

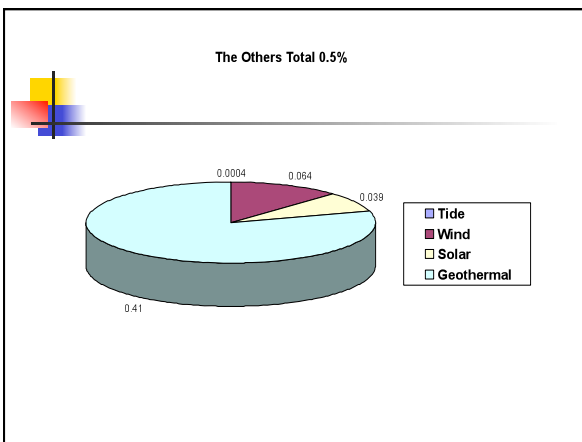
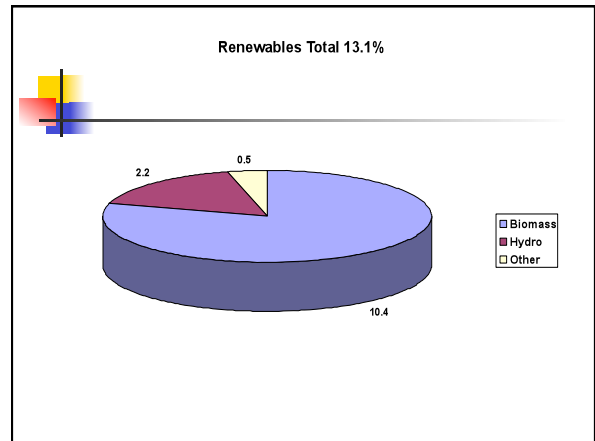
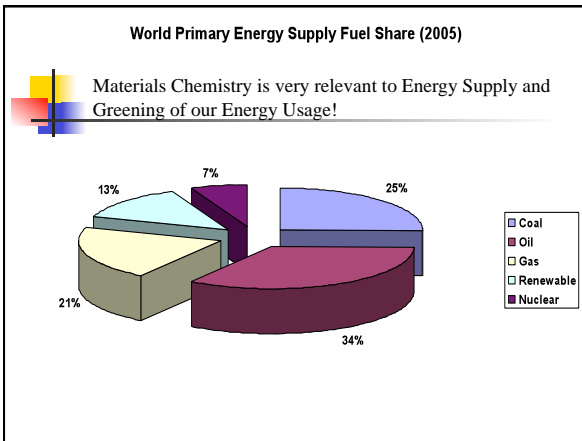
UNIVERSITY OF CAMBRIDGE

Materials Chemistry

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What is Materials Chemistry?

- A discipline at the interface of Materials Science & Chemistry to shape the technology of our materials world
 - In a fuel cell / battery, energy from chemical reactions are harnessed to produce electricity, and choice of materials and design are crucial
 - In order to recycle materials from equipment/ devices, choice of chemical reactions or reagents to impart selectivity and sustainability


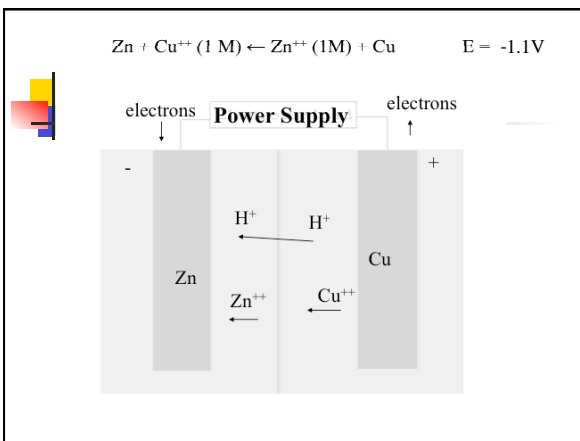
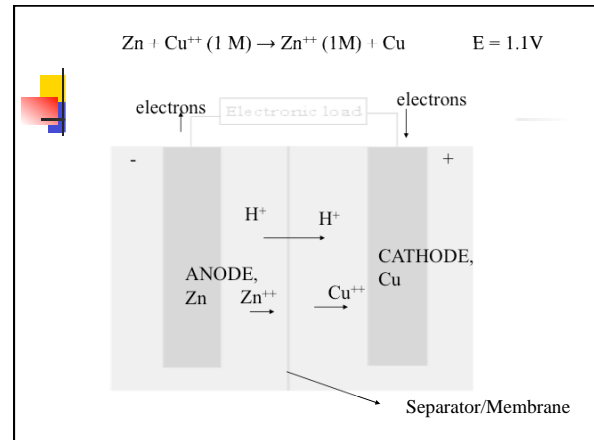


Fossil Fuels C emissions (Total 10 billion tonnes per year)

Fuel	Calorific Value MJ/kg	Mass fraction of C	Plant efficiency	Kg C emission per GJ
Gas	50	0.75	0.5-0.6	30
Oil	40	0.85	0.4-0.6	53
Coal	30	0.7-0.9	0.3-0.6	78

Batteries

- Storage of Electricity from renewable sources
- Low-energy route for recycling of batteries
- Use in transportation

Batteries are Electrochemical Cells

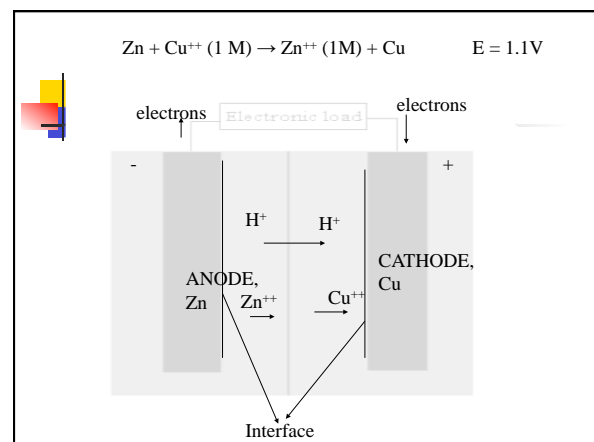
- $A + B \rightarrow C + D$ The change in free energy is converted to electrical potential
- ΔG (Joules) = $-z F E$ where z = no. of electrons involved in the reaction, e.g.

$Zn \rightarrow Zn^{++} + 2 e^-$ (Anode) or
 $Cu^{++} + 2 e^- \rightarrow Cu$ (Cathode)

F is Faraday's Constant = 96540 J/V and E is electrical potential in Volts
 zF is the number of moles of electrons per mole of Zn or Cu

Electrochemical Cells

- Two electrodes – connect the external load (during discharge) or the power supply (during charging) to the electrolyte
- Electrolyte is the medium in which electricity is carried by ions (charged molecules or atoms)
- Electrochemical reactions involve molecules, ions and electrons and occur at the electrode/electrolyte interface



Electrolytes

- Aqueous solutions of acids (in lead acid batteries), alkali (Alkaline or Ni-Cd batteries), salts in water (Metal – Air Batteries)
- Salts dissolved in Organic Solvents (Li batteries)
- Polymers (Li polymer batteries, Fuel Cells)
- Ceramics (Solid Oxide Fuel Cells)

Electrodes

- Conduit for electrons and offer surface for electrochemical reaction (chemically inert) – Pt in Polymer Fuel Cells
- Consumed but can not be regenerated – Zn in “primary” alkali cells
- Consumed and can be regenerated – Li in Li ion cells; Pb and PbO₂ in automotive batteries – “secondary or rechargeable” cells

The Electrical Double Layer

Electrolyte

Positively Charged Electrode

Storage of charge as in a capacitor

Structure of a double layer at the electrode/electrolyte interface

World-wide Battery Demand

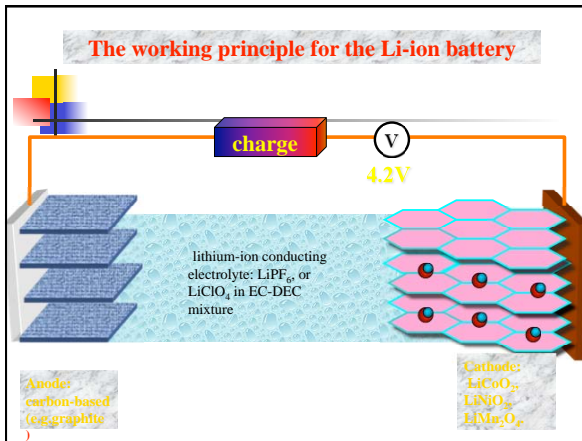
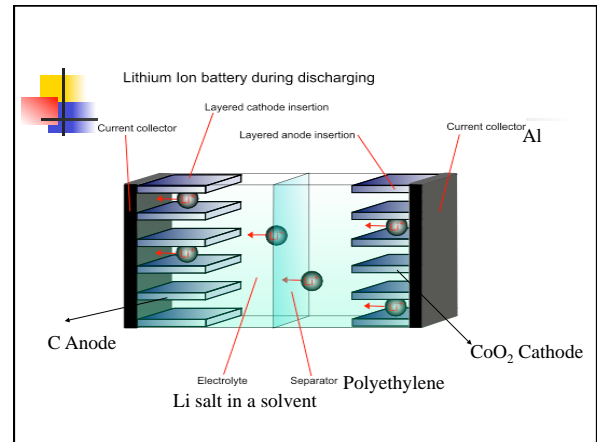
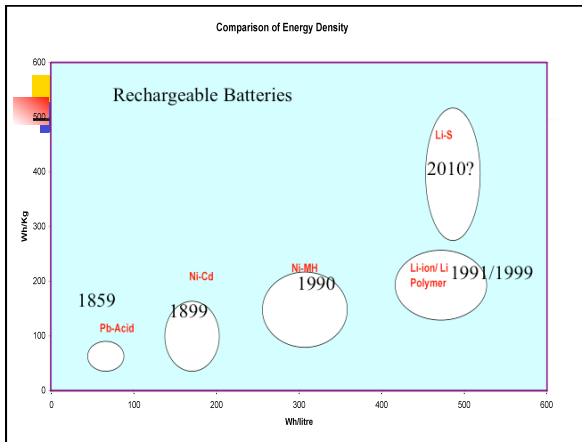
- Current Estimated Annual Sales: > \$100b
- Primary Cells (dominated by Alkaline Cells) at over \$30b per year
- Secondary Cells at around \$50b per year, over 50 % of which is Lead-Acid Batteries
- Ni- based and Li-ion based secondary batteries have markets of \$10b per year each

Lead Batteries (> 80 % Lead Usage)

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Lead-Acid Batteries

- Anode – Pb paste on a Pb-Sb-Ca alloy grid
- Cathode – PbO₂ paste on a Pb-Sb-Ca alloy grid
- Electrolyte – H₂SO₄ (aq)
- Specific Capacity – 18 Ah/kg of the battery weight
- Specific Energy – 35 Wh / kg of the battery weight



- ### Cell Potential
- Large free energy decrease for the cell reaction ($-\Delta G / z F = E$) → Products are much more stable than the reactants
 - Li to LiCoO₂
 - Pb and PbO₂ to PbSO₄
 - A small value of no of electrons in the reaction (z): $\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$ (z = 1)

- ### Cell Reactions
- $\text{Li}_y\text{C}_6 + \text{Li}_{1-y}\text{CoO}_2 \rightarrow \text{Li}_{y-x}\text{C}_6 + \text{Li}_{1-y+x}\text{CoO}_2$
 - z = 1 (per Li); $E_{\text{max}} = 4.2 \text{ V}$
 - y = 1; x increases from 0 to 0.5 and E decreases from 4.2 to 2.8 V
 - $\text{Pb} + \text{PbO}_2 + \text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O}$
 - z = 2 (per Pb); $E_{\text{max}} = 2.1 \text{ V}$
 - $2\text{Li} + \text{S} \rightarrow \text{Li}_2\text{S}$
 - z = 1 (per Li); $E_{\text{max}} = 2.2 \text{ V}$

- ### Cell Capacity
- 1 mole of element can carry zF Coulombs (Amperes. Seconds) of charge
 - Ah/kg is defined as the specific capacity = $zF / 3.6 \times \text{Mol. Wt. of the element}$
 - A large value of z and low Mol. Wt. elements would give a large value of specific capacity per kg of the element
 - Cell voltage decreases with increasing current derived

Specific Cell Capacity

- Li Chemistries: 3860 Ah/kg of Li
- Pb Chemistries: 260 Ah/kg of Pb
- Al Chemistries: 2980 Ah/kg of Al

Specific Energy

- Specific Energy = Specific Capacity x Cell Voltage x wt of the element per kg wt of the cell = ΔG (per wt of the element per kg wt of the cell) / 3.6 x Mol. Wt.
- Very stable products and low molecular weight would give high energy storage per unit wt of the battery
- Weight required to support the reacting element should be low for a high energy density

Specific Energy

- In a typical Li-ion cell, the wt of anode is 21x wt of Li, while the wt of cathode is 50x wt of Li – only 2 wt % of the total wt is usable Li in the battery: Specific Energy in the 110 – 180 Wh/kg of the battery
- In a typical Pb-acid battery, usable Pb is 10 wt% of the battery wt: Specific Energy in the 30 – 50 Wh/kg of the battery

Comparison of Rechargeable Batteries

Cell	Pb-acid	Ni-Cd	Ni-MH	Li-ion	Li-poly
Wh/kg	30-50	45-80	60-120	110-180	100-130
Wh/l	30-50	180	300	250-400	450
Cell V	2	1.25	1.25	3.6	3.6
Self-discharge	5 %	20 %	30 %	10 %	10 %
cycle	300	1500	500	1000	500
Max. Wh/kg	150			250	250
Cost \$/kWh	150	250	500	2000	2500
Market, \$/yr	30 b	7.5 b	2.5 b	10 b	0.8 b

Assuming 100 % EV ??

- Assuming world vehicle population: **1.5 b**
- 150 m new vehicles per year + 350 m replacement batteries per year
- Demand for **500 m** batteries per year

Type	Lead-Acid	Li-ion
Metal, mtpy	150	100
Current supply, mtpy	6	0.12

Energy Sustainability??

- Energy required to make Li: 80,000 Wh/kg of Li and energy derived from a battery: 10,000 Wh/kg of Li + energy losses of 5,000 Wh/kg of Li for each recharging cycle (x 1000 cycles)
- Research into low energy Li recycling methods is critical

Hydrogen Economy

- Hydrogen from renewable energy source by electrolysing water and using hydrogen as a fuel in engines or in fuel cells
- Photochemical splitting of water to directly produce hydrogen and oxygen
- Hydrogen storage issues need improved solutions

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SOLID OXIDE FUEL CELLS

- H₂ gas fuel presented at anode
- O₂ from air as oxidant present at cathode
- Oxygen ions transport across the electrolyte
- Electrons carried to external circuit

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The cell

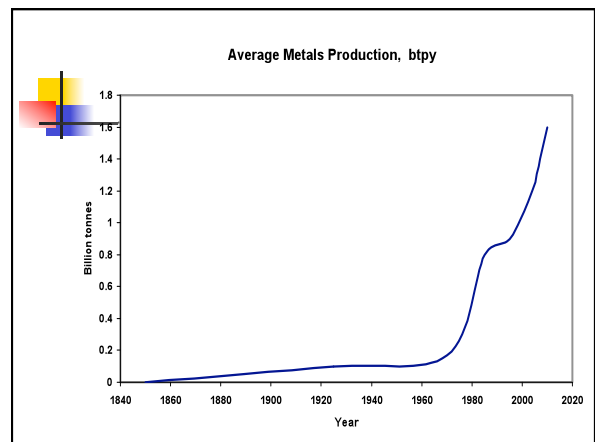
LSM cathode
YSZ electrolyte
NiO anode

Sustainability in Materials

- Conservation – avoid unnecessary usage
- Dematerialization – use less materials
- Substitution
- Recycling
- Recovery from wastes

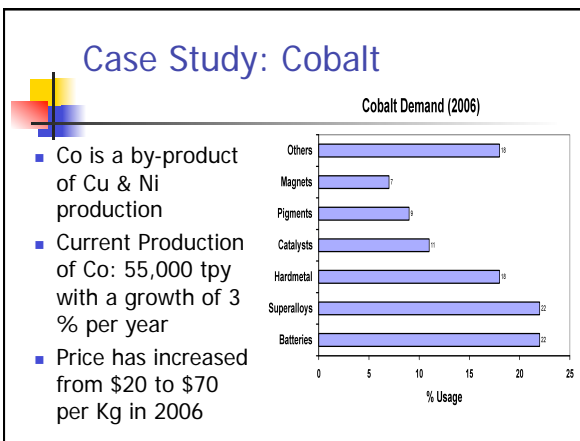
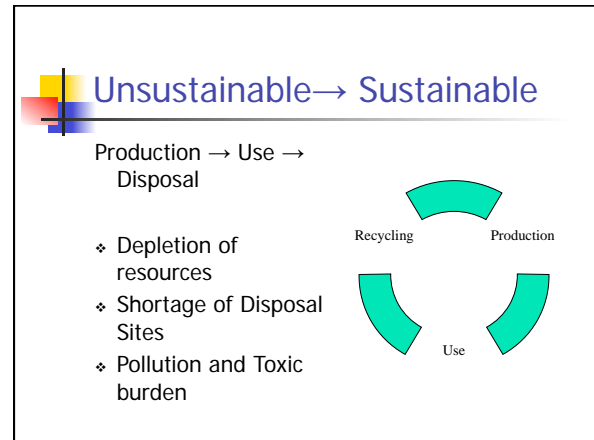
Metal Usage

Period	Amount in billion tons
Antiquity - 1900	1
1900 – 1950	5
1950-1980	5
1980 – 1990	8
1990 - 2000	9
2001 - 2010	12.5
2010 - 2020	15
2020 - 2030	20



Metal Recycling (2006)


Metal	Total MTPY	From ores, MTPY	Recycling, MTPY
Steel	1200	700	500
Aluminium	30	20	10
Copper	24	16	8
Lead	8	4	4



- ### Cobalt in Li-ion Batteries
- 1.4 b cells a year use 9000 tpy of Co in the electrodes
 - Each Hybrid Car uses 2.5 kg of Co
 - For a future scenario (2020) of 1 b cars per year, the total Co demand for the battery market alone will be 2.5 Mtpy (current demand in the same market is: 0.09 Mtpy)

- ### Energy & Materials
- The interlocked issues of materials & energy sustainability offer challenges
 - Some materials may be successfully recycled or recovered to improve sustainability but at a huge energy cost
 - Energy minimisation may be successfully applied at the expense of un-sustainability in the material

- ### The Environmental Paradox Trap
- Strategy for energy efficient and/or green technologies such as fuel cells and oil desulphurization (PGMs), hybrid cars (Co), Solar cells (Te, In); car magnets (Nd) impact on Materials Sustainability
 - Strategy for Materials Sustainability such as recycling of batteries impact on energy sustainability



Our Challenges

- If much of the hope is rooted in technological progress then our task is even larger than the adventure of the industrial revolution (which is still incomplete, for a majority of peoples)
- The past technological success was rooted in labour productivity, but labour is now abundant
- My view: focus on resource productivity, even at the cost of decrease in labour productivity