Electrical Storage

Batteries, Fuel Cells and Ultra-capacitors

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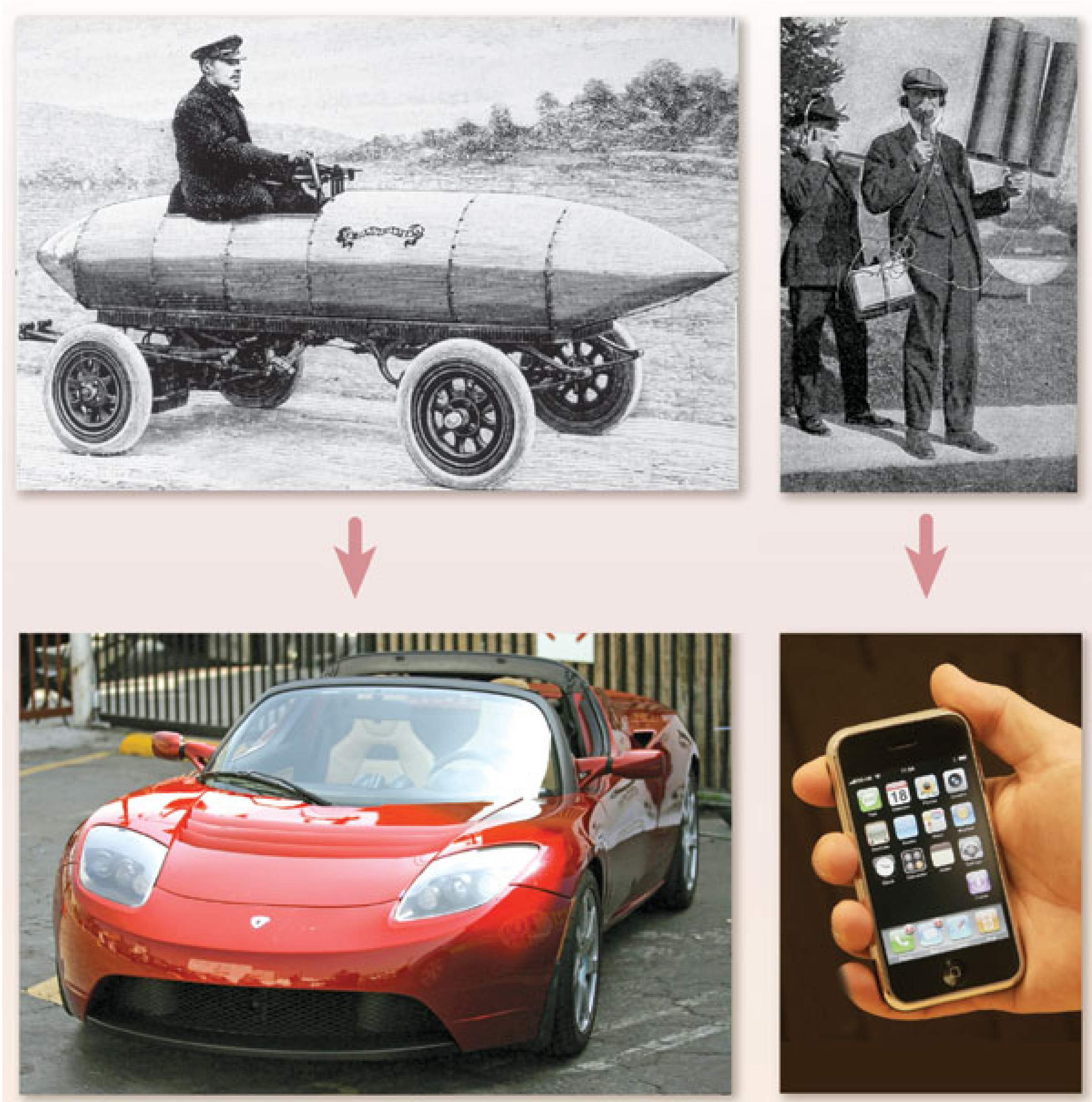


In 1899 a Belgian car, *La jamais contente* (top left), equipped with lead–acid batteries, reached a speed of 30 meters per second . In the same year, at a car competition in Paris, the only petrol-driven car was disqualified for having unpractically high consumption. Inside the United States, between 1900 and 1920, the proportion of electrical cars produced fell from 60% to 4% of the total. One century later, fully electrical cars, such as the Tesla roadster (bottom left), are coming back into the picture. Meanwhile, the first wireless communication took place in Pennsylvania in 1920 (top right). Nearly 100 years later, the latest mobile phones (bottom right) can perform a wide range of functions.

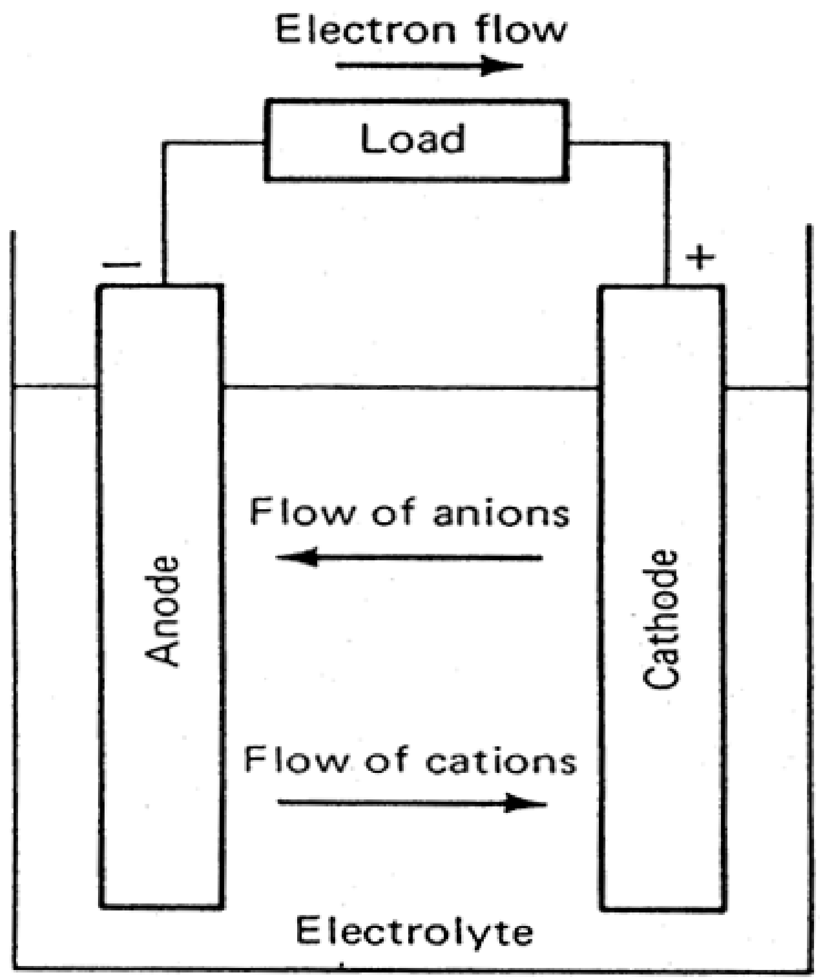
What is a “Battery“?

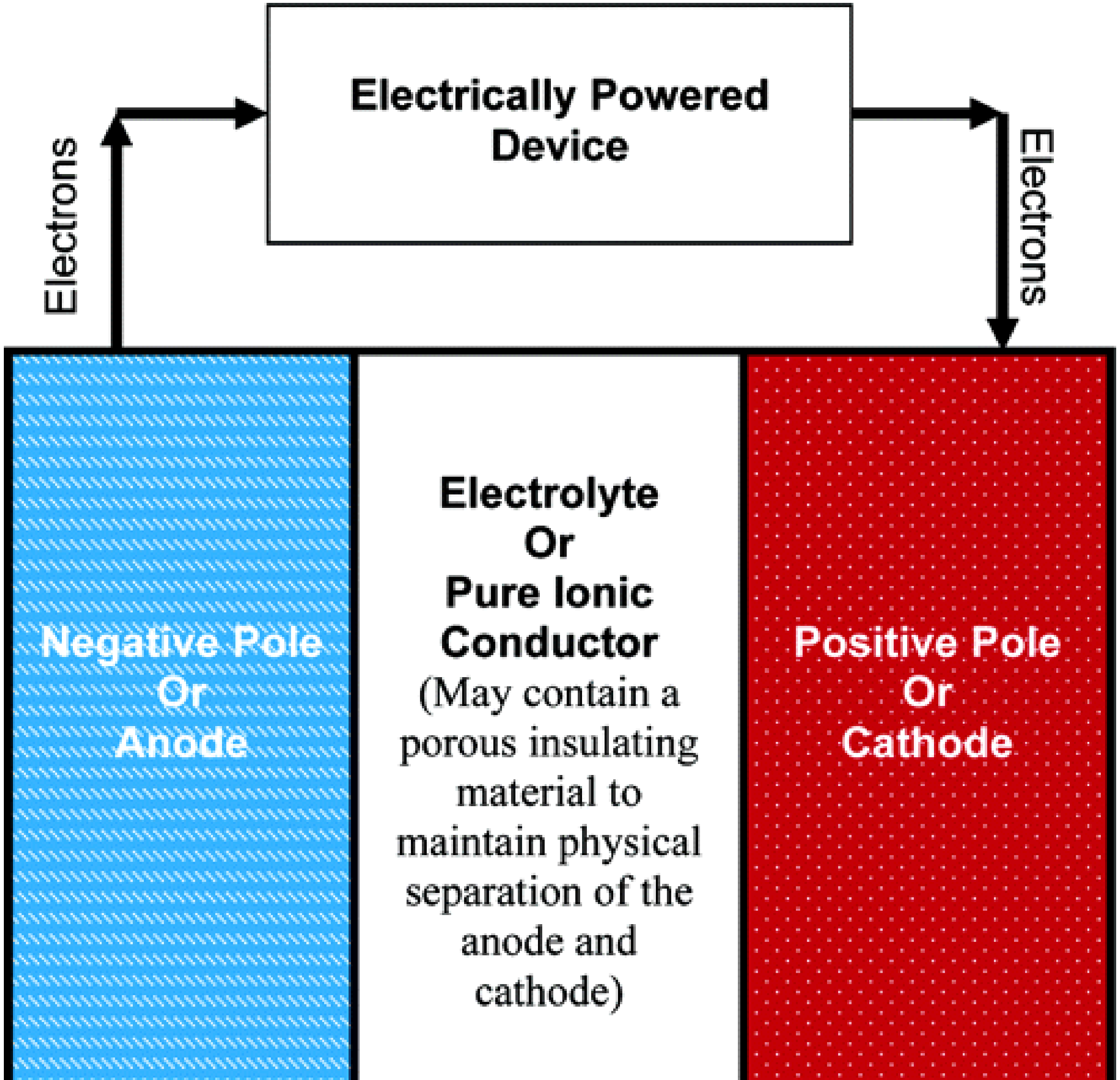
- Portable Source of Electrical Power
- Energy Storage/Conversion Device
- Converts Chemical Energy Into Electrical Energy
- Works on Electrochemistry Principles
- Volta Invented in 1800

Chemical *vs.* Electrochemical

- **Chemical**
  - Chemical energy converted to thermal energy
  - Energy producing chemicals: Fuel and Oxidant
  - Fuel and oxidant are brought together. Resultant combustion reaction produces heat
  - Fuel + Oxidant → Heat
- **Electrochemical**
  - Chemical energy converted to electrochemical energy
  - Energy Producing chemicals: Anode Material, Cathode material
  - Anode and cathode materials are kept separately
  - electrons pass through out side loop
  - electrolyte to complete circuit

Electrochemical Cell Configuration





Block diagram of a cell or battery powering a device. If a battery is recharged, the load is replaced with an energy source that imposes a reverse voltage that is larger than the battery voltage and the flow of electrons is reversed.

Battery Terminology

- **Cell-Basic Unit**
  - Contains Anode, Cathode, Electrolyte, Separator etc.
- **Battery:**
  - Contains 2 or more cells in series or parallel
- **Discharging**
  - Removing energy from the cell/Battery
- **Charging**
  - Returning energy to the cell/battery

Basic Electrochemical Cell
Five essential components of a cell

The Anode
The Cathode
The Ionic Conductor (electrolyte)
The Metallic Conductor (electrical connection)
The separator

The Anode

The anode has the lowest potential and is oxidized in the process by a loss of electrons:

$$M \rightarrow M^{z+} + ze^-$$

Anodic reaction
Oxidation reaction
Electron generation

The Separator

Electrical insulator membrane, allowing ionic transfer and solvent wetting.

The Cathode

The cathode has a high potential, leading to a consumption of electrons.

$$MO + z\mathit{e} \rightarrow [MO]^{z-}$$

Cathodic reaction
Reduction reaction
Electron consumption

The Electrolyte

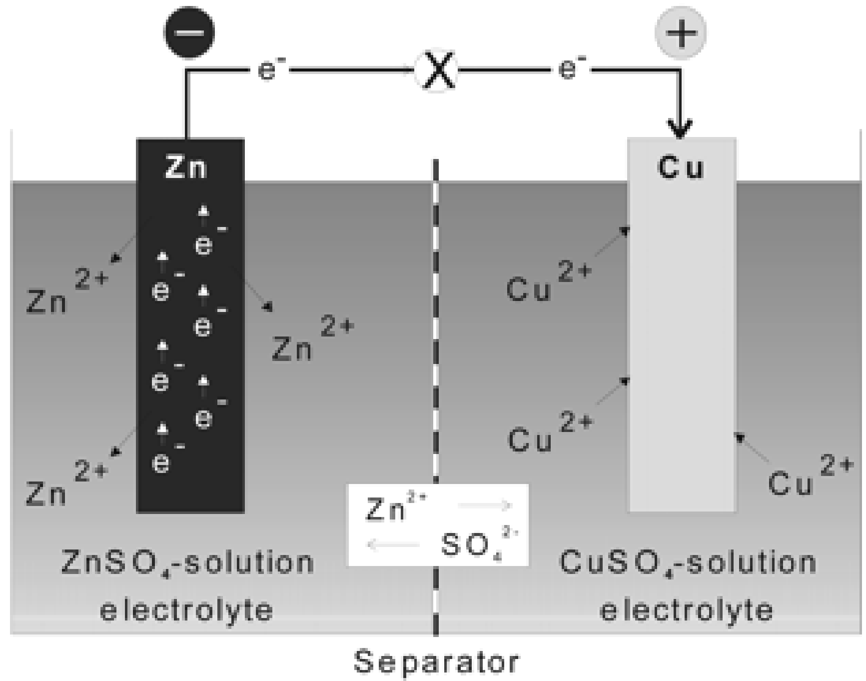
a solution conducting ions

Electrical Connections

the anode and cathode in an electrochemical cell must be in electrical contact in order to generate power and energy. Difference in free energies between the anode and the cathode produces electrical potential which is the driving force for electrochemical reaction.

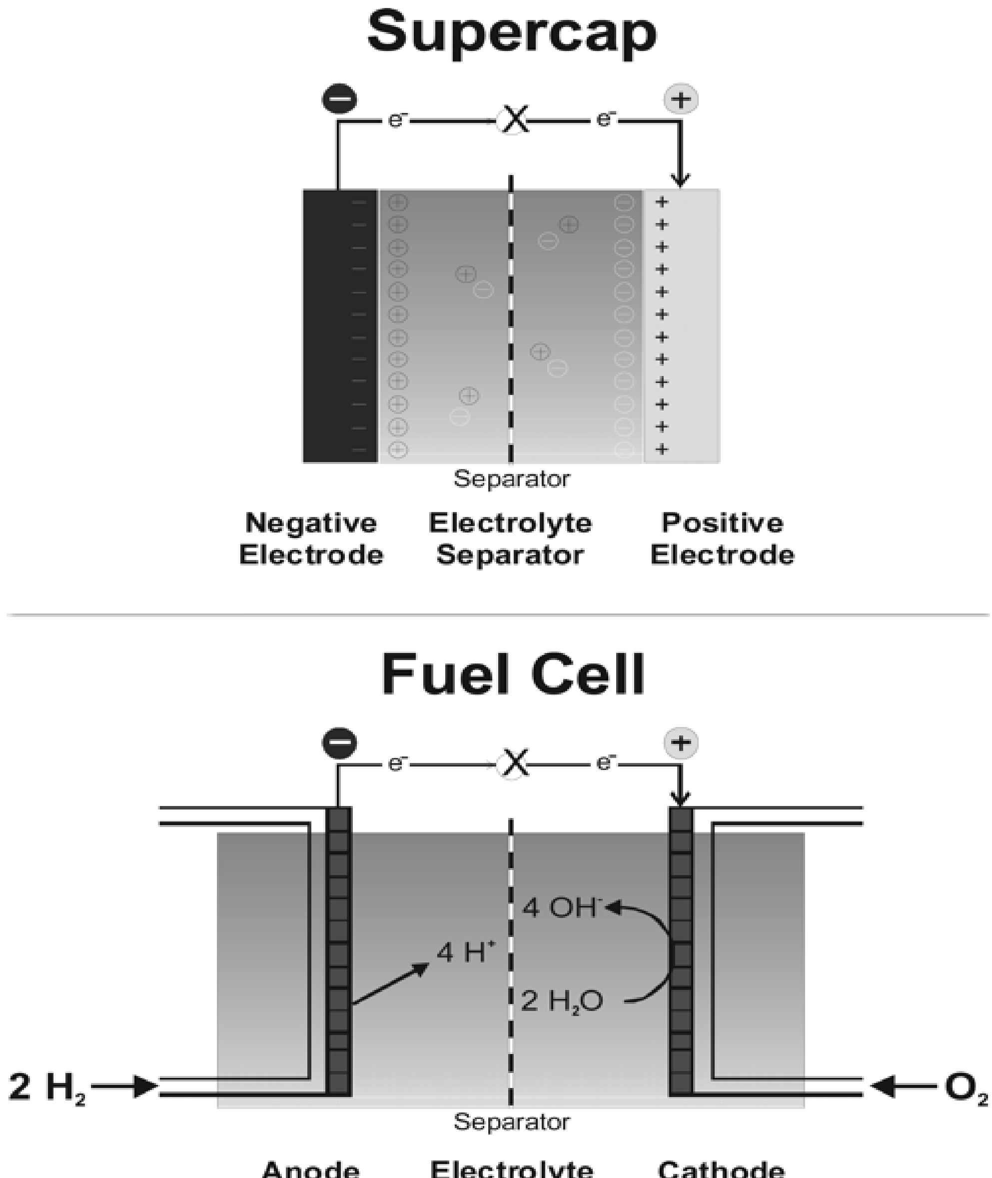
Current collectors

Battery



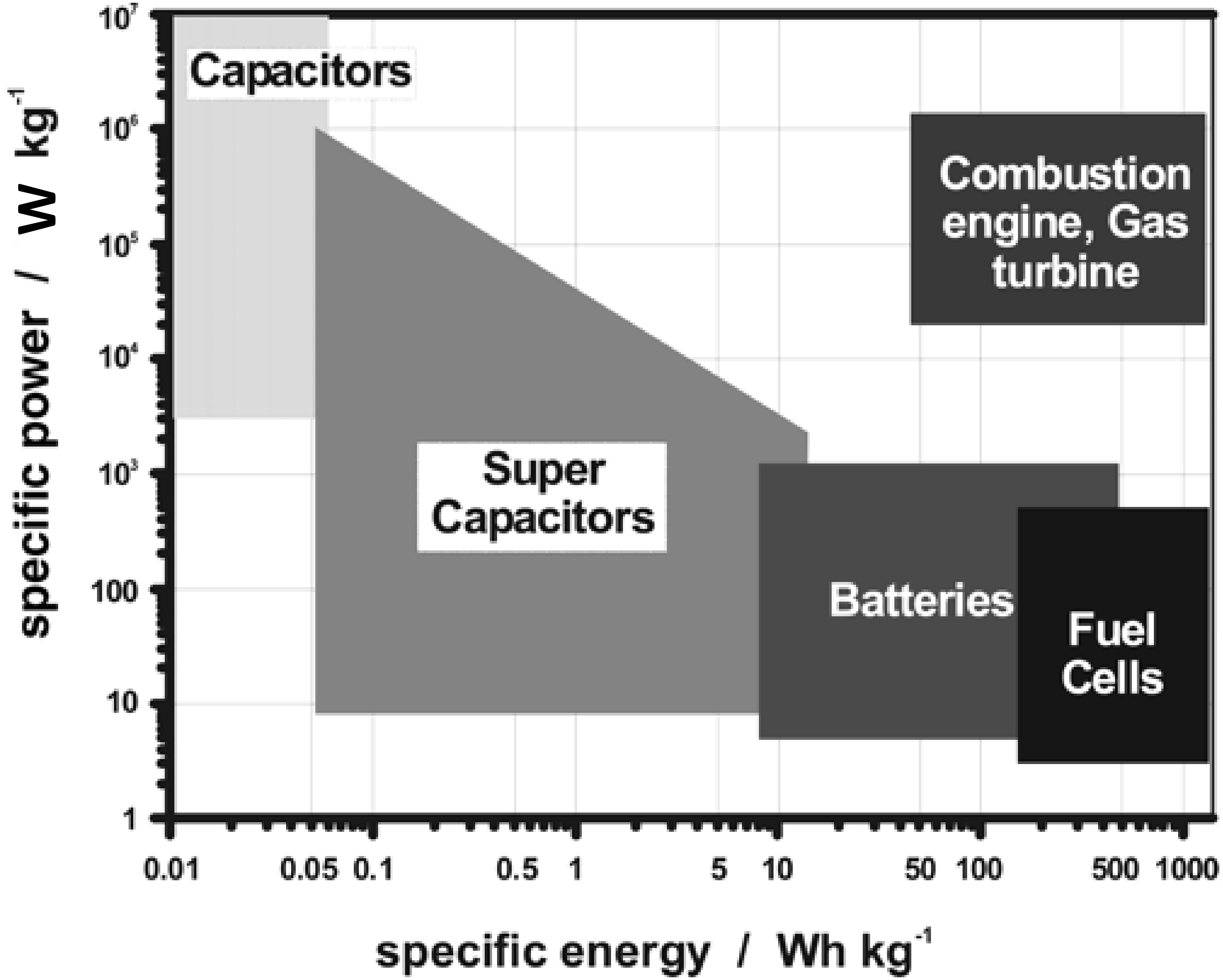
	Anode	Electrolyte Separator	Cathode
Requirements on			
electron conduction:	must	no	must
ion conduction:	can	must	can

Representation of a battery (Daniell cell) showing the key features of battery operation and the requirements on electron and ion conduction.



Representation of (top) an electrochemical capacitor (supercapacitor), illustrating the energy storage in the electric double layers at the electrode−electrolyte interfaces, and (bottom) a fuel cell showing the continuous supply of reactants (hydrogen at the anode and oxygen at the cathode) and redox reactions in the cell.

Power(ful) vs. Energ(etic) Devices?



Simplified Ragone plot of the energy storage domains for the various electrochemical energy conversion systems compared to an internal combustion engine and turbines and conventional capacitors.

Power vs. Energy...

- $P_{[W]} = E/t = J/t_{[sec]} = I_{[amp]} V_{[volt]} =$
  $\underline{(C_{[coulomb]} / t_{[sec]}) V_{[volt]}}$

- $E_{(J, Wh)} = Pt = Q_{[amp\ h]} V_{[volt]} = \underline{I_{[amp]} t_{[sec]} V_{[volt]}}$

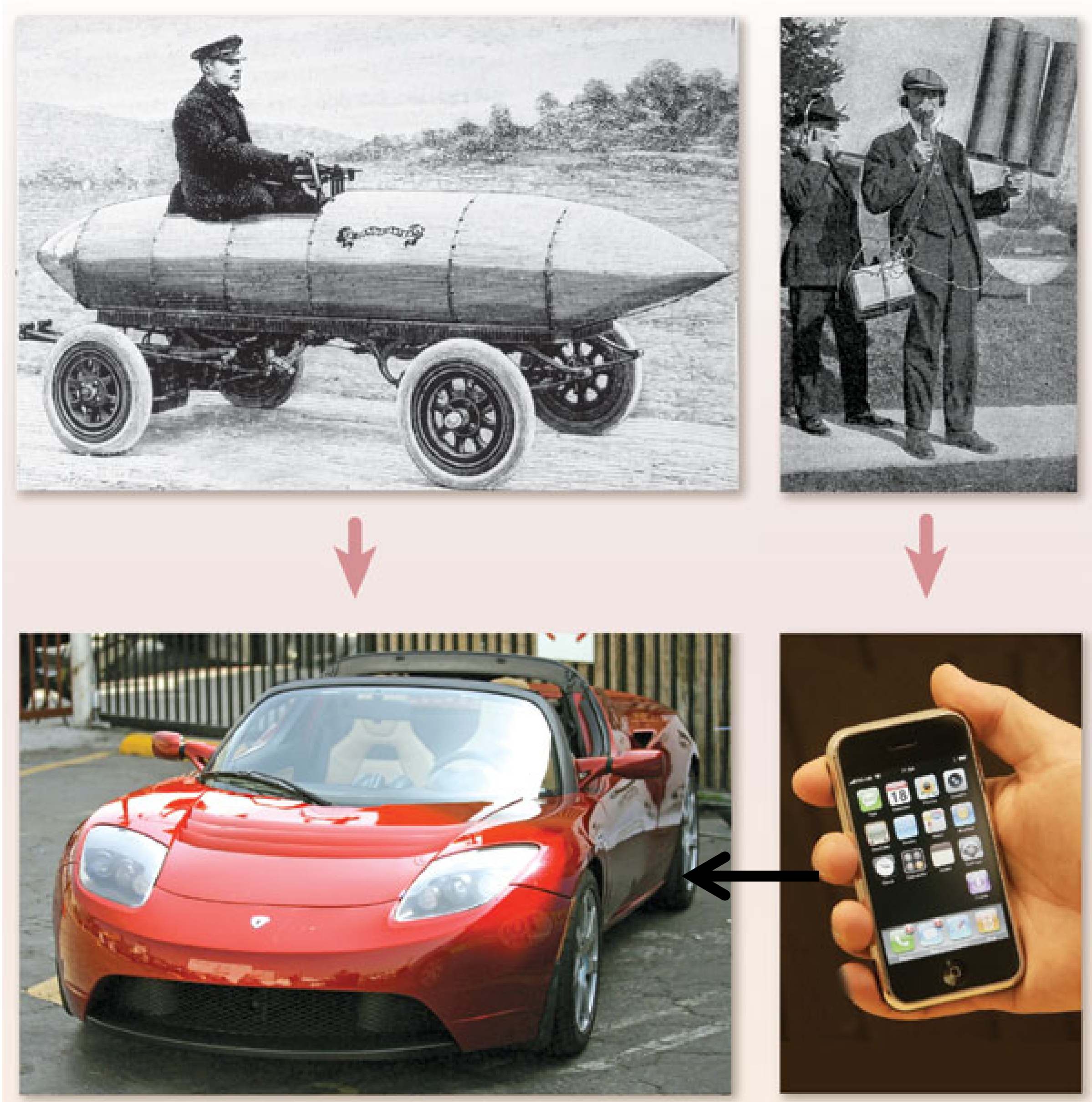
Conclusion

$t\downarrow \quad P\uparrow \quad ; \quad t\uparrow \quad E\uparrow$

Therefore, high energy density batteries *MUST* have low power capabilities, while high power device (U-cap) has, by nature, low energy density.

EV…EV…EV!!!
Fame or…Shame

http://www.evdriven.com/li-ion/presentations/



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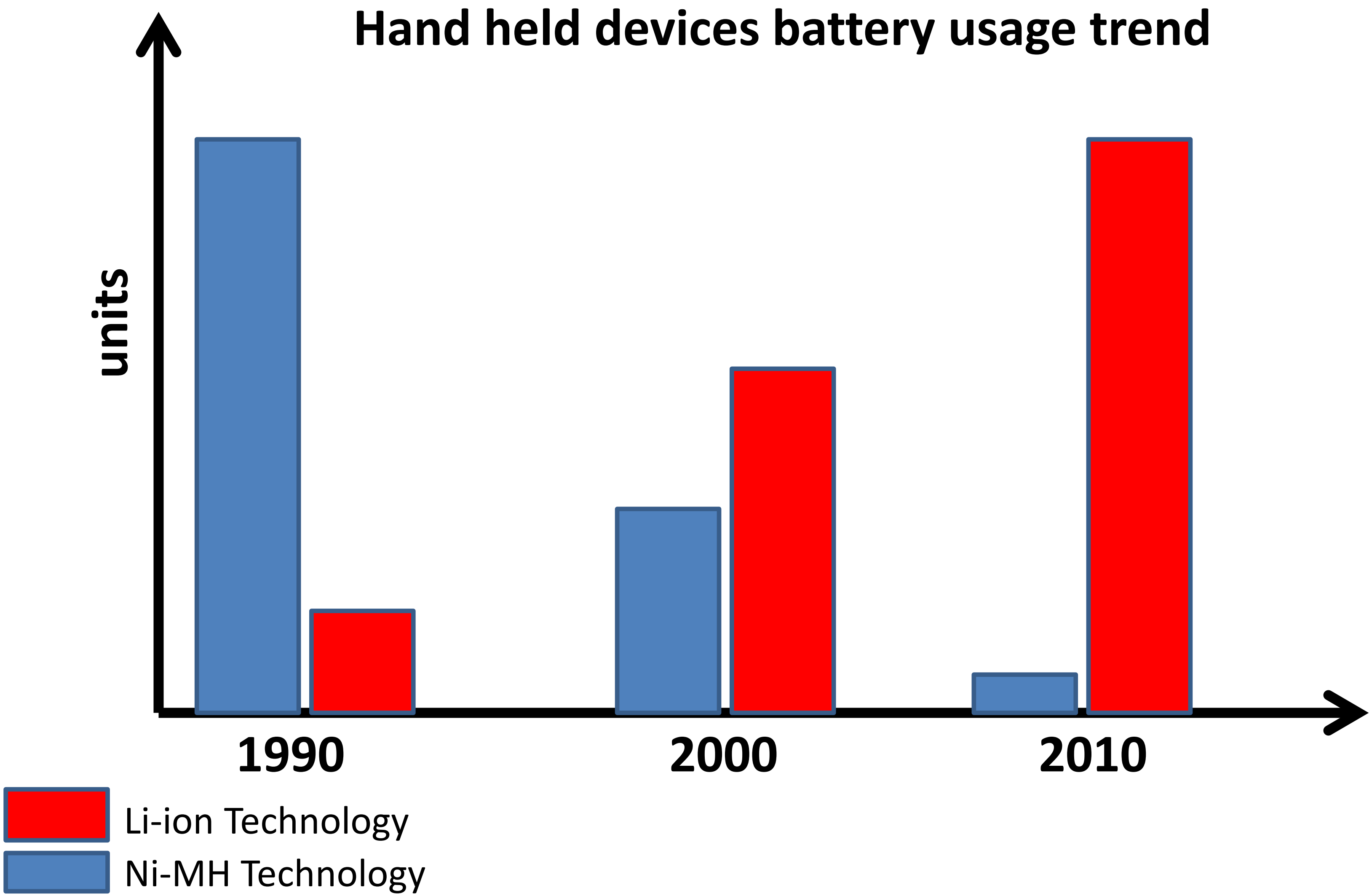
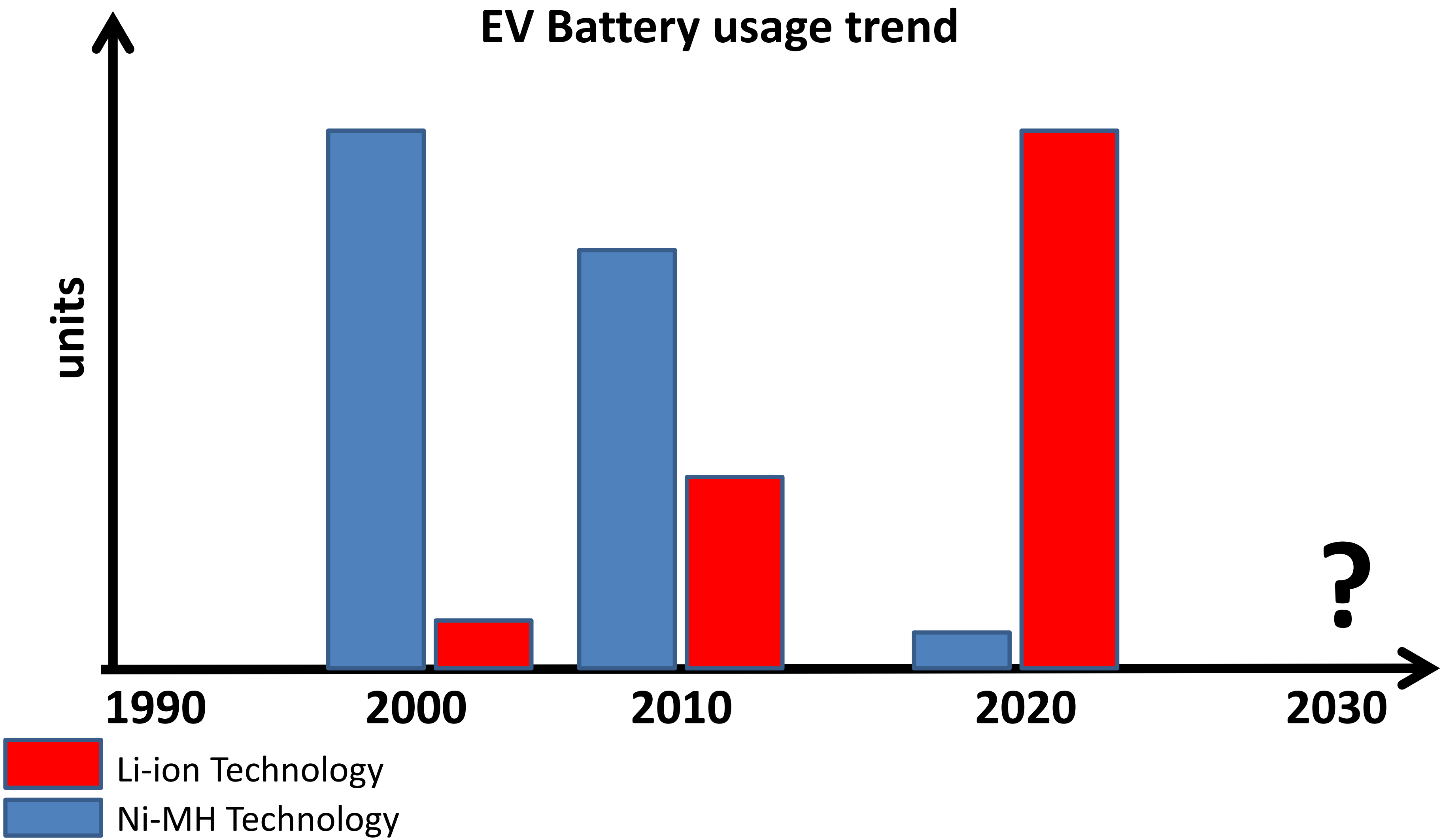
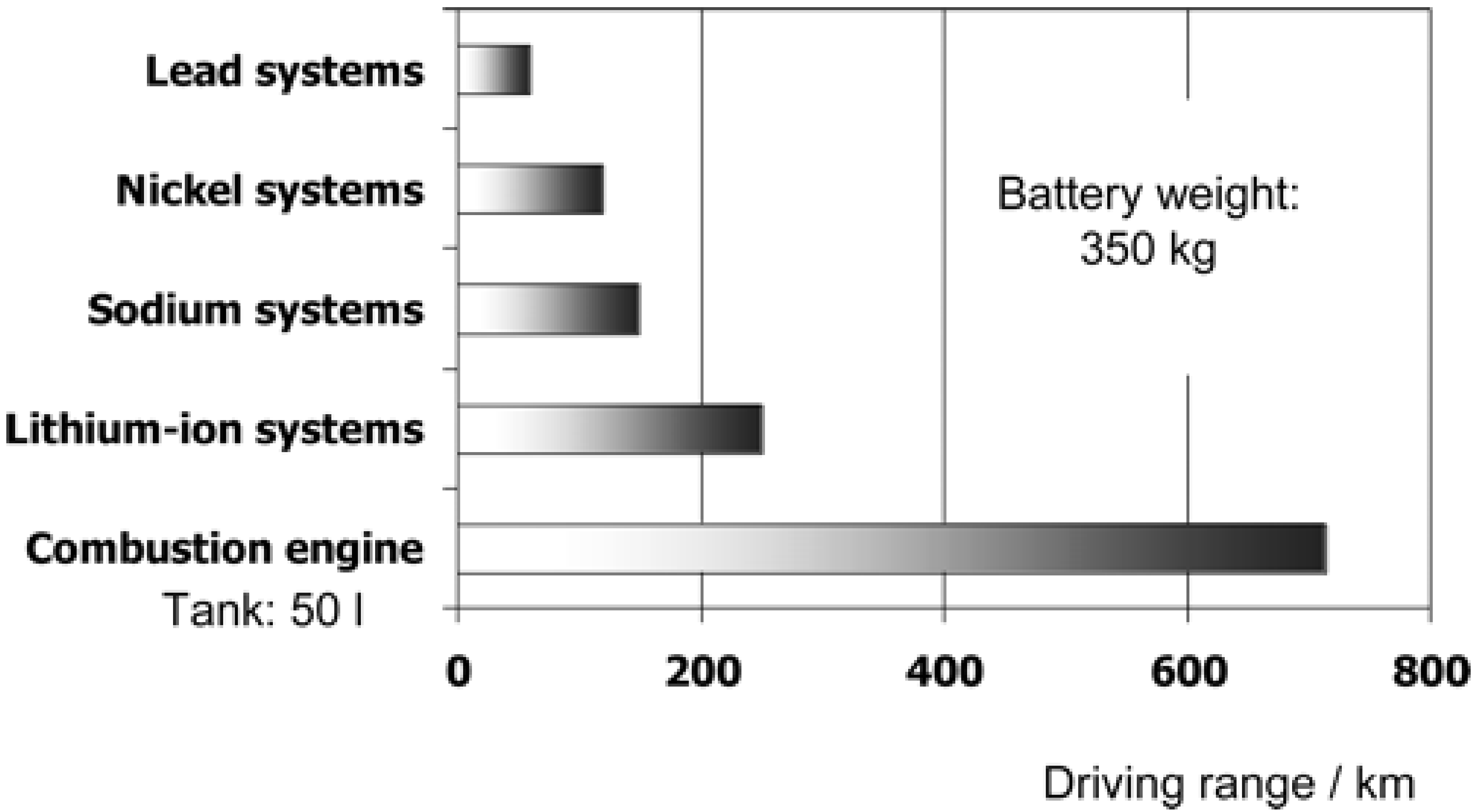
Sinusoidal Technology Transfer-Phase Lagging



Sinusoidal Technology Transfer-Phase Lagging

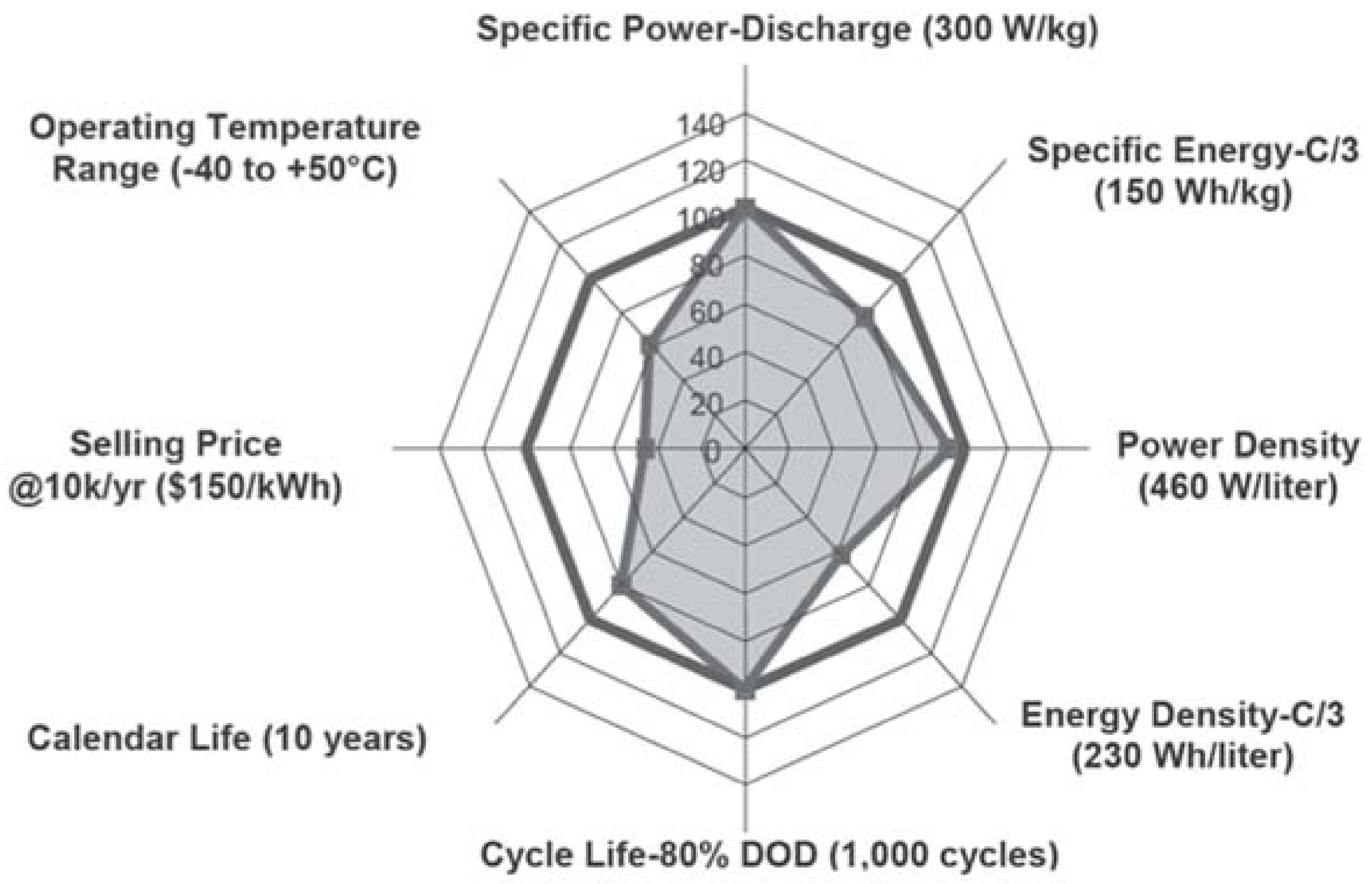


Driving Distance and "Technology"

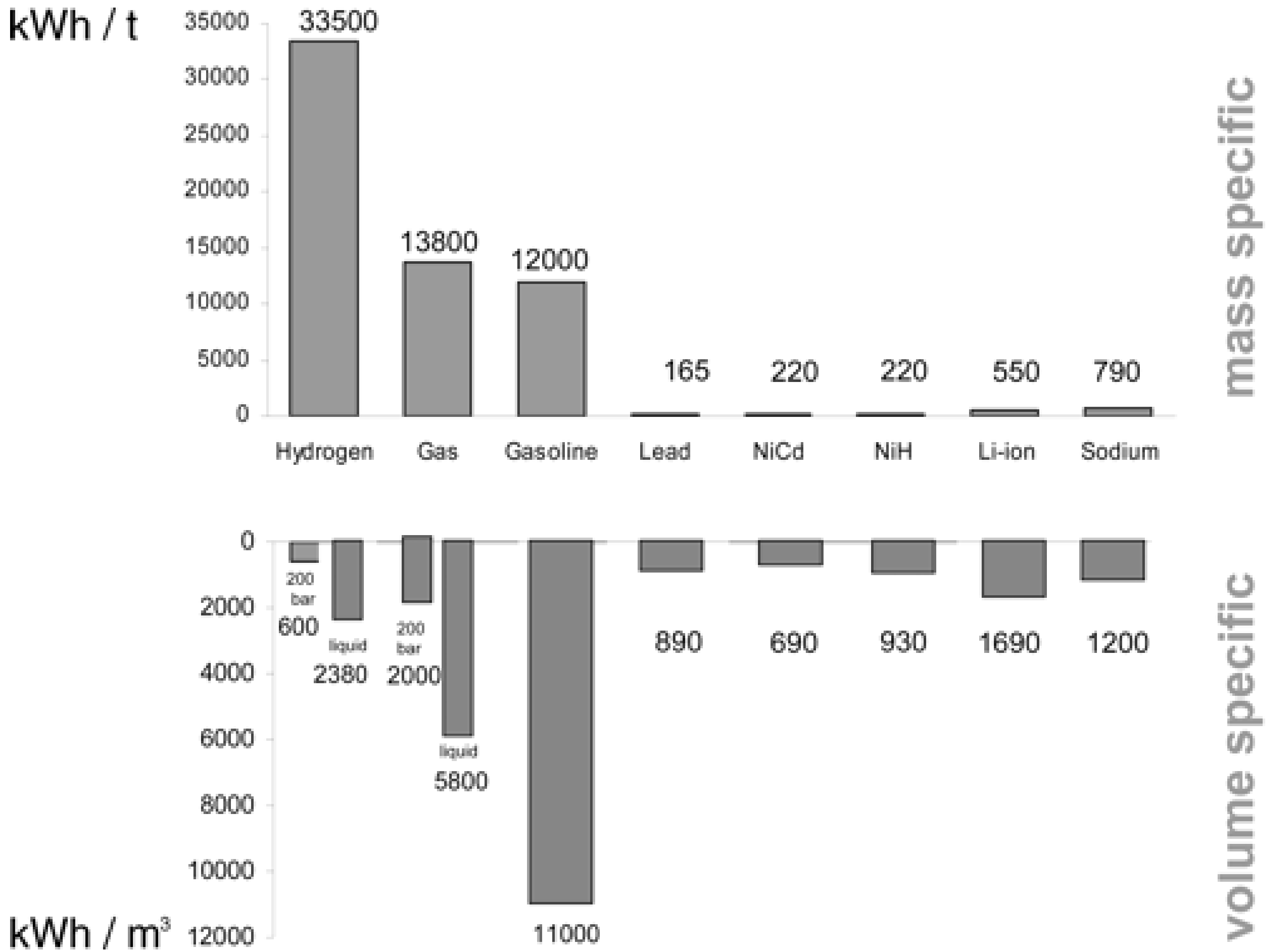


Comparison of the driving ranges for a vehicle powered by various battery systems or a gasoline-powered combustion engine.

The Challenges to Meet…



A battery technology spider chart for EVs. The 100% line equals the DOE target for HEVs and USABC target for EVs; the gray area and line represent technological achievements



Theoretical specific energies [(kW h)/ton] and energy densities [(kW h)/m^3] of various rechargeable battery systems compared to fuels, such as gasoline, natural gas, and hydrogen.

Nernst Equation

$$b\text{B} + c\text{C} + \dots \rightleftharpoons m\text{M} + n\text{N} + \dots$$

$$\Delta G = -zF\varepsilon$$

$$\Delta G = \Delta G^0 + RT\ln Q$$

$$Q = \frac{a_M^m\, a_N^n\, \dots}{a_A^a a_B^b\, \dots} = \frac{\Pi[\,products\,]}{\Pi[\,reactants\,]}$$

$$\Delta G^0 = -zF\varepsilon^0$$

$$-zF\varepsilon = -zF\varepsilon^0 + RT\ln Q$$

$$\varepsilon = \varepsilon^0 - \frac{RT}{zF}\ln Q$$

$$\varepsilon = \varepsilon^0 + \frac{RT}{zF}\ln\frac{1}{Q}$$

$$\varepsilon = \varepsilon^0 + \frac{RT}{zF}\ln\frac{\Pi[\,reactants\,]}{\Pi[\,products\,]}$$

Metal-Metal (M/M^{+z}) ion Potential

$$E = E^0 + \frac{RT}{zF} ln \frac{[M^{z+}][e]^z}{[M]}$$

$$E = E^0 + \frac{RT}{zF} ln [M^{z+}]$$

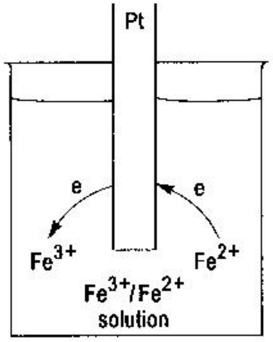
$$E = E^0 + 2.303 \frac{RT}{zF} log [M^{z+}]$$

$$E = E^0 , [M^{z+}] = 1$$

$$E = E^0 + \frac{0.0592}{z} log [M^{z+}]$$

When $T = 298\ ^oK$

RedOx Potentials



$$Fe^{+3} + e \rightleftharpoons Fe^{+2}$$

$$Ox + ze \rightleftharpoons Red$$

$$MnO_4^- + 5e + 8H^+ \rightleftharpoons Mn^{+2} + 4H_2O$$

In the RedOx system the electrode must be made of an inert metal, usually Pt.
This electrode act as a sink or source for electrons. The electrolyte system contains two substances; electron donors and electron acceptors.

Nernst Equation for *RedOx* Couple

$$E = E^0 + \frac{RT}{zF} ln \frac{Ox}{Red}$$

or

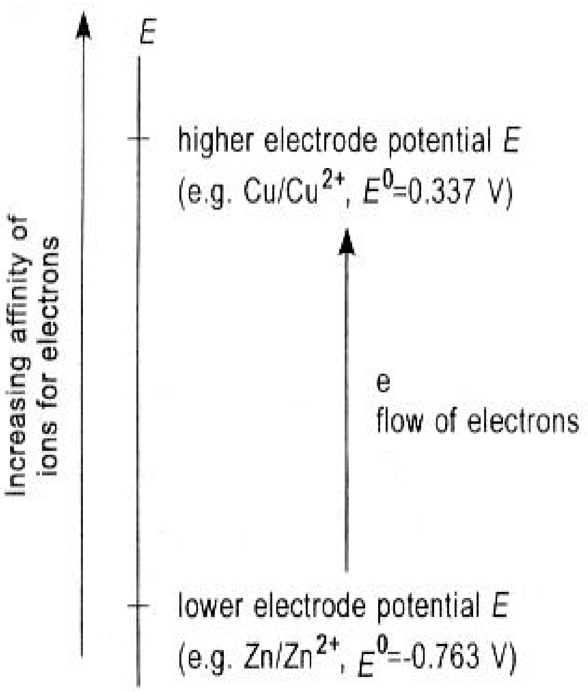
$$E = E^0 + 2.303 \frac{RT}{zF} log \frac{Ox}{Red}$$

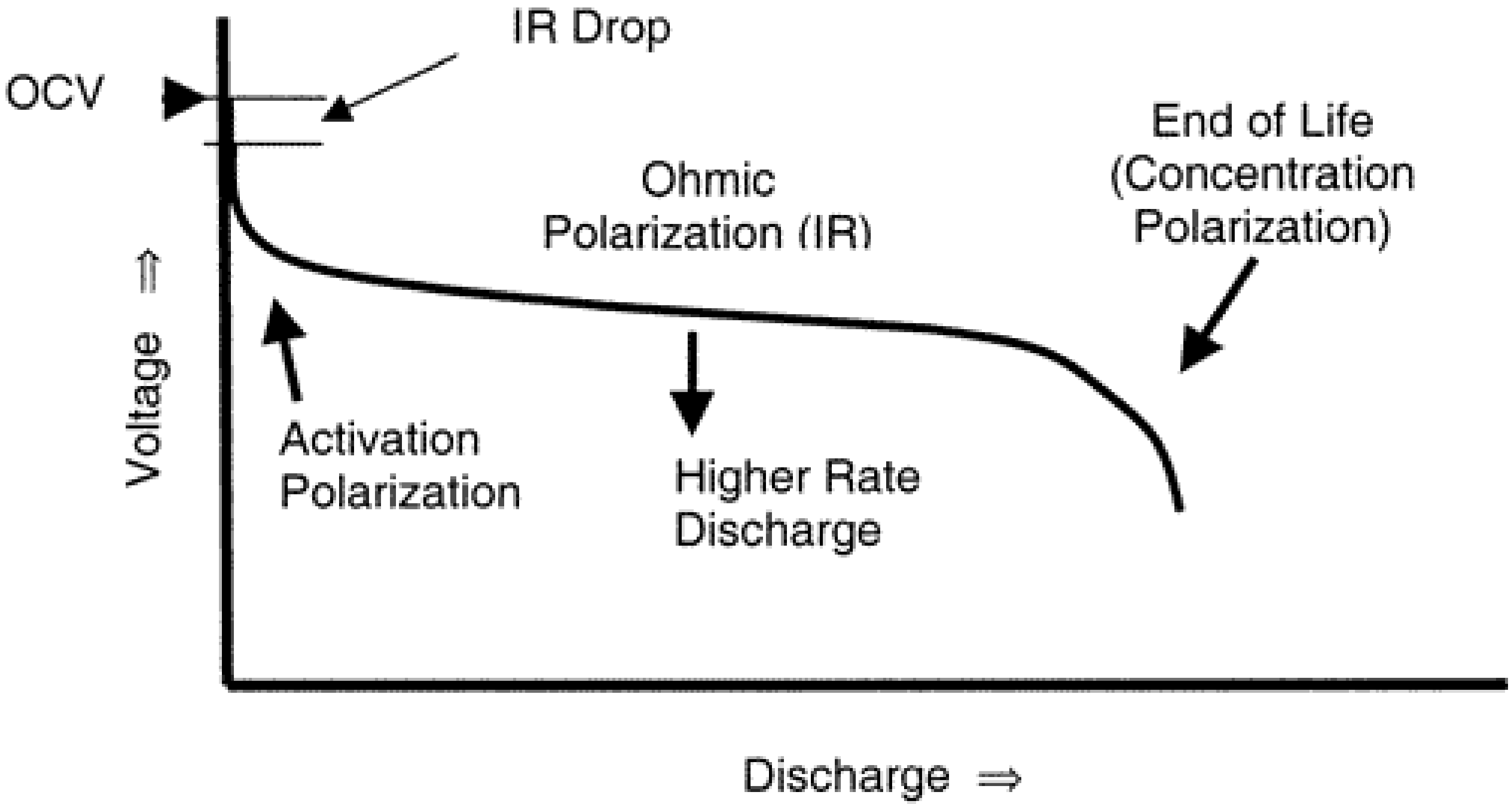
$$when\ [Red] = 1\ and\ [Ox] = 1$$

$$E = E^0$$

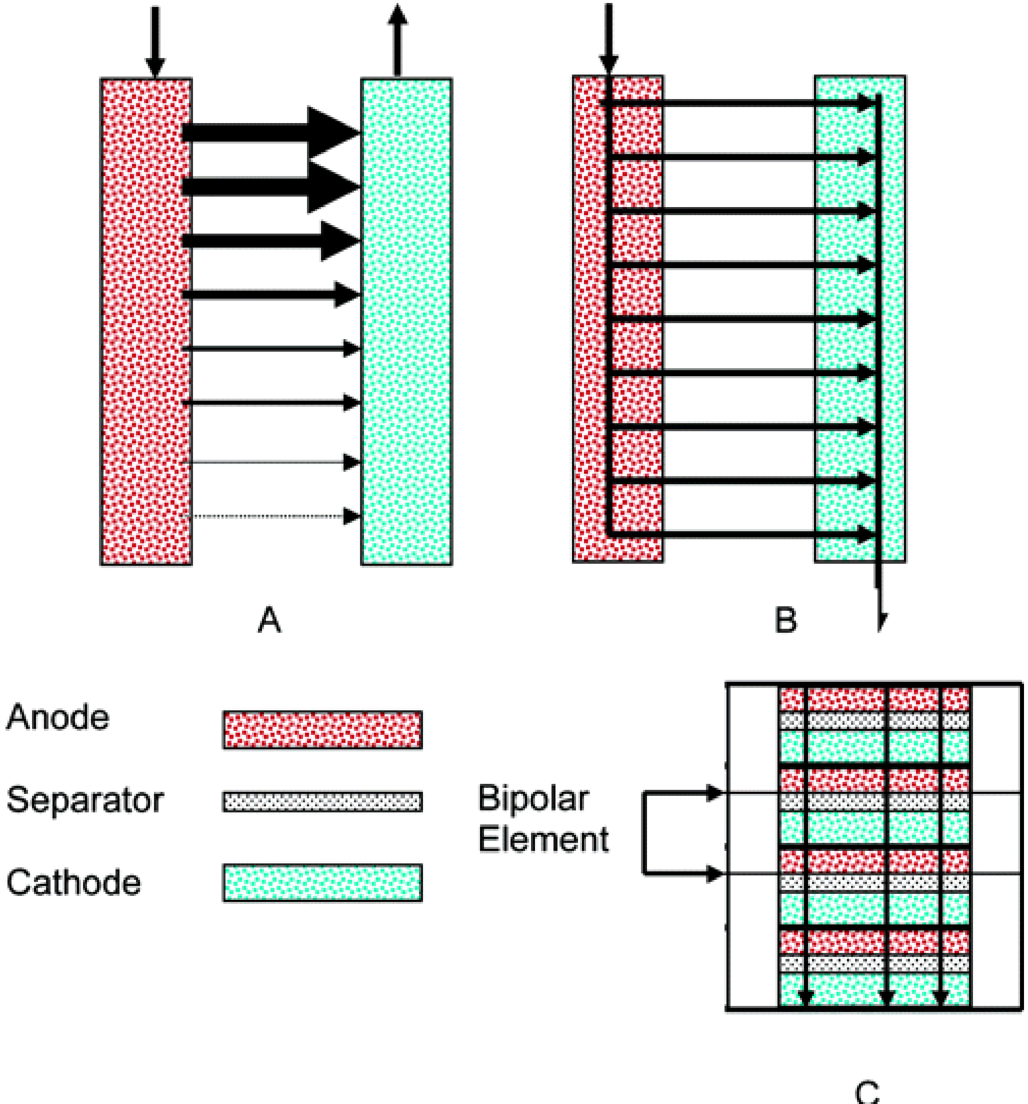
Standard Electrode Potentials

Metal/Metal-ion Couple	Electrode Reaction	Standard Value (V)
Au/Au^{+}	$Au^{+} + e \Leftrightarrow Au$	1.692
Au/Au^{3+}	$Au^{3+} + 3e \Leftrightarrow Au$	1.498
Pd/Pd^{2+}	$Pd^{2+} + 2 \Leftrightarrow Pd$	0.951
Cu/Cu^{+}	$Cu^{+} + e \Leftrightarrow Cu$	0.521
Cu/Cu^{2+}	$Cu^{2+} + 2e \Leftrightarrow Cu$	0.3419
Fe/Fe^{3+}	$Fe^{3+} + 3e \Leftrightarrow Fe$	−0.037
Pb/Pb^{2+}	$Pb^{2+} + 2e \Leftrightarrow Pb$	−0.1262
Ni/Ni^{2+}	$Ni^{2+} + 2e \Leftrightarrow Ni$	−0.257
Co/Co^{2+}	$Co^{2+} + 2e \Leftrightarrow Co$	−0.28
Fe/Fe^{2+}	$Fe^{2+} + 2e \Leftrightarrow Fe$	−0.447
Zn/Zn^{2+}	$Zn^{2+} + 2e \Leftrightarrow Zn$	−0.7618
Al/Al^{3+}	$Al^{3+} + 3e \Leftrightarrow Al$	−1.662
Na/Na^{+}	$Na^{+} + e \Leftrightarrow Na$	−2.71

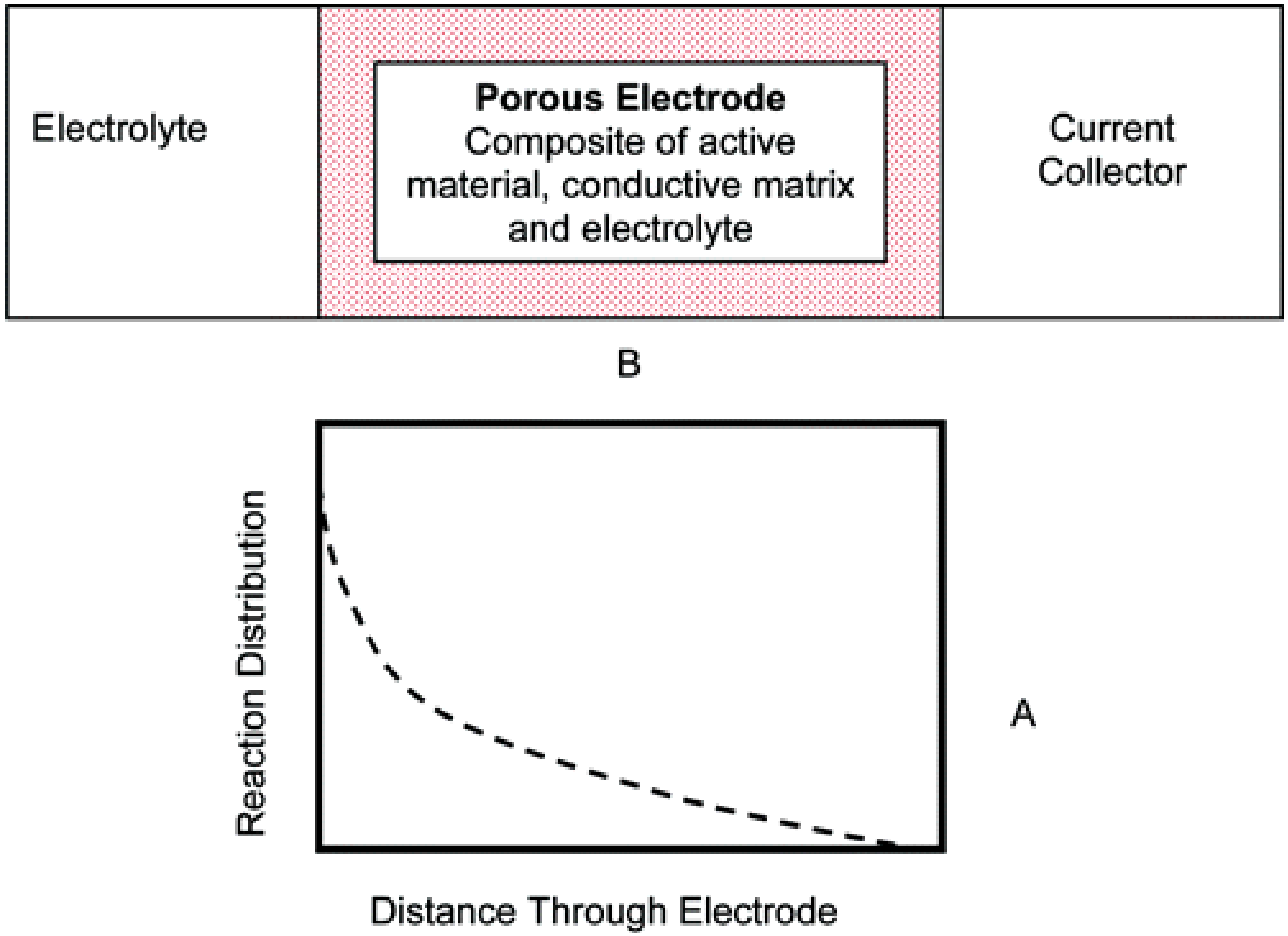




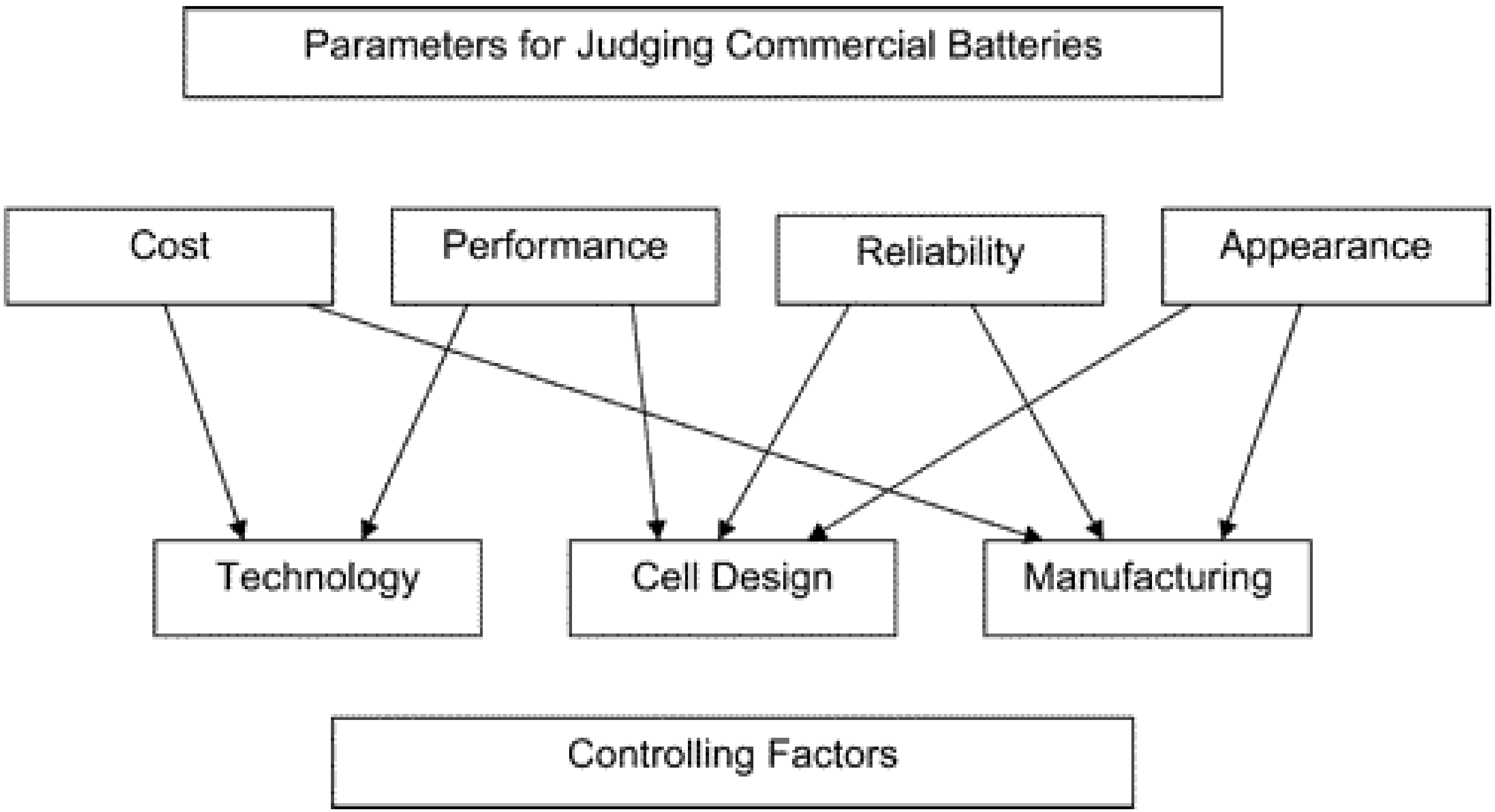
Typical discharge curve of a battery, showing the influence of the various types of polarization.



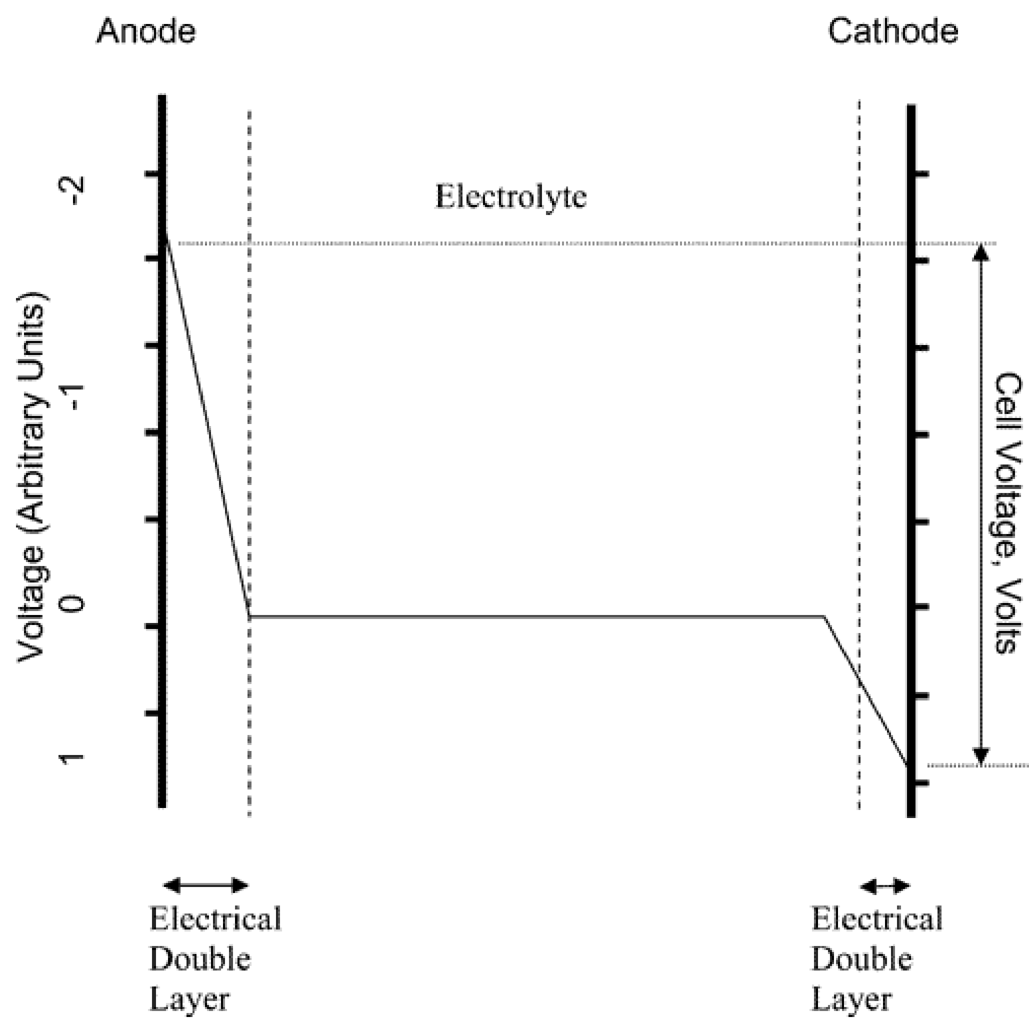
Primary current distribution on the front surface of the electrodes based on Kirkhof's law calculation for three different cell constructions: (A) Both connections to the cell are at the top. The higher resistance path at the bottom sections of the electrode reduces the current flow and results in a nonuniform current distribution. (B) All paths have equal resistance, and a uniform current distribution results. (C) The bipolar construction has equal resistance from one end to the other.



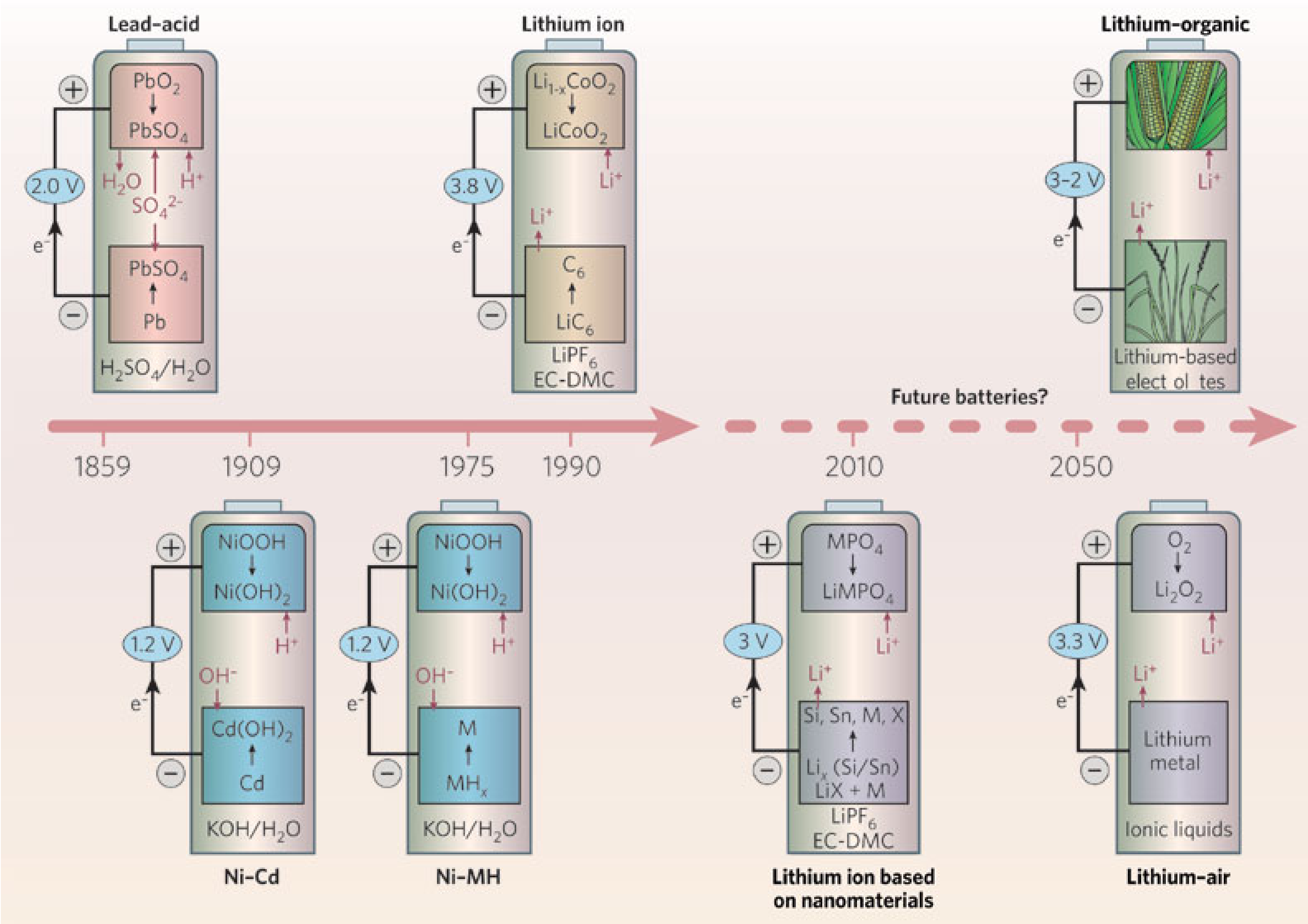
Schematic porous electrode structure: (A) Electrons from the external circuit flow in the current collector which has contact to the conductive matrix in the electrode structure. The redox reaction at the electrode produces electrons that enter the external circuit and flow through the load to the cathode, where the reduction reaction at the cathode accepts the electron from the external circuit and the reduction reaction. The ions in the electrolyte carry the current through the device. (B) The reaction distribution in the porous electrode is shown for the case where the conductivity of the electrode matrix is higher than the conductivity of the electrolyte.



How batteries are judged by users and the factors that control these criteria.



Voltage levels in the various sections of the unit cell of a battery, fuel cell, or electrochemical capacitor. The structure and composition of the electrical double layer differ at the anode and cathode.



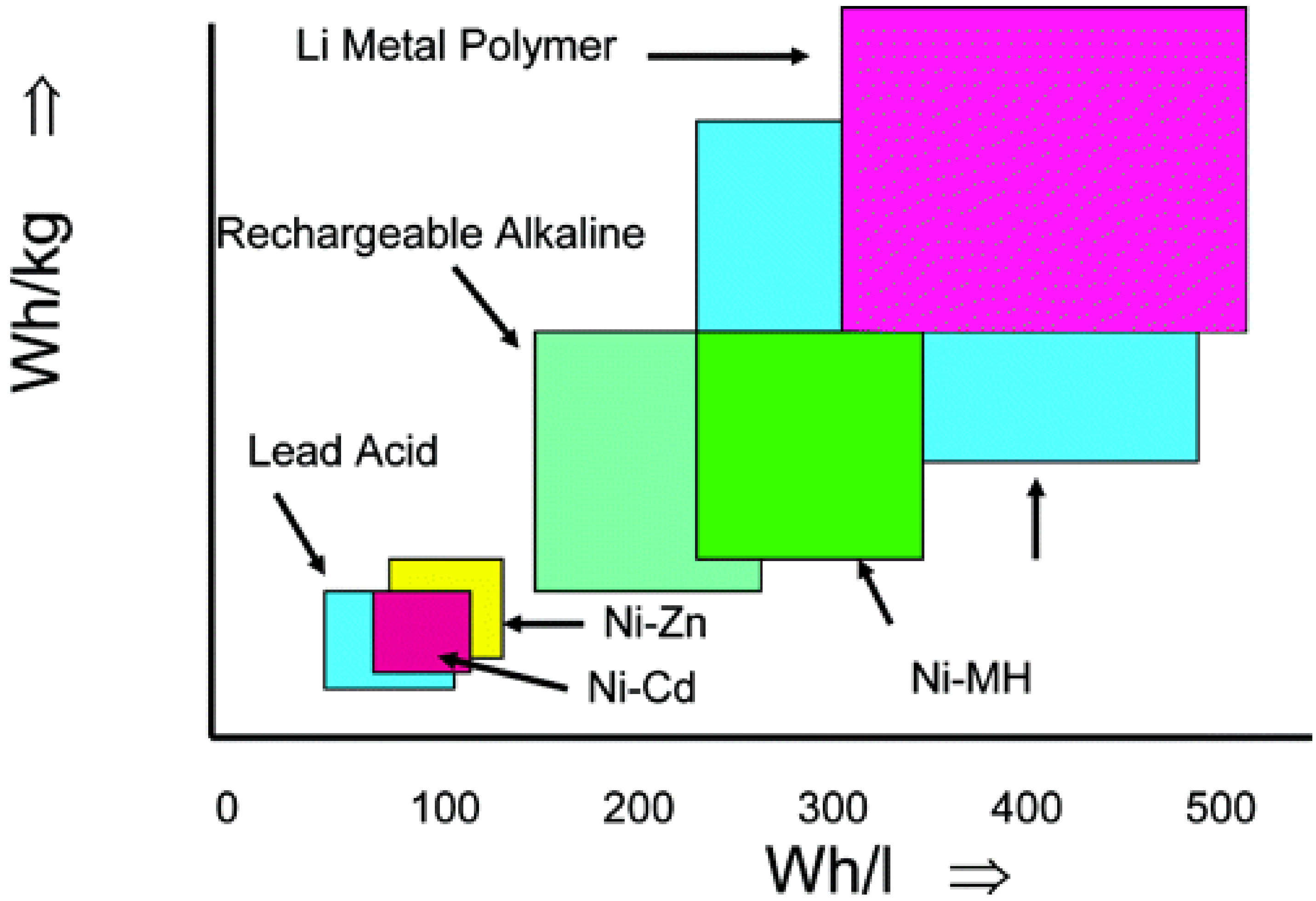
Present-day battery technologies are being outpaced by the ever-increasing power demands from new applications. As well as being inherently safe, batteries of the future will have to integrate the concept of environmental sustainability.

Energy Storage-Primary Systems

CELL TYPE	OCV	PROFILE	Wh/kg	Wh/l	OPER TEMP
LECLANCHE	1.5	SLOPING	65	100	-5 TO 45 C
ALKALINE	1.5	MOD SLOPE	95	220	-20 TO 55 C
MERCURY	1.35	FLAT	325	470	0 TO 55 C
SILVER ZINC	1.6	FLAT	130	515	0 TO 55 C
ZINC AIR	1.45	FLAT	290	905	0 TO 50 C
Li/MnO_2	3.5	FLAT	200	400	-20 TO 55 C
Li/CF_X	3.1	FLAT	240	450	-20 TO 55 C
Li/FeS_2	1.6	FLAT	130	385	-20 TO 55 C
$Li/SOCl_2$	3.65	FLAT	350	900	-40 TO >70 C

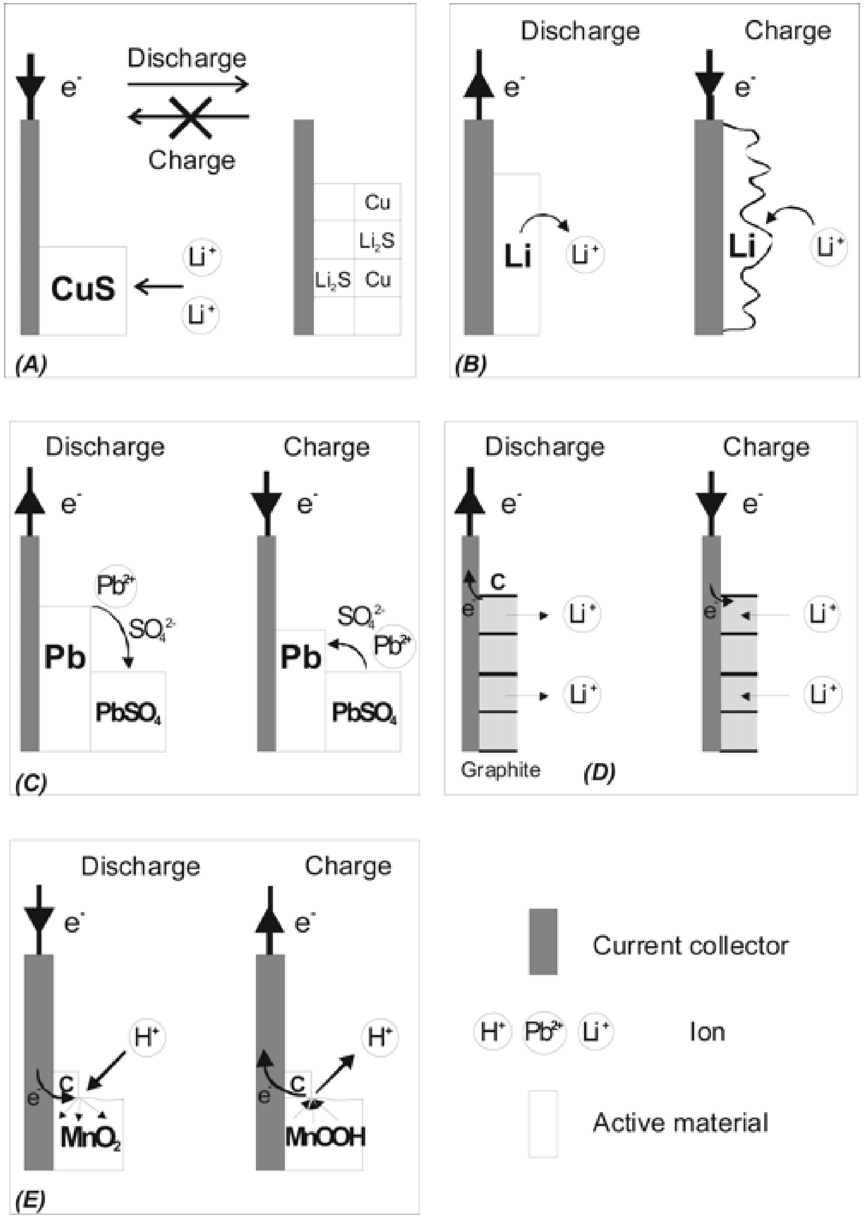
Energy storage capability of common commercial primary battery systems.

Energy Storage-Secondary Systems



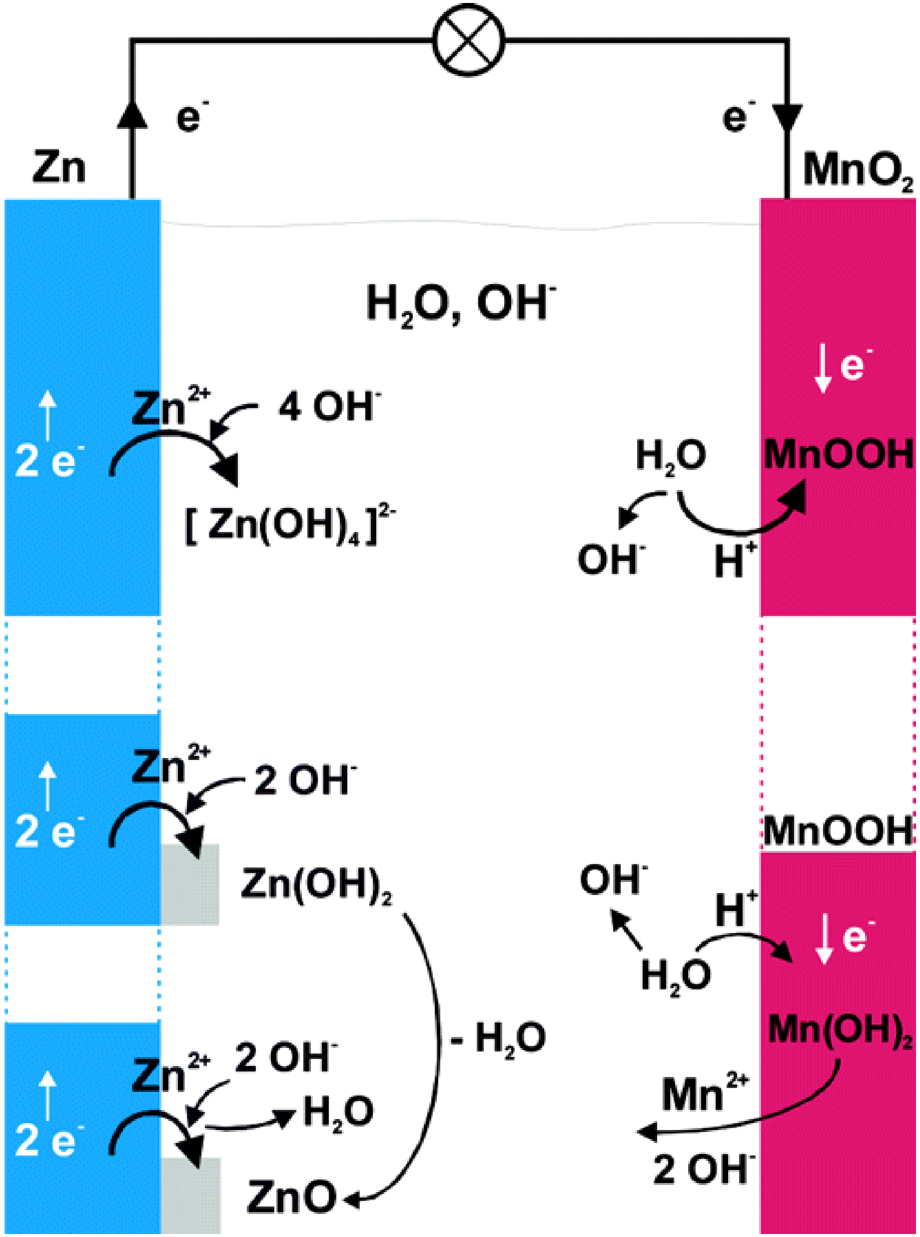
Energy storage capability of common rechargeable battery systems.

Charge-Discharge Mechanisms



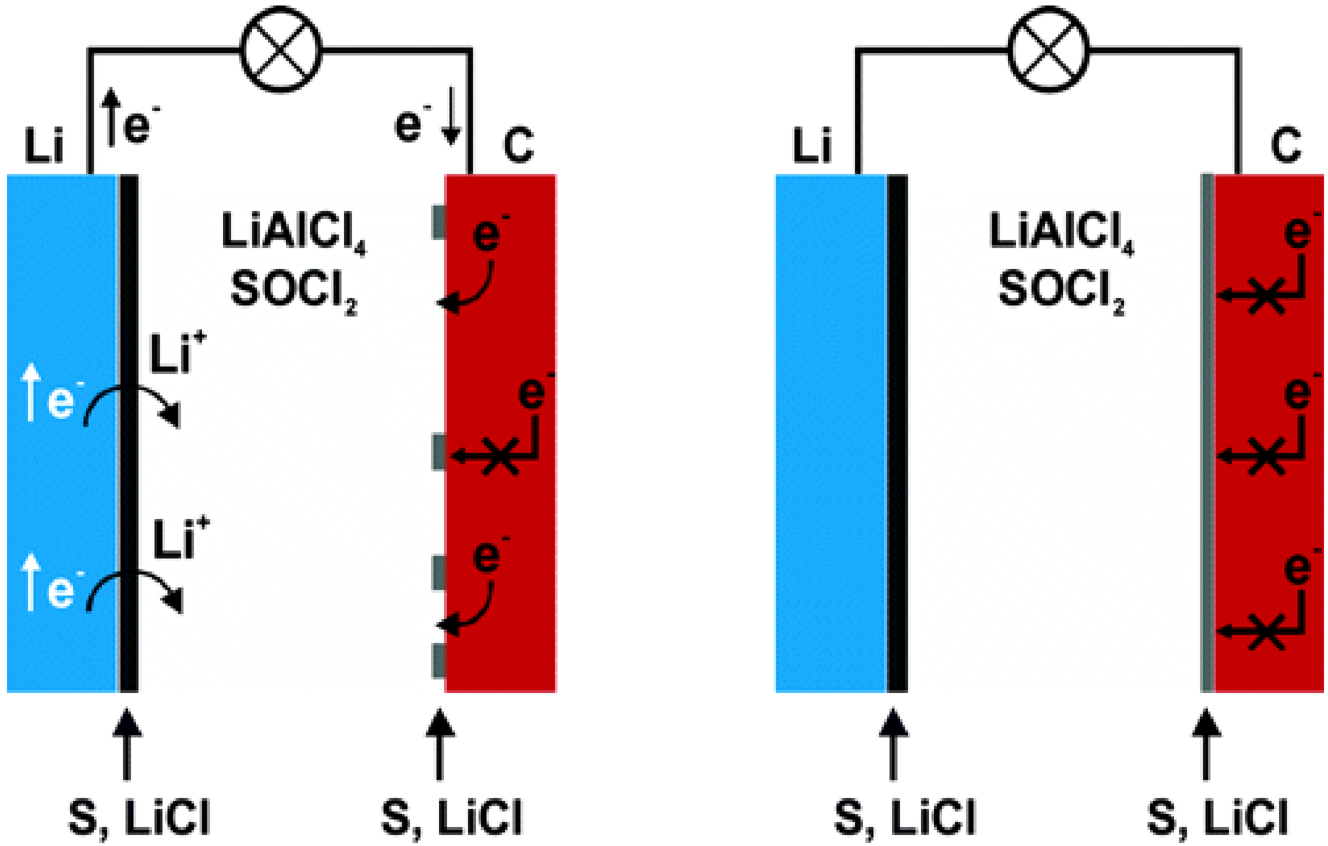
Schematics showing various discharge and charge mechanisms of battery electrodes, which serve as examples of the battery electrode charge/discharge mechanisms.

Discharge Mechanism of a Zn–MnO_2 Cell



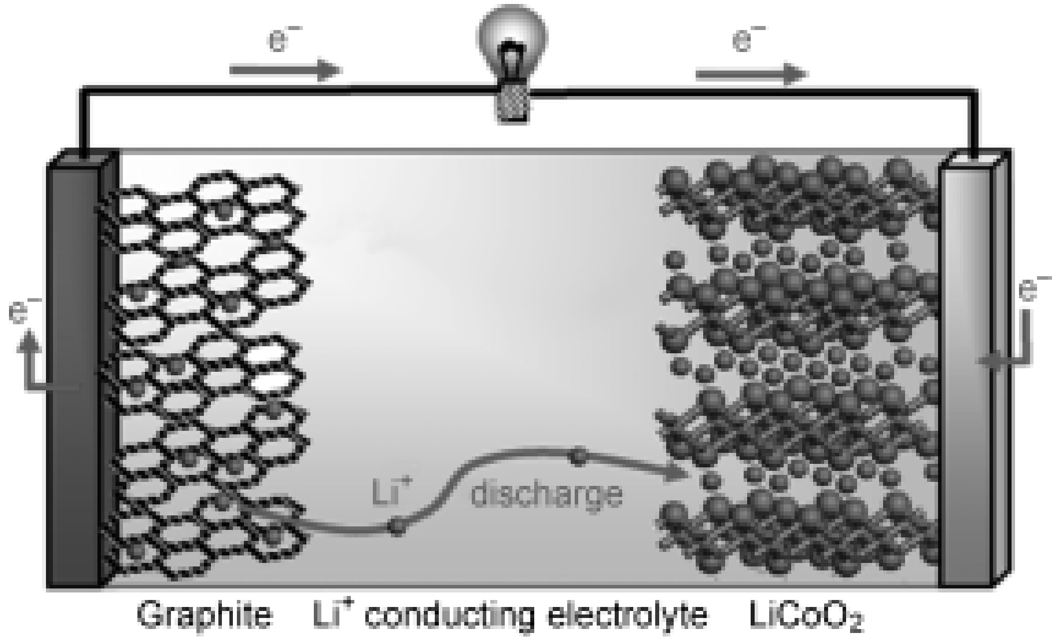
Discharge mechanism of a Zn–MnO_2 cell. From top to bottom, various stages of the discharge reaction are depicted. On the Zn side, the local change of the pH alters the composition of the discharge product.

Discharge Mechanism of a Li–$SOCl_2$ Cell



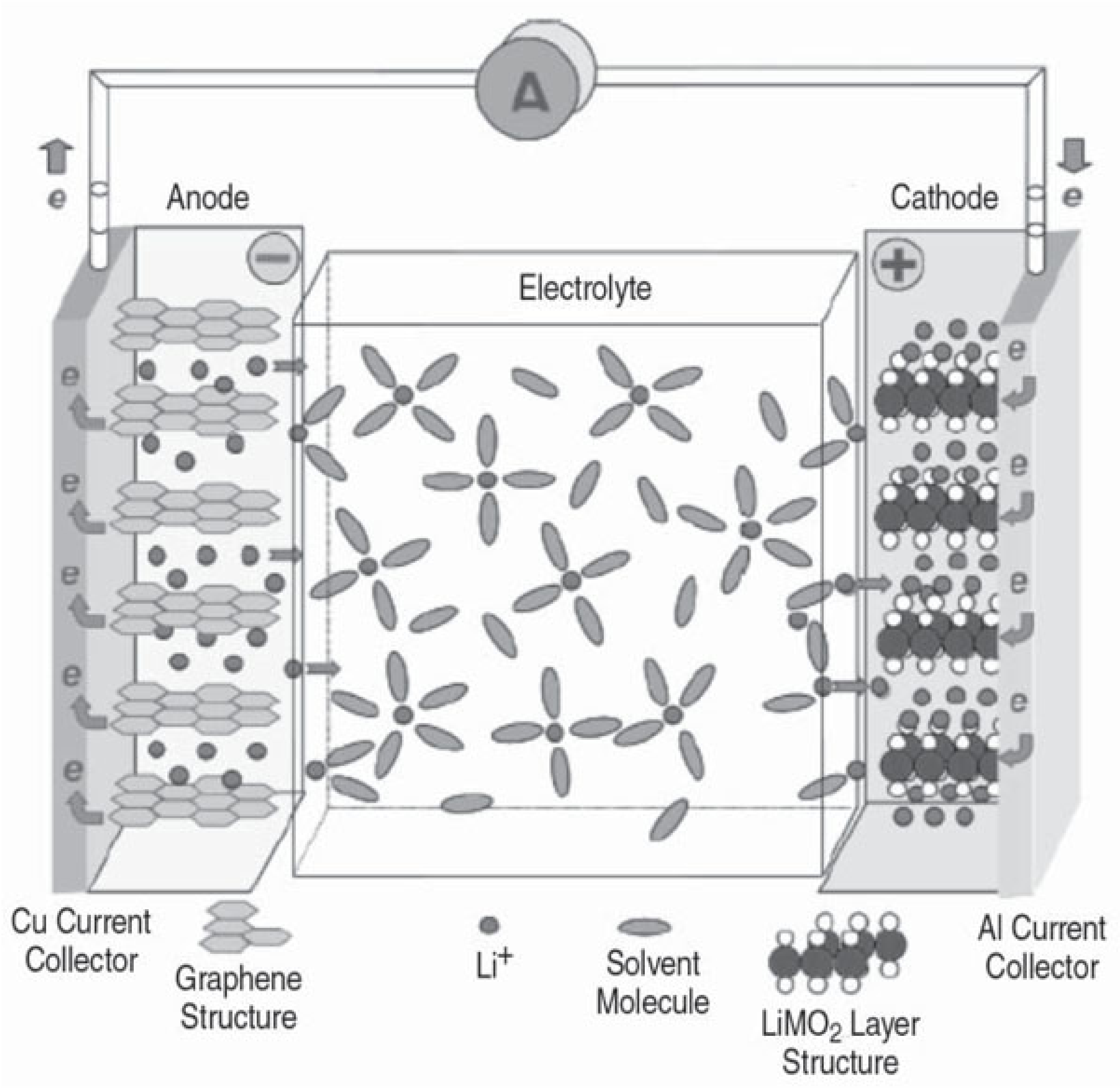
Discharge mechanism of a Li–$SOCl_2$ cell. The cell can operate until the surface of the carbon cathode is fully covered by electronically insulating LiCl and S discharge products. The Li–SO_2 cell is also a soluble cathode system with a cell construction similar to that of the Li–$SOCl_2$ cell. It follows a similar discharge reaction where the reaction product is LiS_2O_4.

Schematic of Li ion cells

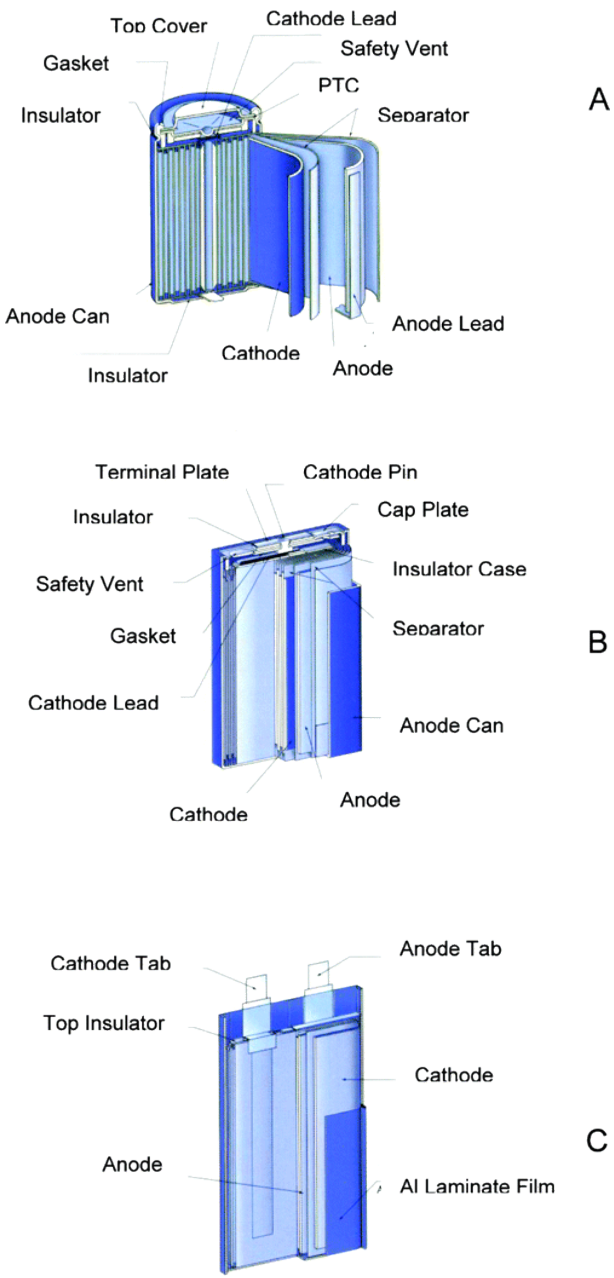


$$Li_xC_6 + Li_{1-x}CoO_2 \rightleftharpoons 6C + LiCoO_2$$

Schematic of Li ion cell

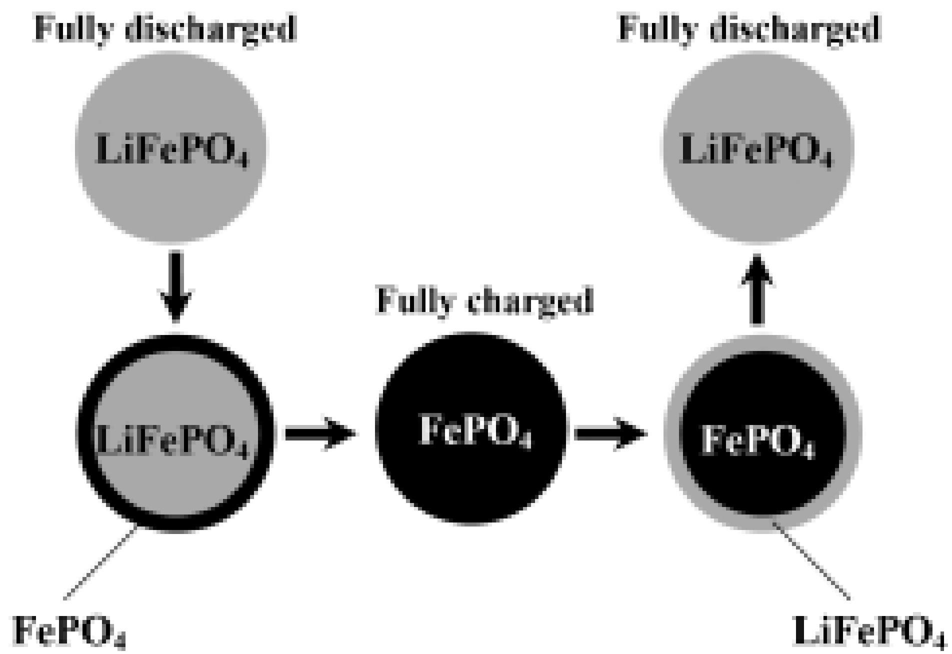


Construction of Li ion cells

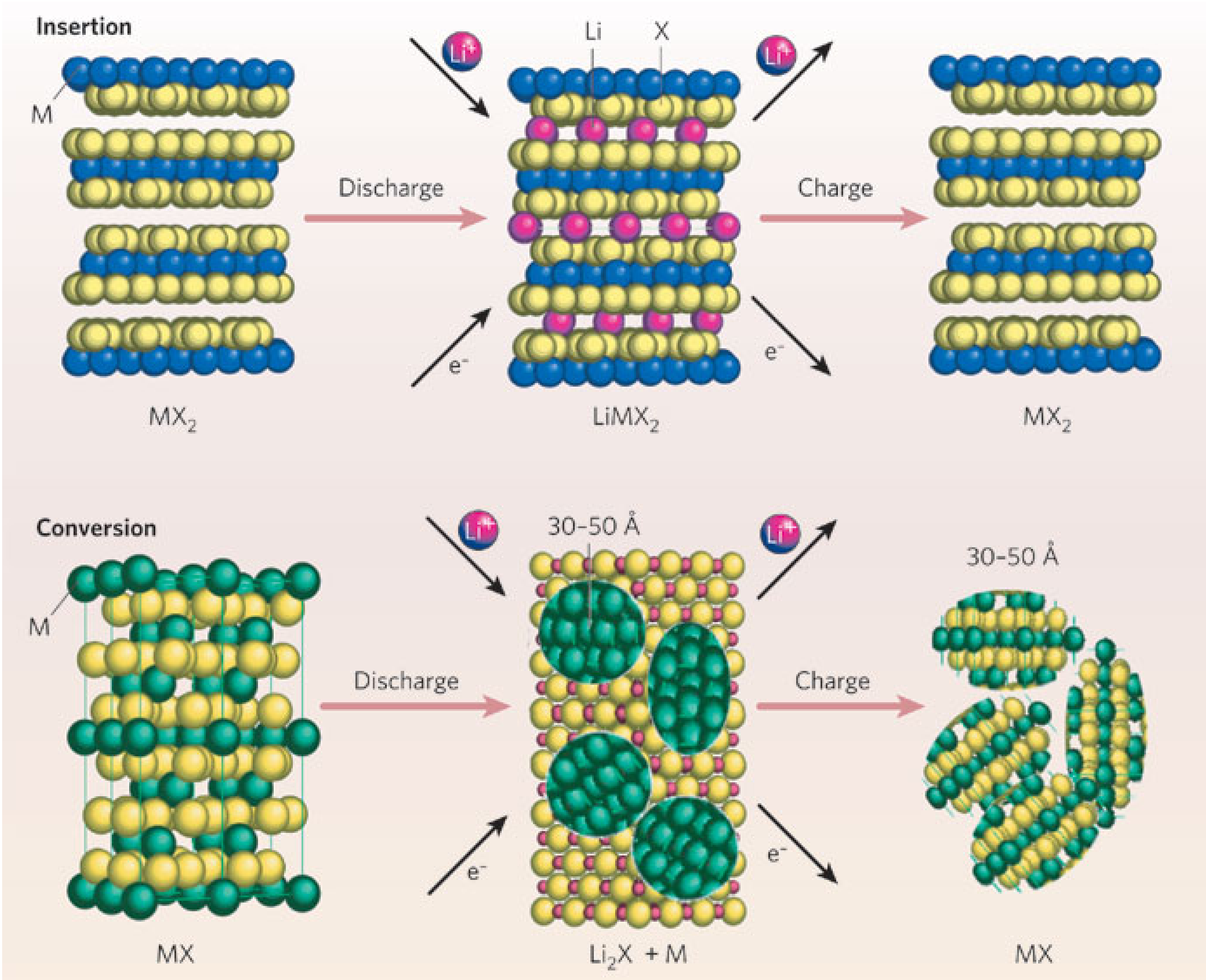


Construction of (A) cylindrical, (B) prismatic, and (C) polymer Li ion cells.

Charge/discharge of $LiFePO_4$

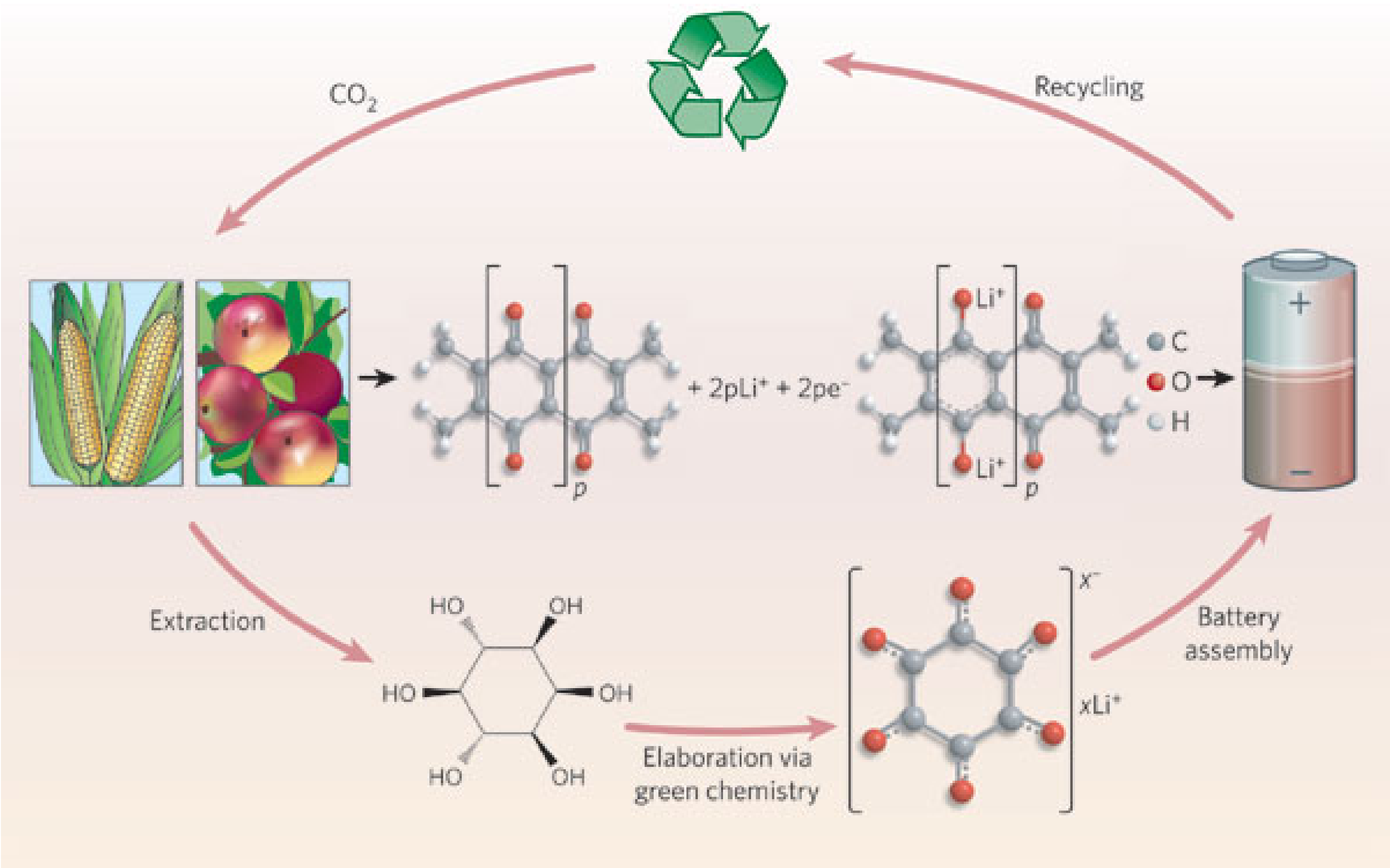


Schematic representation of the processes during charge/discharge of $LiFePO_4$.



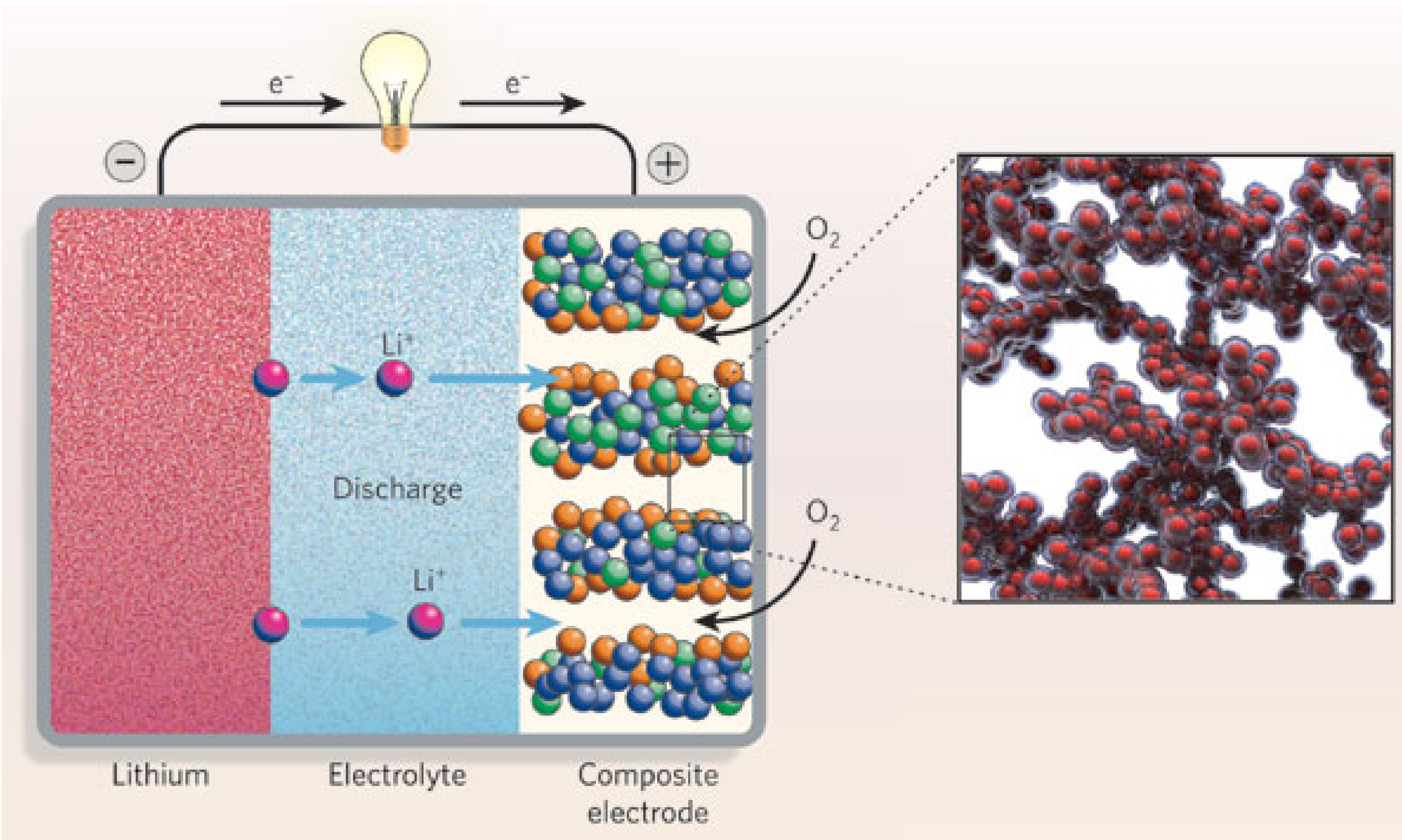
Schematic representation showing the contrasting reaction mechanisms occurring during discharge for insertion (top) and conversion reactions (bottom). The insertion reaction demonstrates a maximum of 1 electron transfer per transition metal (here designated M), whereas the conversion reaction can transfer 2 to 6 electrons

Green Future for Li Batteries



Proposed sustainable organic-based batteries based on electrode materials made from biomass. *Myo*-inositol extracted from corn can be used to prepare electrochemically active $Li_2C_6O_6$, whereas malic acid from apples can undergo polycondensation to a polyquinone that is electrochemically active to lithium (centre).

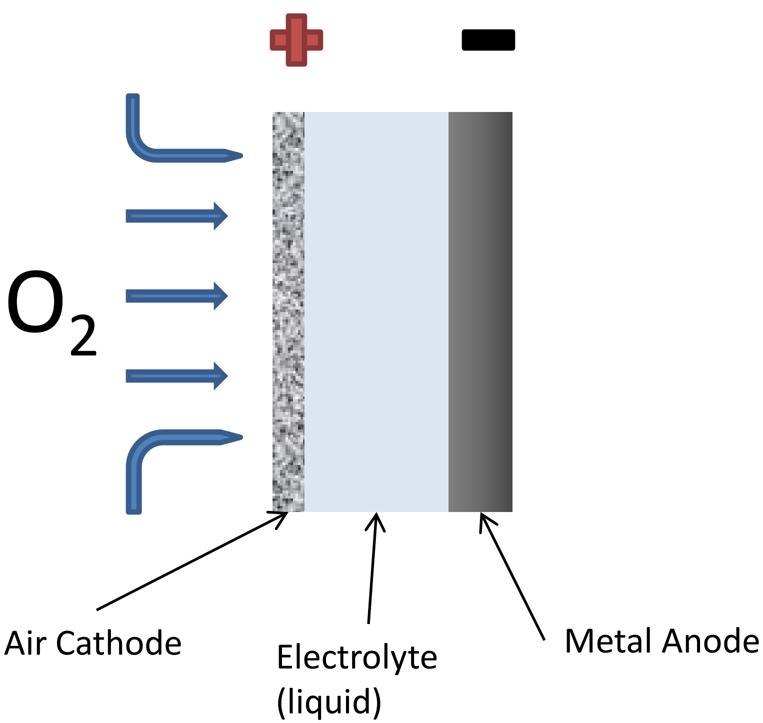
Air (Luft) Future for Li Batteries

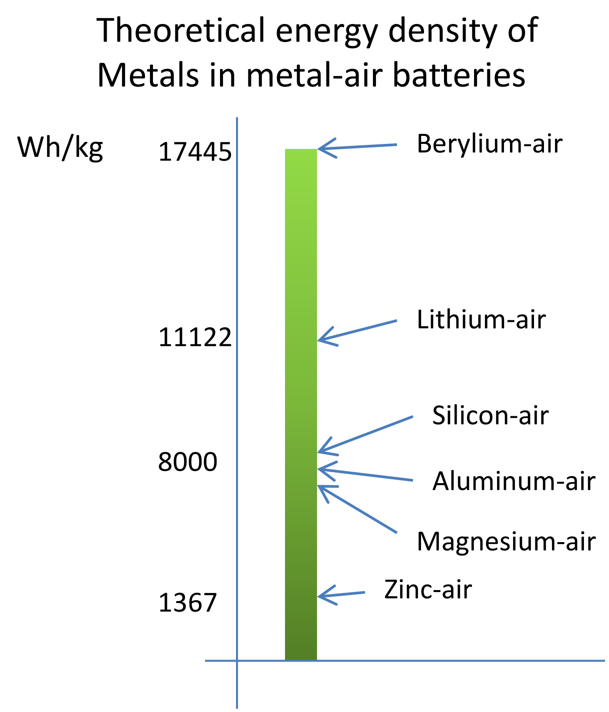


Left, the mechanism used in lithium–air batteries. Right, three-dimensional nano-architectured electrodes made from depositing 10- to 20-nm-thick layers of MnO_2 onto a carbon foam using a low-temperature process that could be used to enhance the kinetics of the lithium–air electrode

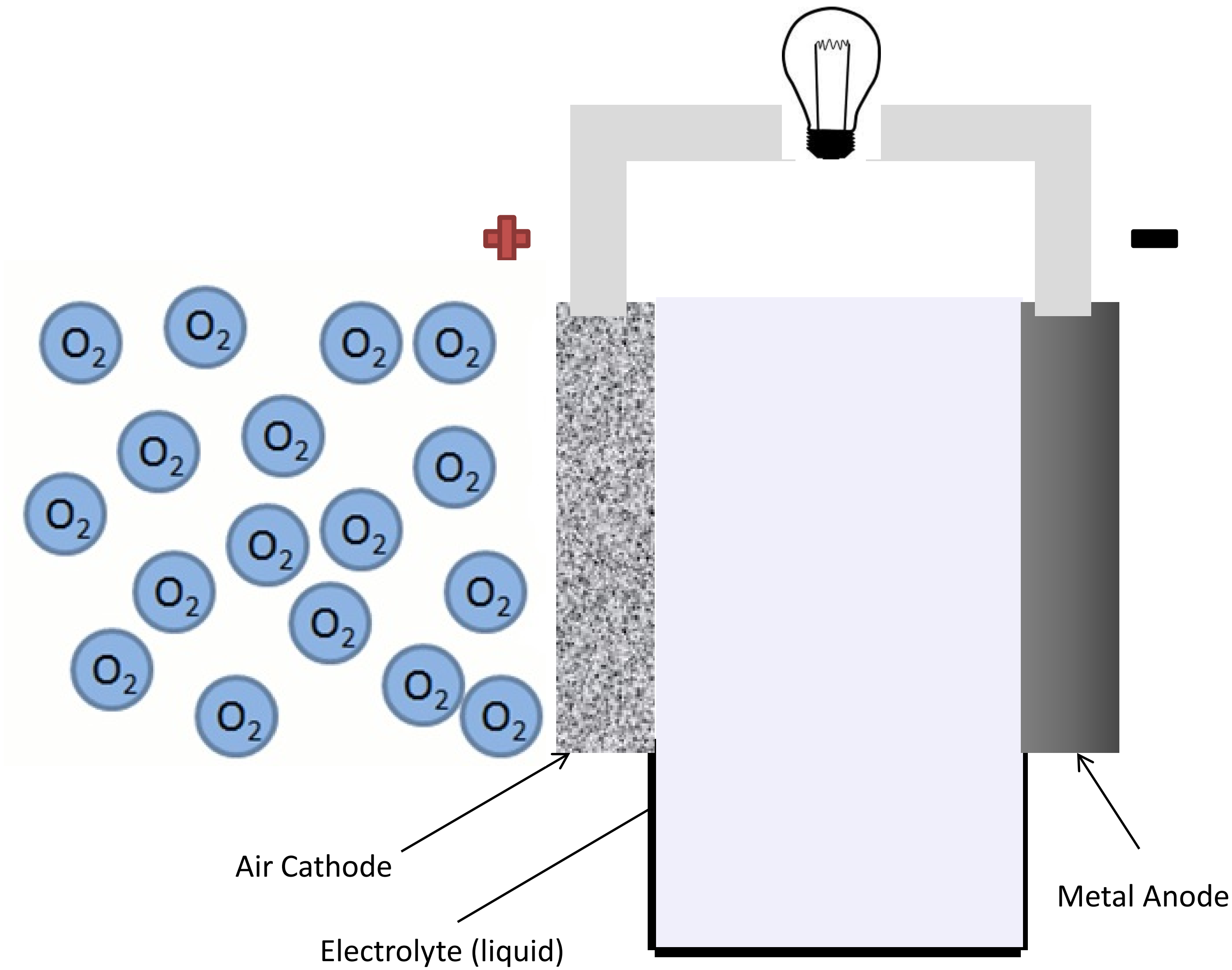
Metal-Air Batteries

- Oxidation of metal generates electricity
  - Results in metal oxide waste

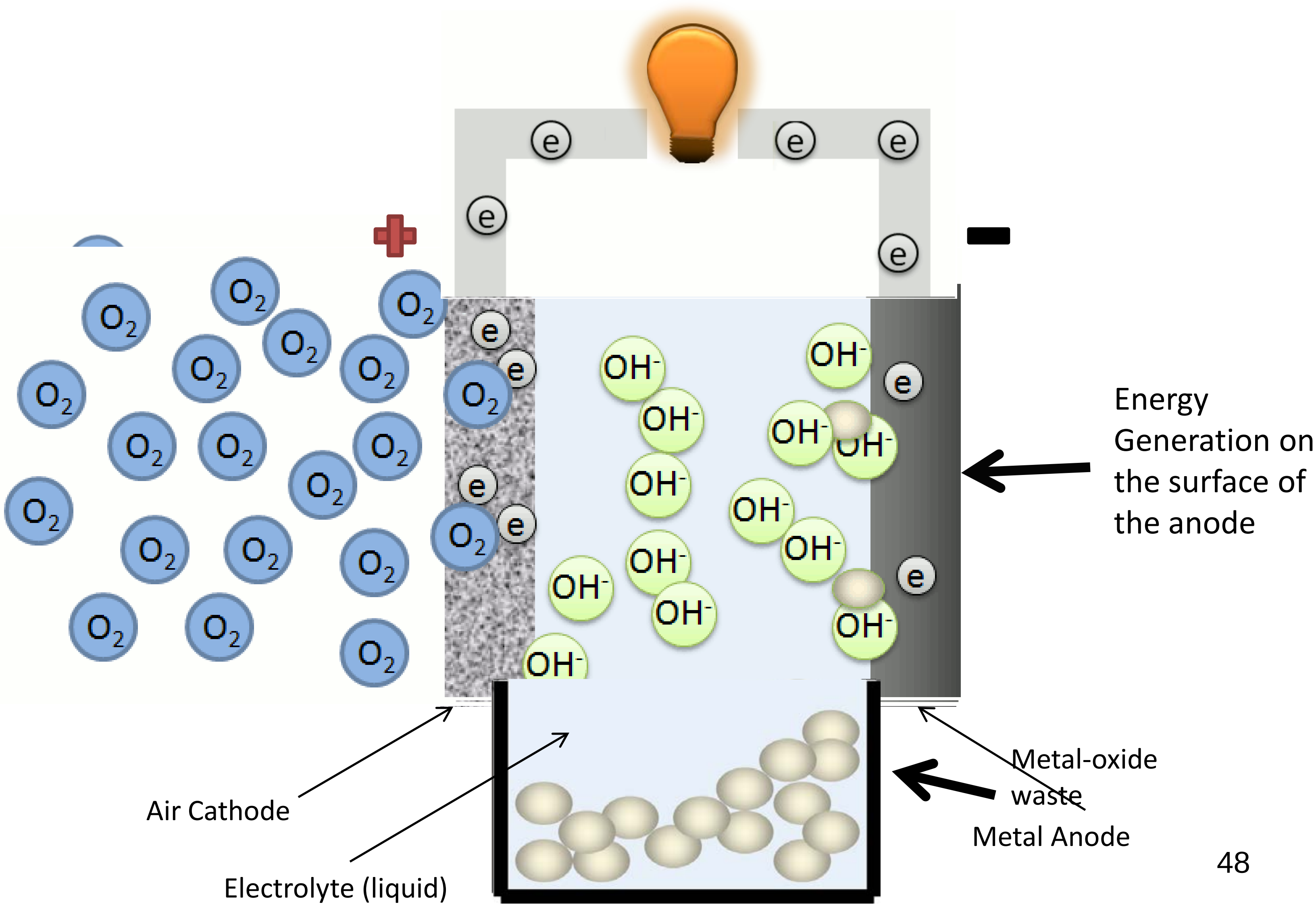




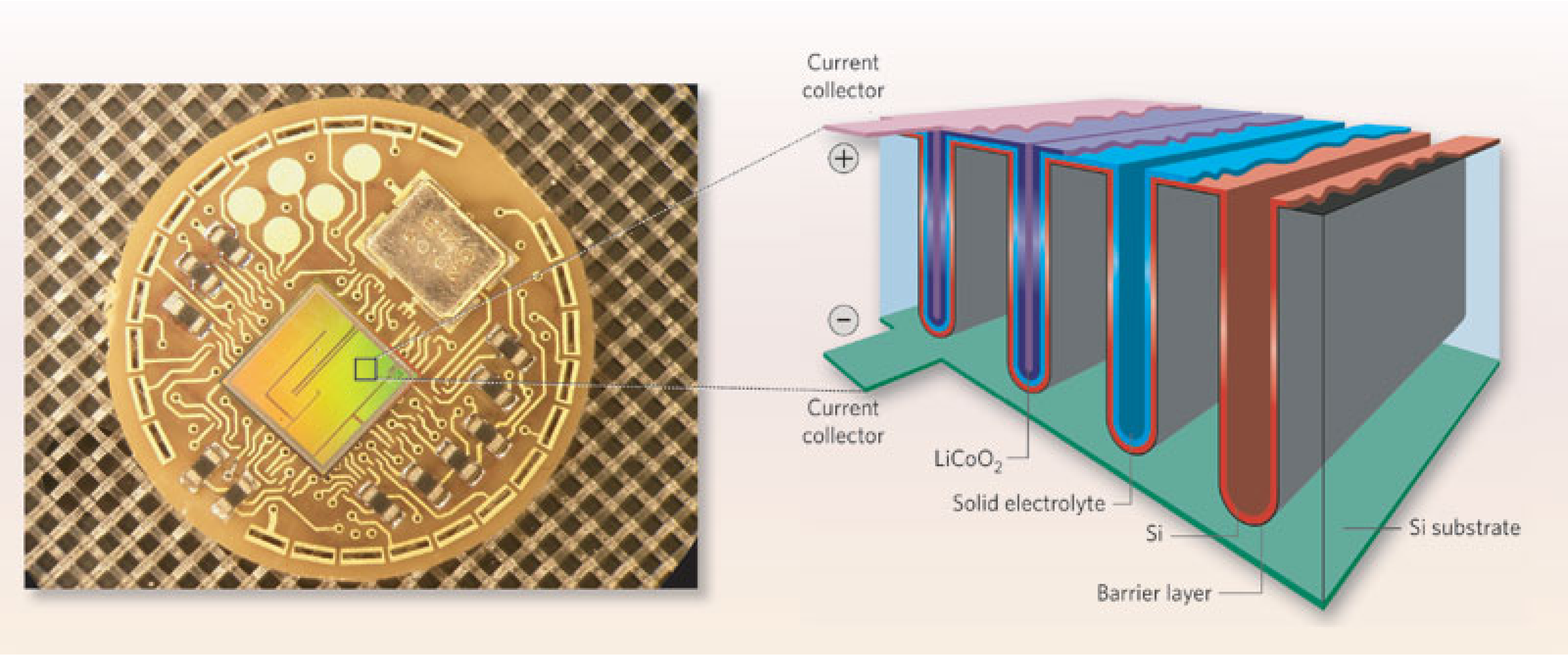
Metal-Air Battery



Metal-Air Battery

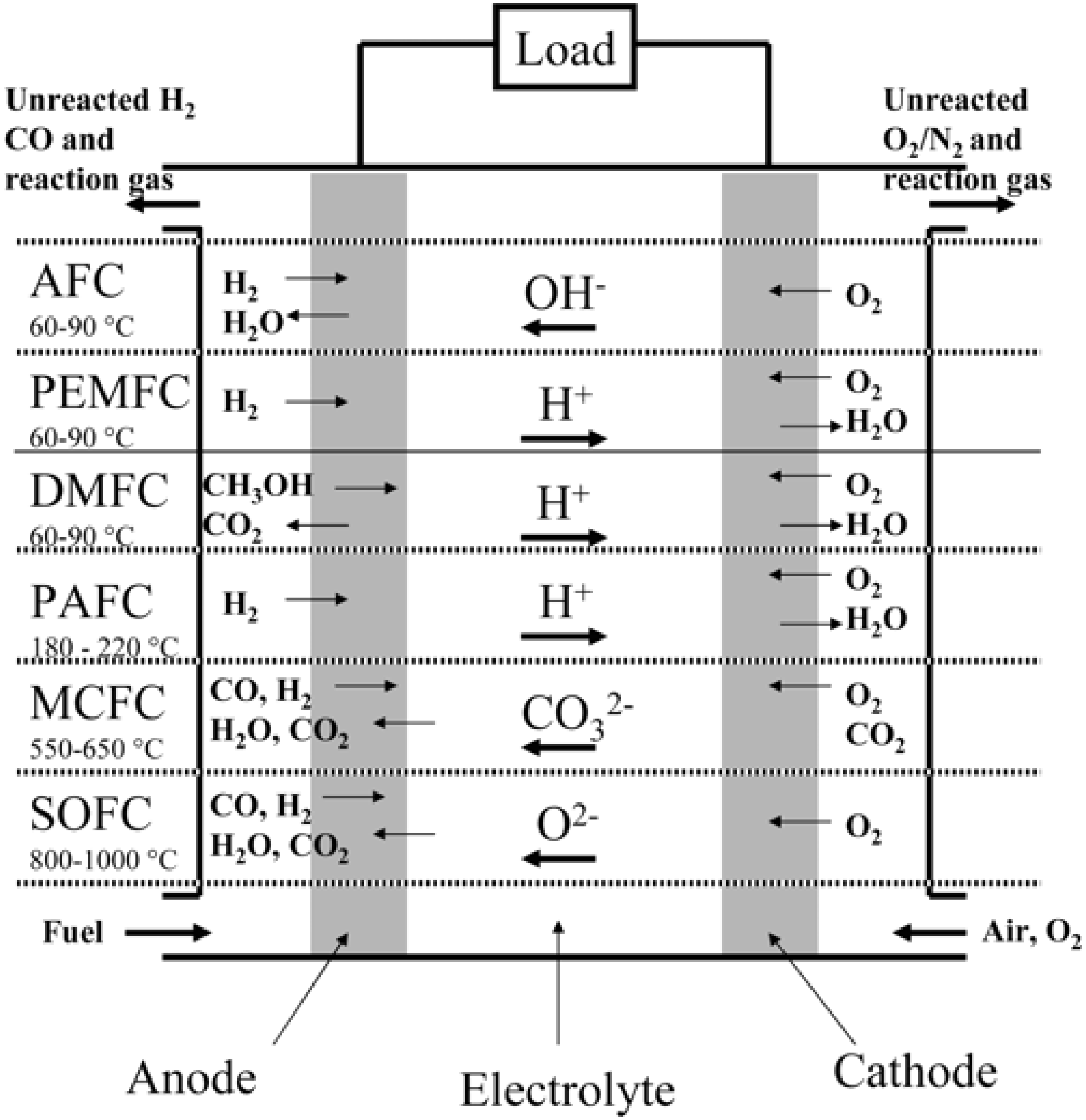


Going Miniature in Li Batteries

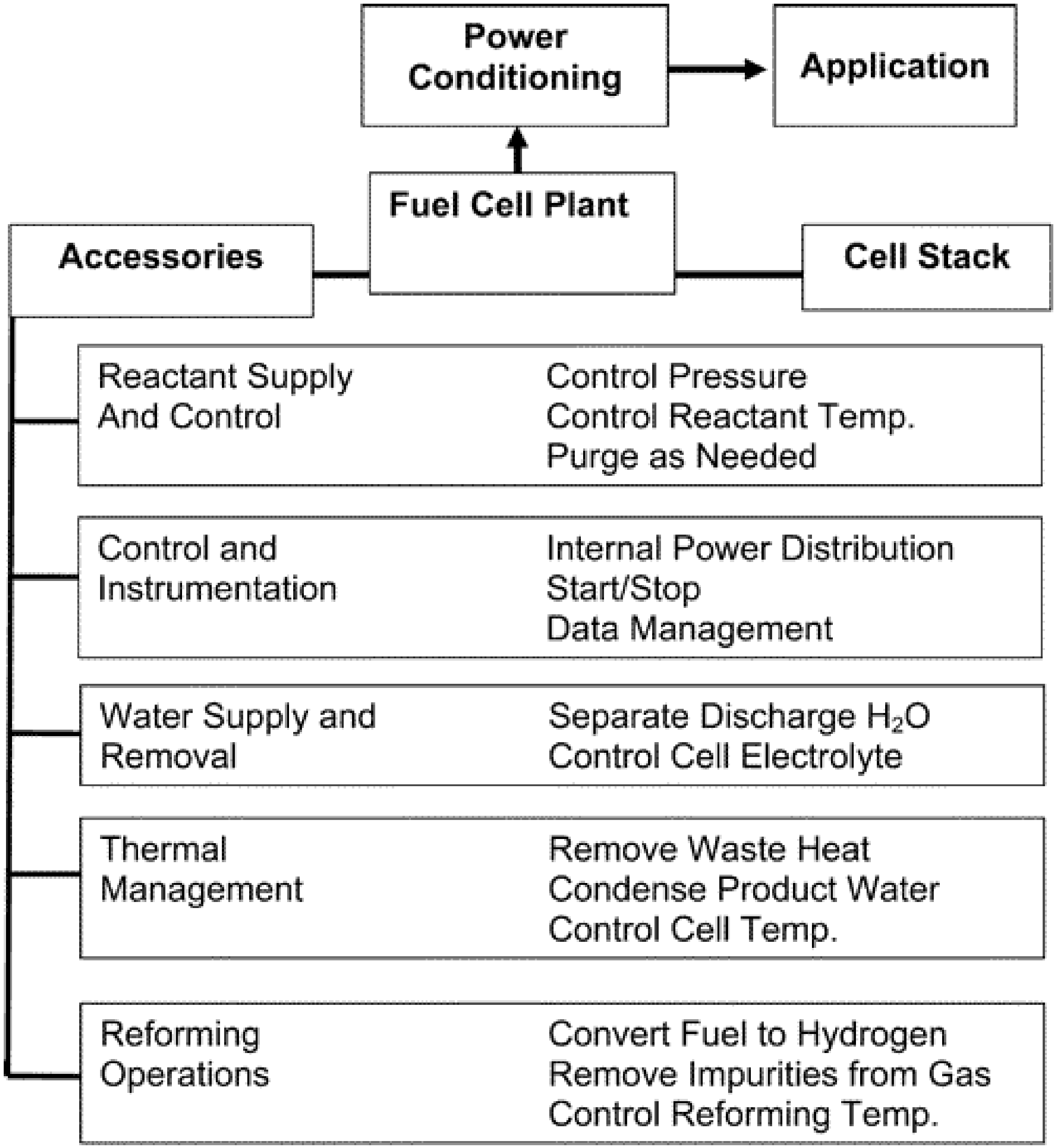


Schematic representation of a three-dimensional, integrated, solid-state lithium-ion battery. The surface area of the battery has increased 25-fold compared with a two-dimensional thin-film battery with the same footprint surface area, and will therefore be able to provide enough energy to power smart autonomous network devices related to sensing applications.

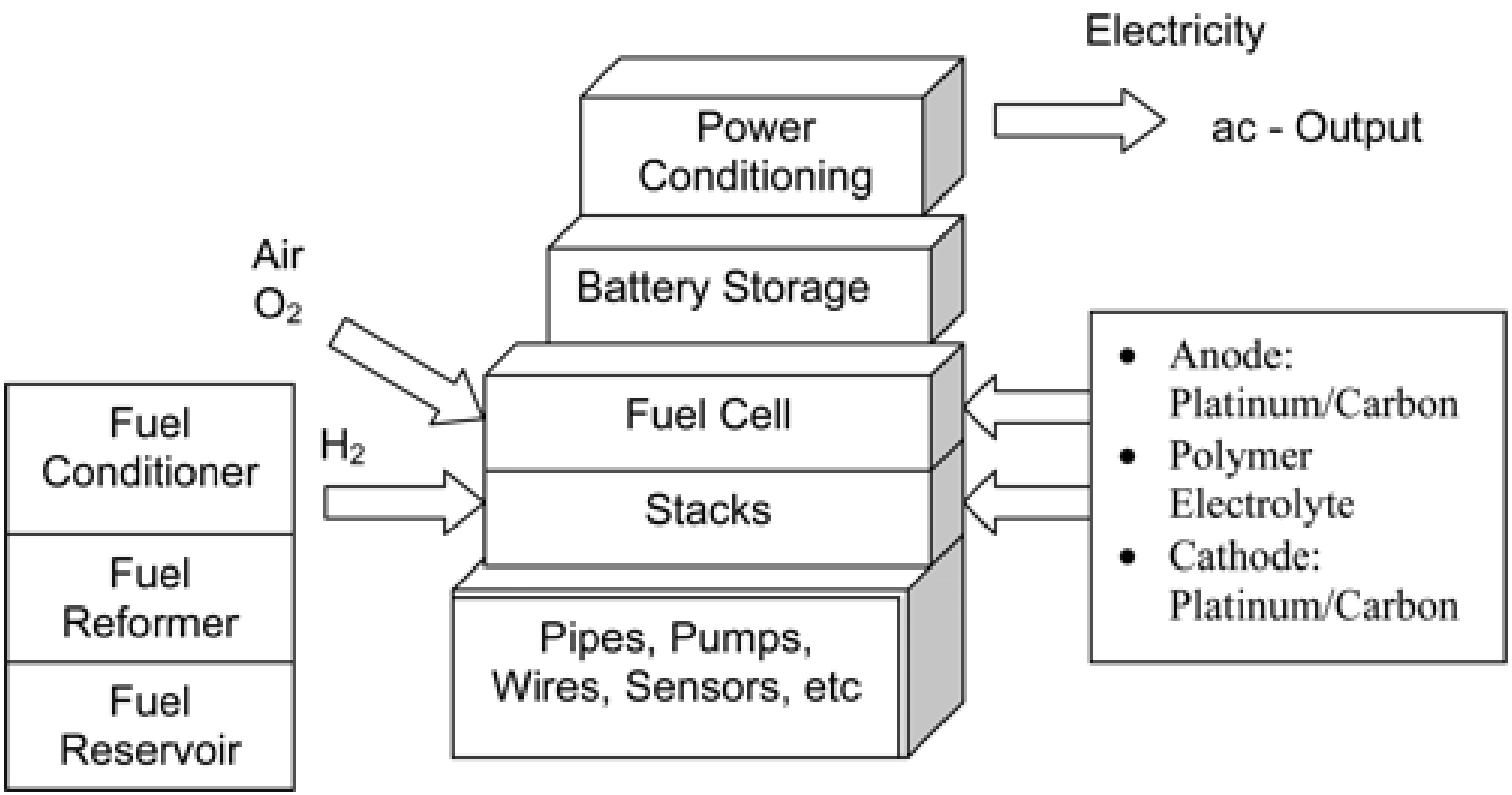
fuel cell systems



Summary of the reactions and processes that occur in the various fuel cell systems.

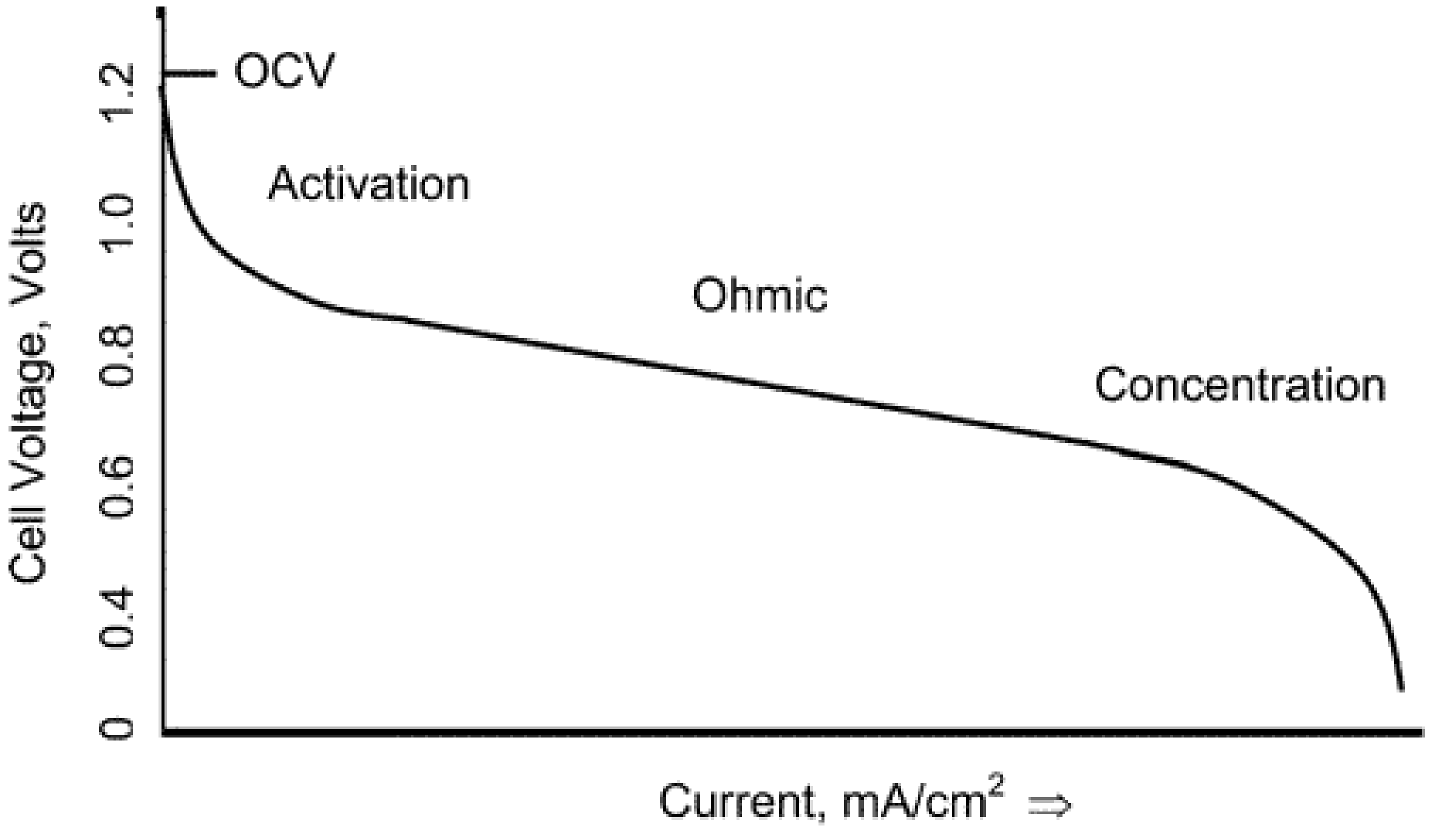


Block diagram of the component parts of a functioning fuel cell.



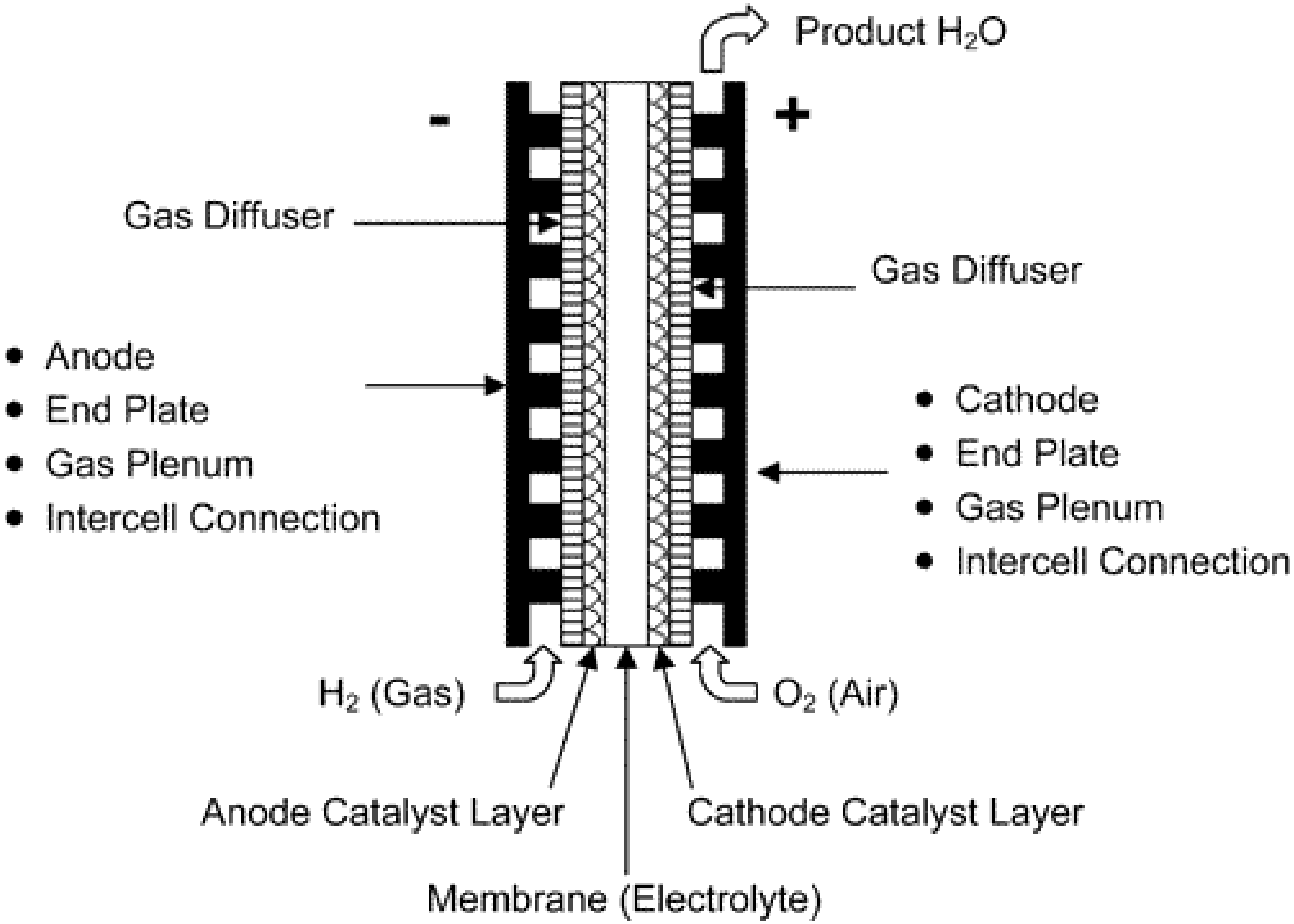
Depiction of the components of a complete fuel cell system including the re-former and power conditioning unit.

Power Curve for a Fuel Cell



Typical power curve for a fuel cell. The voltage drops quickly from the OCV due to the formation of the peroxide intermediate. Operation of the fuel cell at the knee of the curve where concentration is limiting performance can damage the electrodes and lead to rapid deterioration of cell operation.

PEM Fuel Cell



Schematic of a polymer electrolyte membrane (PEM) fuel cell. The fuel cell stacks operate at 30−180 °C with 30−60% efficiency. Fuel options include pure hydrogen, methanol, natural gas, and gasoline.

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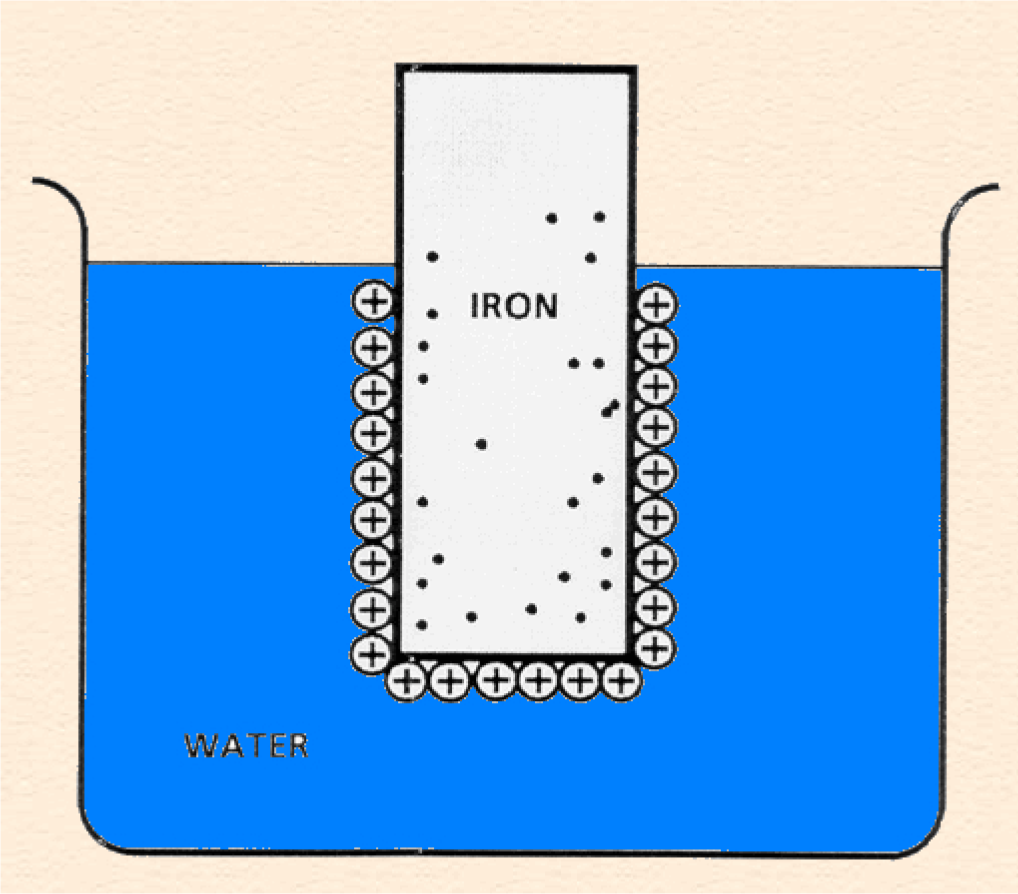
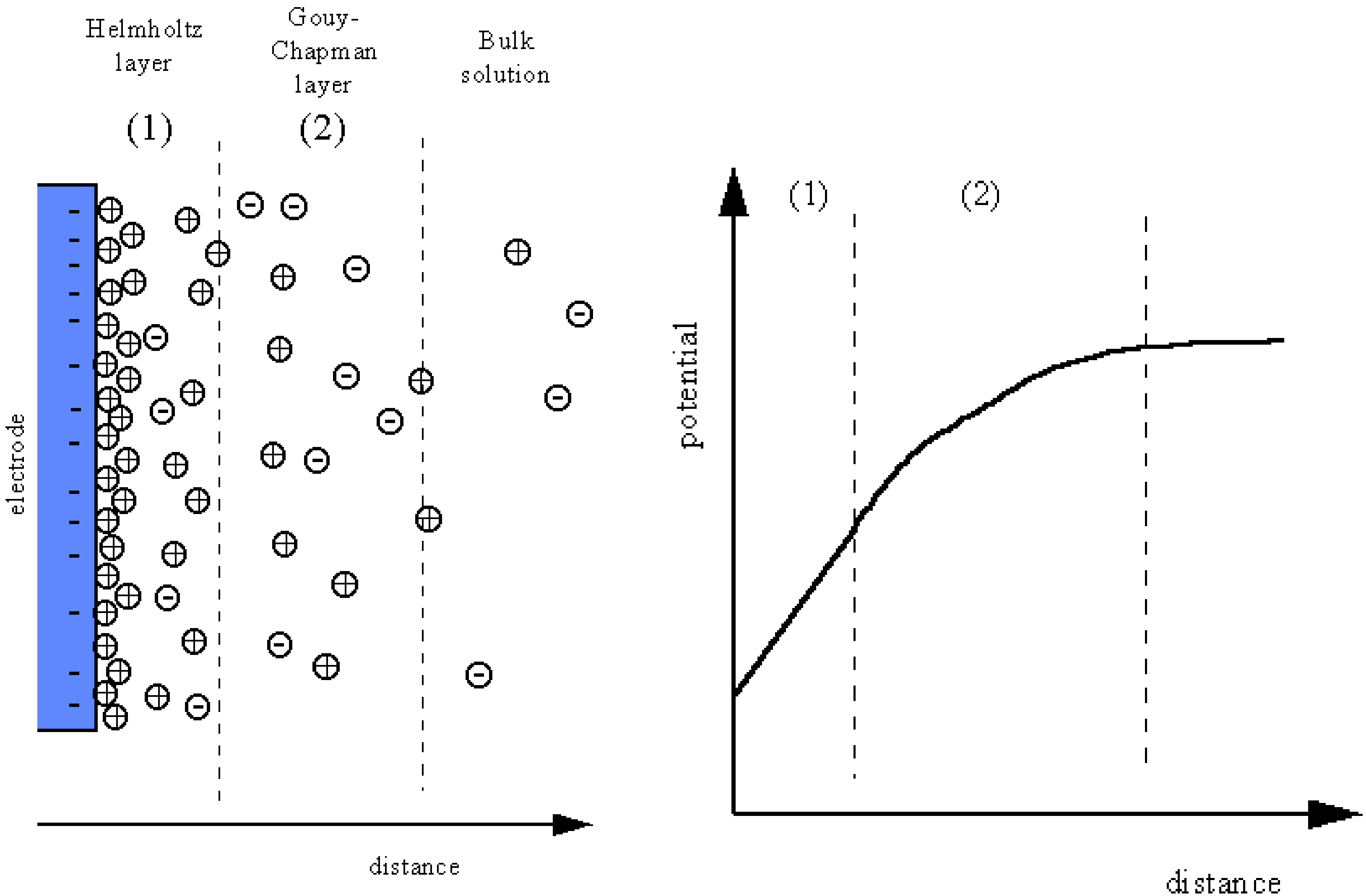


The following animation shows the process of ionization of a metallic substrate immersed in water and the formation of the double layer.



The distribution of ions at the metal/solution interface and the variation of potential

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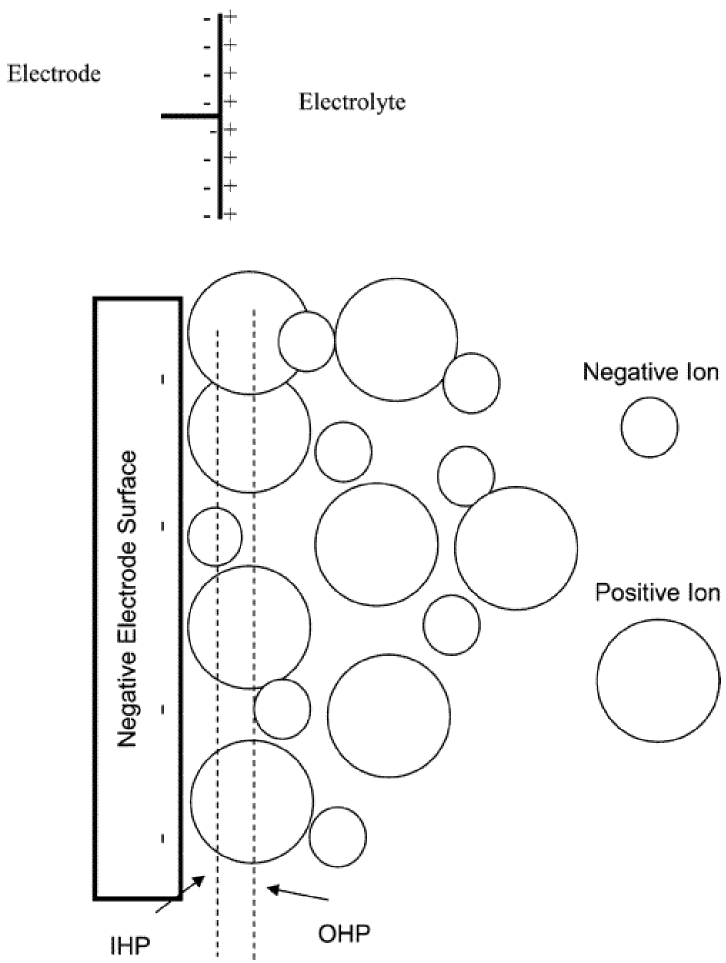
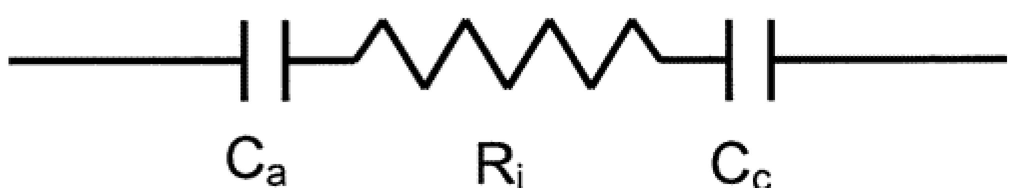


(A, top) Simple Helmholtz model of the electrical double layer. It is essentially a picture of a conventional capacitor. (B, bottom) Depiction of the electrical double layer at the surface of the negative electrode showing the outer Helmholtz plane (OHP) and the inner Helmholtz plane (IHP). The inner Helmholtz plane (IHP) refers to the distance of closest approach of specifically adsorbed ions and solvent molecules to the electrode surface. The outer Helmholtz plane (OHP) refers to the distance of ions, which are oriented at the interface by coulomb forces.



Some slides were adopted from…

- M. Winter, Chem. Rev., **2004,** 104, 4245-4269.
- M. Armand and J.-M. Tarascon, Nature, **2008**, 451, 652-657.
- Private collection…

Danke Schoen and Toda!