches)</li> <li>• Zinc air</li> </ul>	<ul style="list-style-type: none"> <li>• Nickel cadmium</li> <li>• Nickel metal hydride</li> <li>• Alkaline</li> <li>• Lithium ion</li> <li>• Lithium ion polymer</li> <li>• Lead acid</li> </ul>

**Dry Cell:** Common, inexpensive, primary use only. 1.5V, typically 500-1000 mAh.

*Anode:*  $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$

*Cathode:*  $2\text{NH}_4^+ + 2\text{e}^- \rightarrow 2\text{NH}_3 + \text{H}_2$

**Alkaline:** Common, inexpensive, primary use, sometimes rechargeable. 1.5V, typically 2100-3000 mAh.

*Anode:*  $\text{Zn} + 2\text{OH}^- \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2\text{e}^-$

*Cathode:*  $2\text{NH}_4^+ + 2\text{e}^- \rightarrow 2\text{NH}_3 + \text{H}_2$

**Lead Acid:** Rechargeable battery, 2.2V, typically 2000 mAh. Most commonly used in cars.

*Anode:*  $\text{E}^0 = +0.36 \text{ V}$   $\text{Pb} + \text{HSO}_4^- \rightarrow \text{PbSO}_4 + \text{H}^+ + 2\text{e}^-$

*Cathode:*  $\text{E}^0 = +1.68 \text{ V}$   $\text{PbO}_2 + \text{HSO}_4^- + 3\text{H}^+ + 2\text{e}^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$

**Ni-Cd:** Common, inexpensive, primary use, sometimes rechargeable. 1.5V, typically 2100-3000 mAh.

*Anode:*  $\text{Cd} + 2\text{OH}^- \rightarrow \text{Cd}(\text{OH})_2 + 2\text{e}^-$

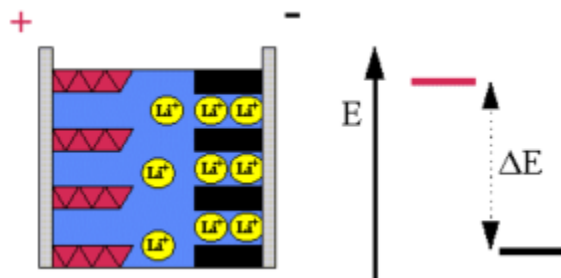
*Cathode:*  $\text{NiO}(\text{OH}) + 2\text{NH}_4^+ + 2\text{e}^- \rightarrow 2\text{NH}_3 + \text{H}_2$

**Lithium-Ion:** Most common form of rechargeable battery, used in electronics and electric vehicles.

*Anode:*  $\text{Li} \rightarrow \text{Li}^+ + 2\text{e}^-$

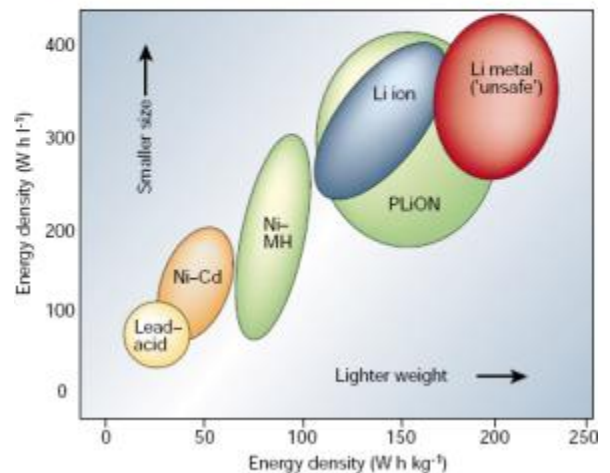
*Cathode:*  $\text{Li}^+ + 2\text{e}^- \rightarrow \text{Li}$

Li-Ion batteries tend to have lighter weight and a higher energy density compared to other types of secondary use batteries. They can also be recycled as well as formed from used Silicon wafers that are used for manufacturing silicon-based electronics chips.



#### Rechargeable batteries: Cell technology

- Ni-Cd (Nickel Cadmium/ 1.2 volts per cell)
- Ni-MH (Nickel Metal hydride/ 1.2 volts per cell)
- Li-ion (Lithium Ion/ 3.7 volts per cell)





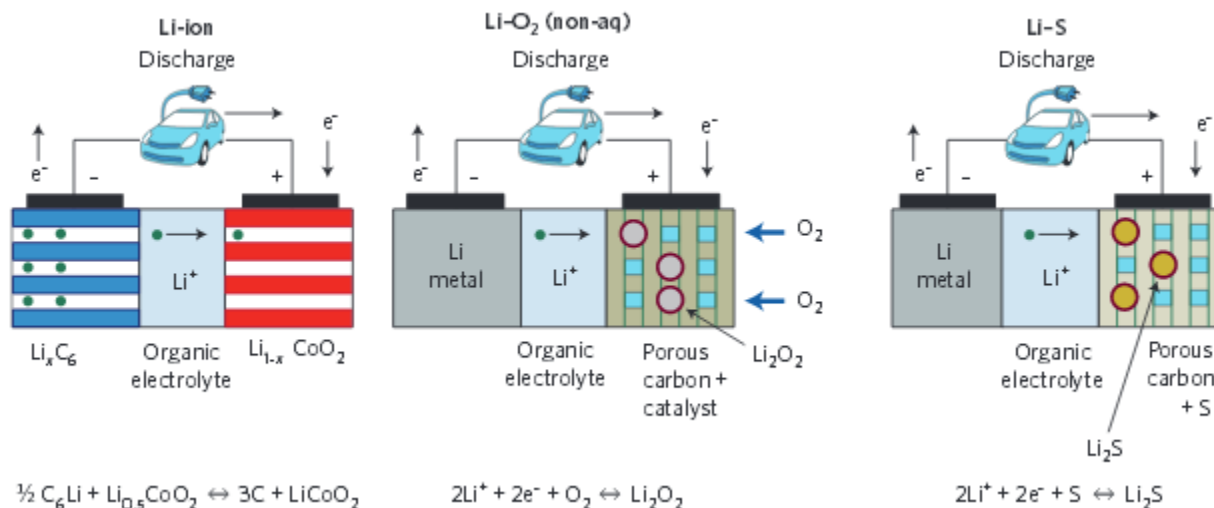
**Lithium-Sulfur Batteries:** Rechargeable battery that uses Sulfur as the element for positive electrode. They have a higher voltage, capacity and thermal capacity than Lithium-Ion batteries. However, they tend to have a lower cycle life.

**Comparison of various secondary batteries.**

System	Negative electrode	Positive electrode	Voltage (V)	Th. Cap. (mAh/g)	Th. En. (Wh/kg)
Ni-Cd	Cd	NiOOH	1.2	162	219
Ni-MH	MH alloy	NiOOH	1.2	~178	~240
Li-Ion	$\text{Li}_x\text{C}_6$	$\text{Li}_{1-x}\text{CoO}_2$	3.6	137 (for $x=0.5$ )	360
<b>Li-S</b>	<b>Li</b>	<b>S</b>	<b>2.1</b>	<b>1,675</b>	<b>2,600</b>
Li-FeS <sub>2</sub>	Li	FeS <sub>2</sub>	1.5	893	1,273

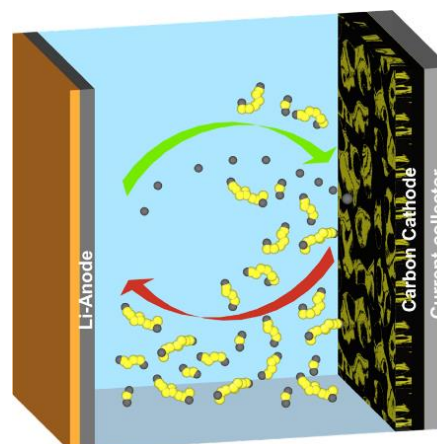
**Comparison of various raw materials for lithium secondary batteries.**

	Iron (Fe)	Nickel (Ni)	Manganese (Mn)	Cobalt (Co)	Copper (Cu)	Molybdenum (Mo)	<b>Sulfur (S)</b>
Cost (US\$/ton)	135 (Fe ore)	12,350	564 (Mn ore)	41,850	2,770	46,260	<b>28</b>
Atomic weight (g/mol)	55.85	58.69	54.94	58.93	63.55	95.94	<b>32.06</b>



Lithium-Sulfur batteries often contain a layer of porous carbon on the cathode. This layer is often composed of graphite, carbon nanofibers, carbon nanotubes, graphene, and/or polymer carbon.

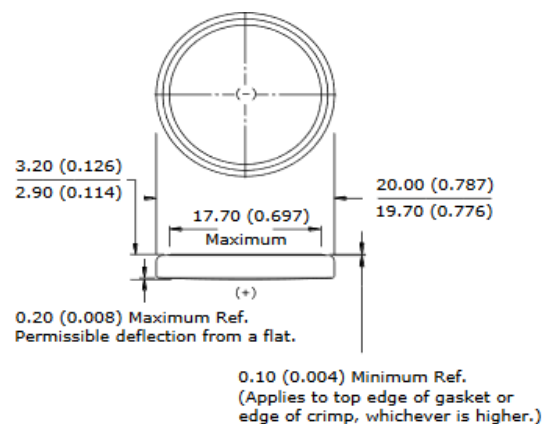
The diagram on the right shows the schematic of an Li-S battery. On the left, we have the Lithium based anode. On the right, we have the current collector, or the Sulfur based cathode, coated in the black layer of Carbon.



## 6. Making a Watch Battery (CR2032)

A button cell, or more commonly known as a watch battery, is a small single cell battery shaped as a squat cylinder. They are typically 5 to 25 mm in diameter and 1 to 6 mm in height. A metal can forms the anode and cathode of the cells. They are most popular for powering small electronics such as watches, calculators and keyless entry transmitters for cars. In the lab, a CR2032 Lithium cell will be assembled.

The CR2032 watch battery contains contents that are composed of nanomaterials and are very delicate. They must be manufactured within a sealed container filled with inert gas. This container is called a *Glove Box* and is filled with *Argon gas*.



### **Required Materials:**

1. Can Structure, two halves (Cathode Can, and Anode Can)
2. Stainless-Steel Disc
3. Clamping Spring
4. Lithium hexafluorophosphate ( $\text{LiPF}_6$ ) Electrolyte
5. Lithium Metal Piece for Anode
6. Manganese Dioxide Metal Piece for Cathode
7. Polycarbonate Separator

### **Assembly Instructions:**

1. Obtain the two halves of the cell 'Can' structure and place them on the working area in an appropriate manner. One will be the cathode can and the other will be the anode can.
2. Obtain an appropriate size of Lithium metal. This will be acting as the anode of the battery.
3. Pick up the lithium metal piece and check for oxidation. If oxidation is present, use a spatula to scrape off the oxidation.
4. Place the Manganese Dioxide metal piece for the cathode into the cathode can. Try your best to make the metal sheet and the cathode can concentric.
5. Place the Polycarbonate Separator on top of the anode inside the cathode can.
6. Using an accurate pipette, draw an appropriate amount of  $\text{LiPF}_6$  Electrolyte, and pour it into the can.
7. Obtain an appropriately sized Lithium piece to act as the anode. Again, check for oxidation and remove with spatula if any. Place the Lithium piece on top of the separator.
8. Place the Stainless-Steel Disc on top of the whole assembly so far. This disc will act as a current collector once the cell is fully manufactured.
9. Place the clamping spring on top of the disc. This will ensure that the cell does not come apart.
10. Place the anode side can on top of the entire assembly, encapsulating it. Push the structure down firmly to ensure that the two halves of the cell are together.
11. Take the newly assembled structure and place it inside the watch battery press. Start the press machine and allow it to clamp down on the structure and seal it permanently.

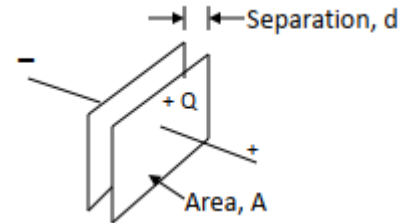


## 7. Electrochemical Capacitors

Capacitors are energy storage devices meant to release 100% of its energy in a short period of time. They are able charge and discharge instantly. We don't use them instead of batteries because they can't hold charge for long.

**Example:** Capacitors are used in car audio systems to reduce the energy load on the engine/alternator when the bass drops, because the bass drop causes a sudden surge in power draw, so the capacitor can take the load instead of bringing down the alternator.

**Example:** Capacitors are used in the Airbus A380 Emergency Door Release system. Boostcap ultracapacitors are used to power emergency actuation systems for doors and evacuation slides in passenger aircraft.



Capacitance is the ratio of the change in an electric charge in a system to the corresponding change in its electric potential. Capacitance is found by the formula:  $C = Q/V$ , where  $Q$  is the charge in Coulomb and  $V$  is the voltage.

**Parallel Plate Capacitor:**  $C = \epsilon_0 \epsilon_r A/d$

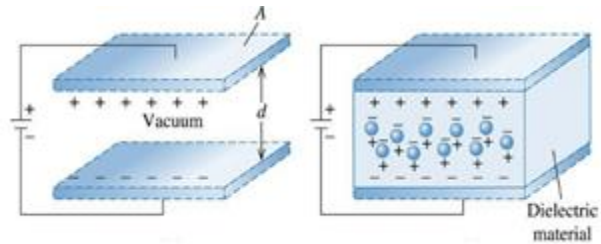
**Spherical Capacitor:**  $C = 4 \pi \epsilon_0 R$

**Increase A:** using materials with large surface area. **Decrease d:** electrochemical double layer. **Increase  $\epsilon_r$ :** Certain oxides (Perovskite) demonstrates extremely high permittivity

Stored Energy:  $E = \frac{1}{2} CV^2 = \frac{1}{2} C(V_i^2 - V_f^2)$

Energy density:  $E/Ad = \frac{1}{2} \epsilon \epsilon_0 (V/d)^2$

**Dielectric Constant:** a quantity measuring the ability of a substance to store electrical energy in an electric field. The presence of an electric field polarizes the electron distribution about an atom creating a dipole moment. The dielectric constant is the relative permittivity of a dielectric material. It is an important parameter in characterizing capacitors.



**Electrochemical Capacitors:** Often called supercapacitor or ultracapacitor. Invented by Standard Oil of Ohio in the 1960's. Product line introduced by NEC in 1978 (SOHIO license). Originally used for computer memory backup. Appreciation of other attractive features in 1990s – Extraordinary power performance – Very high cycle-life – Long maintenance-free operational life – Safe, generally environmentally friendly technologies

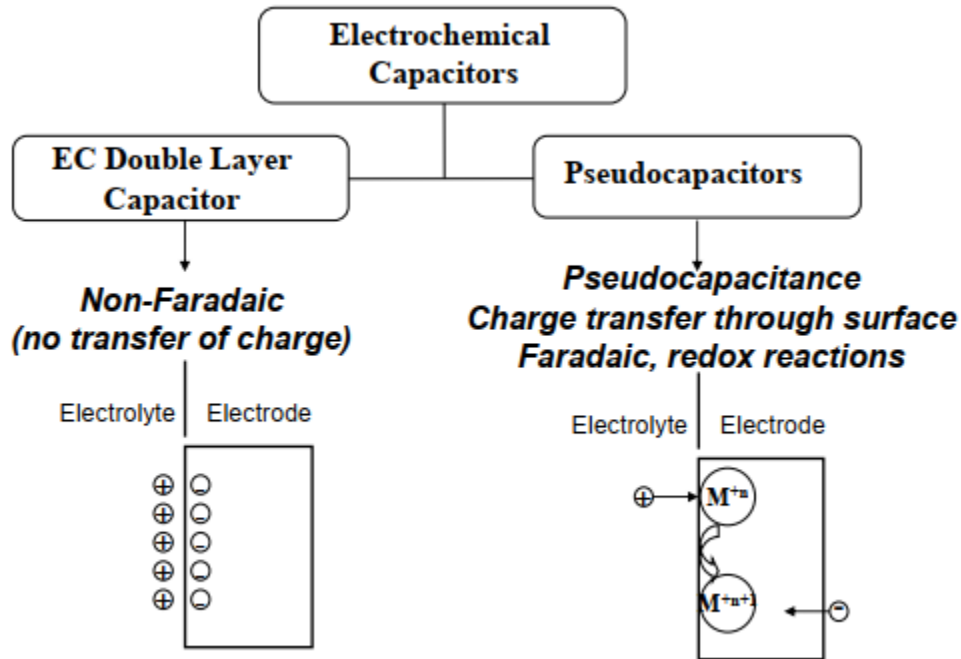
Supercapacitors or ultracapacitors are being widely used for energy storage in many applications, such as UPS, and electrical vehicles, etc

Property	Battery	E.C.
Storage Mechanism	Chemical	Physical
Power Limitation	Depends on reaction kinetics, mass transport	Separator ionic conductivity
Energy Limitation	Electrode mass	Electrode surface area
Output Voltage	Constant Value	Sloping value (SOC known precisely)
Charge Rate	Depends on reaction kinetics, mass transport	Very high, same as discharge rate
Cycle Life Limitations	Depends on physical stability and chemical reversibility	Depends on side reactions
Life Limitation	Depends on thermodynamic stability.	Depends on side reactions

**Status of Supercapacitors:**

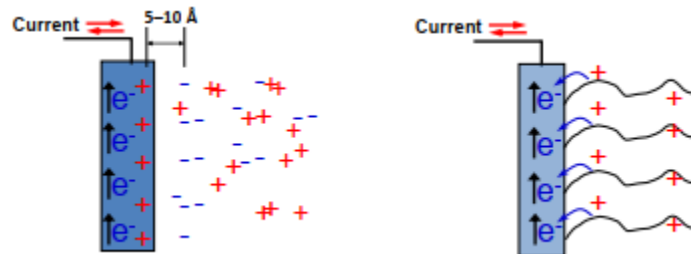
- Extraordinarily high specific capacitance ~100 F/g typical.
- Very low \$/J compared with conventional capacitors.
- Low unit-cell voltage, ~1 to 3 V
- Non-ideal behavior--response time ~1 s
- Expensive, on an energy basis, compared with batteries
- Very powerful when compared with batteries
- Operational life and cycle life can be engineered to exceed application requirements

**Types** - Electrochemical Capacitors can be divided into two types, as shown below:



**Pseudocapacitance:** Faradic process (e.g. metal oxides and conducting polymers); Charge transfer across the metal-solution interface. Oxidation or reduction occurs. Governed by Faraday's law.

**Non-Faradic Process:** (e.g. activated carbon); No charge transfer across the metal-solution interface. Adsorption and desorption.

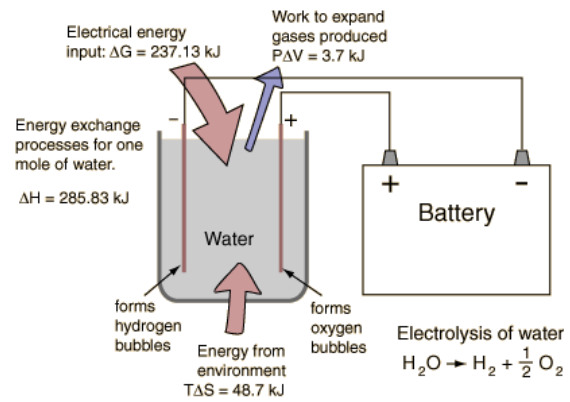


**Pseudocapacitors** have an even higher energy density than ECDL capacitors. However, they suffer from lower power density compared to ECDL, as well as a shorter cycle life. Furthermore, the best metal oxide electrodes are expensive and required aqueous electrolyte at low voltage.

## 8. Fuel Cells

The first fuel cell was built in 1839 by Sir William Grove, a lawyer and a gentleman scientist. Serious interest did not begin until the 1960's when the U.S. Space Program chose fuel cells over riskier nuclear power and expensive solar energy. Fuel cells powered the Gemini and Apollo spacecraft, and they are still in use.

**Electrolysis:** Chemical decomposition produced by passing an electric current through a liquid or solution containing ions. It is used to separate water into Hydrogen and Oxygen. By providing energy from a battery, water ( $\text{H}_2\text{O}$ ) can be dissociated into the diatomic molecules of hydrogen ( $\text{H}_2$ ) and oxygen ( $\text{O}_2$ ).

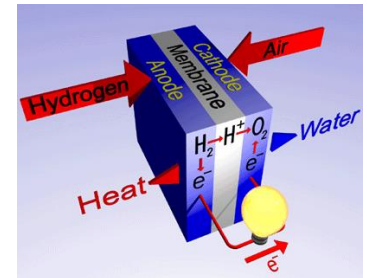
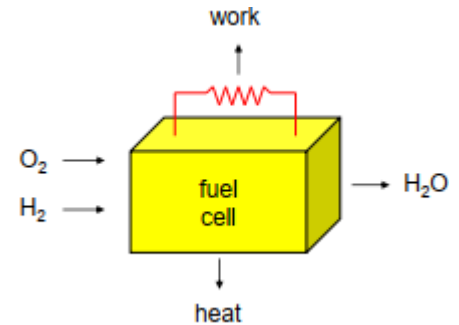


Fuel Cells essentially use Electrolysis, but in the reverse direction. The basic principle is the same as Batteries. Fuel cells generate electricity through an electrochemical process in which the energy stored in a fuel is converted directly into DC electricity. The electrical energy is generated without combusting fuel, which makes it very attractive from an environmental standpoint.

**Advantages:** High energy conversion efficiency, Modular design, very low chemical and acoustical pollution, fuel flexibility, cogeneration capability, rapid load response.

**Components:** Same as batteries, a cathode, an anode and an electrolyte sandwiched between the two.

**Operation:** Oxygen flows through the cathode. A fuel gas containing Hydrogen (i.e. Methane) flows past the anode. Negative Oxygen ions migrate through the electrolyte membrane to react with hydrogen to form water. This reaction generates electrons which flow from the anode to an external load and back to the cathode, a final step that completes the circuit and provides electricity.

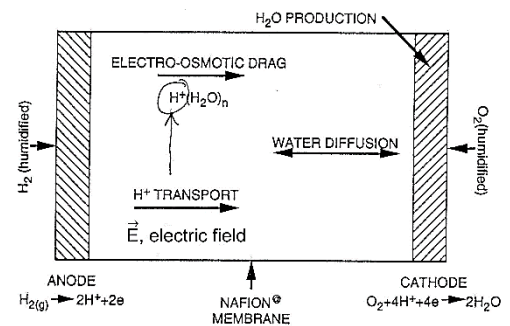


**Proton Exchange Membrane Fuel Cell:** Simplest form of fuel cell. Anode conducts hydrogen molecules, cathode conducts electrons back from circuit and combine the ions with oxygen to form water. The electrolyte is the proton exchange membrane, where it only conducts positively charged ions. The membrane blocks electrons. The catalyst is a special material (usually platinum powder coated onto carbon paper) to facilitate the reaction of oxygen and hydrogen.

**Anode:**  $2\text{H}_2 \rightarrow 4\text{H}^+ + 4\text{e}^-$

**Cathode:**  $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$

**Net Reaction:**  $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$

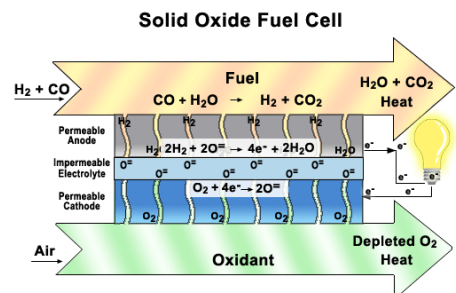


**Solid Oxide Fuel Cell:** Uses a ceramic, solid-phase electrolyte to reduce corrosion and electrolyte management problems. Ceramic needs to operate at about 1000°C.

**Anode:**  $\text{H}_2 + \text{O}^{2-} \leftrightarrow \text{H}_2\text{O} + 2\text{e}^-$

**Cathode:**  $\frac{1}{2}\text{O}_2 + 2\text{e}^- \leftrightarrow \text{O}^{2-}$

**Possible Designs:** Tubular, Segment-type tubular, Planar



**Problems with Fuel Cells:**

1. The fuel cell uses oxygen and hydrogen to produce electricity.
2. The oxygen required for a fuel cell comes from the air. In fact, in the PEM fuel cell, ordinary air is pumped into the cathode.
3. The hydrogen is not so readily available, however.
4. Hydrogen has some limitations that make it impractical for use in most applications.
5. Hydrogen is difficult to store and distribute, so it would be much more convenient if fuel cells could use fuels that are more readily available.

*The problem with storage and distribution is addressed by a device called a reformer. A reformer turns hydrocarbon or alcohol fuels into hydrogen, which is then fed to the fuel cell*

**Electrocatalyst:** Carbon Nanotubes are used as a catalyst support for PEMFC. CNTs allow for electrocatalysts with small particle size and high dispersion, resulting in high electrocatalytic activity. Supporting materials with high surface area are essential to disperse catalyst particles. CNTs, because of their nanometer size and high surface area (1000m<sup>2</sup>/g) have been use as catalyst support for fuel cells

**Hydrogen Storage Methods:**

Hydrogen storage methods	Gravimetric density (wt %)	Volumetric density (kg H <sub>2</sub> /m <sup>3</sup> )	Working temperature (K) and pressure (bar)	(advantages & draw backs)
Compressed gas	13	7	300 150	Laboratory use, high gas pressure
Liquid hydrogen	-	70	21 1	High volumetric density , expensive
Metal hydrides	1.5 – 3.0	100 – 120	300 2-20	Reversibility of uptake & release, high volumetric density, low wt %
Mg based hydrides	3 – 6	100 – 120	573 2-20	High wt % high temperature, slow kinetics
Complex hydrides (NaAlH <sub>4</sub> , LiBH <sub>4</sub> )	5.5; 18	95-120	520-553, 100-120	High wt %, desorption at high temp, rehydrogenation at high temperature & pressure
Adsorbed hydrogen	3.5	100	300 100	High volumetric density, High pressure