# CH5715
# Energy Conversion and Storage

## Part 1: Fundamental Electrochemistry

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**Aims:**

To introduce students to the principals and applications of ionic conductors and electrochemical processes

For lecture notes: http://jtsigroup.wp.st-andrews.ac.uk/ch5715-energy-conversion-and-storage/

# Course

- Basics  and underlying concepts – Irvine
- Fuel Cells – Baker
- Lithium and related batteries - Armstrong

# Outline

**1 Overview and applications**

**2 Ionic Conduction**

**3 Electrochemical Processes**

**4 Electrochemical Characterisation**

**5 Impedance Spectroscopy**

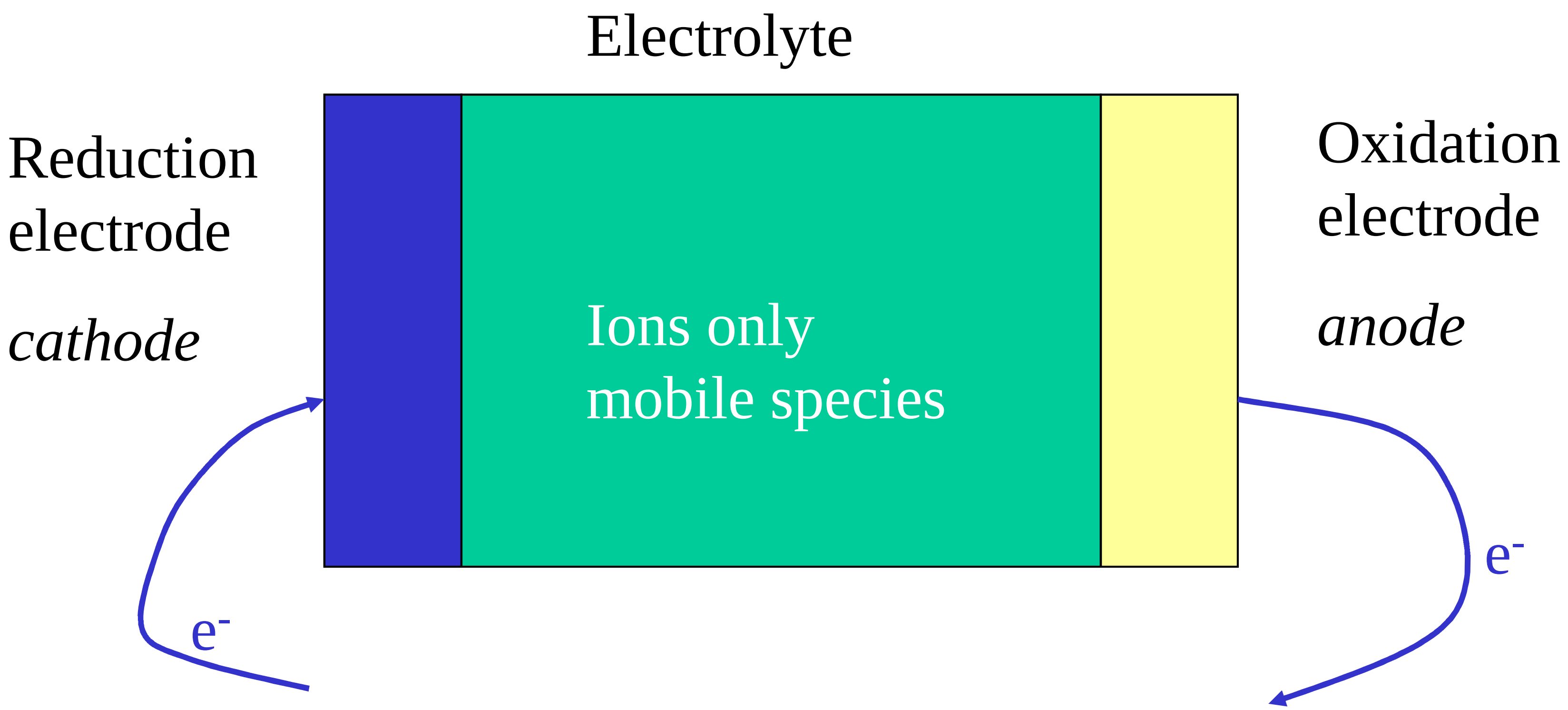
# Lecture 1 Contents

- Electrochemistry absolute basics
- Categories
- Some Applications

# Electrochemistry

| Electrolyte | Interface | Electrodes | Redox process |
|---|---|---|---|
| Molten Salts eg NaCl | | | Intercalation eg $Li_xC_6$ |
| Ceramic Electrolyte eg Naβ alumina | | Metals | Gases eg $H_2/H_2O$ |
| Solution eg $H_2SO_4$ | | semiconductors | Redox couples eg $3I^-/I^{3-}$ |
| Polymers eg poly(ethylene oxide): $NaClO_4$ | | | |

# Electrochemical Cells



**Cathode - reduction**

$X + ne^- \rightarrow X^{n-}$

Fuel Cell $O_2 + 4e^- \rightarrow 2\,O^{2-}$

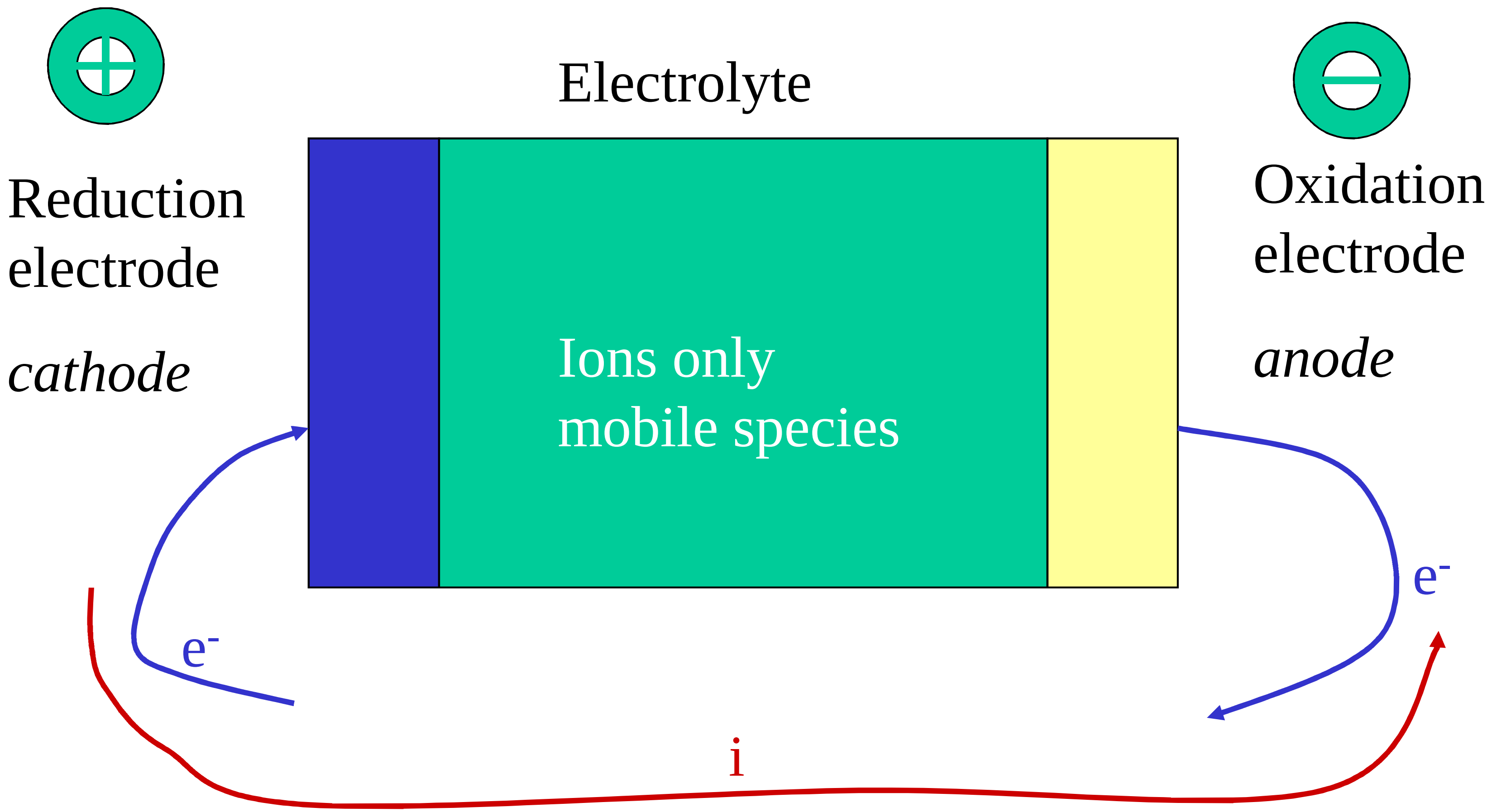
**Anode - oxidation**

$M \rightarrow M^{n+} + ne^-$

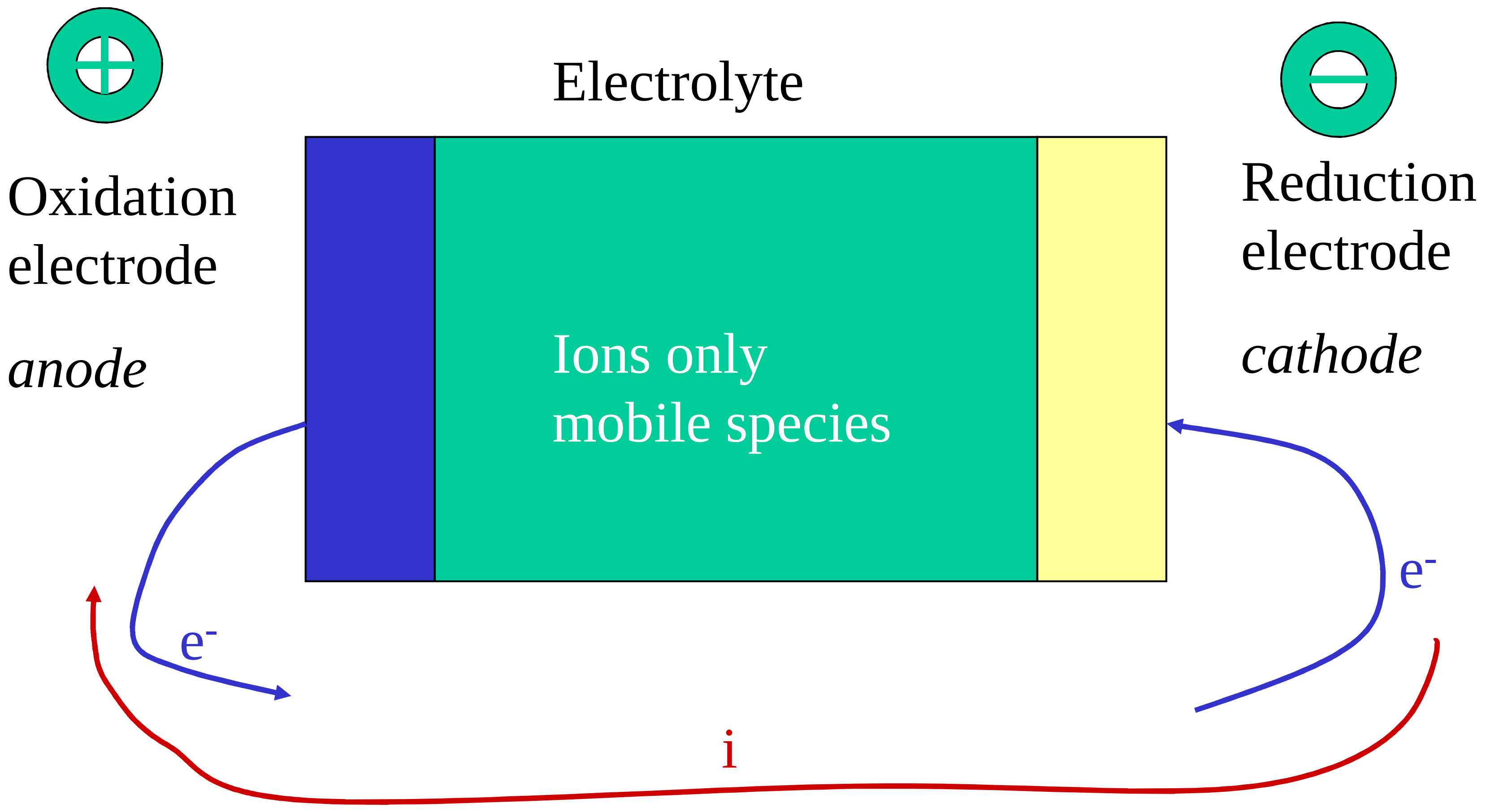
Fuel Cell $H_2 \rightarrow 2H^+ + 2e^-$

- Fuel cells and batteries are electrochemical devices used to provide dc electrical energy
- Fuel Cells similar to battery under discharge
- Electrolysers similar to batteries under charge
- Fuel cells energy source is external
- Batteries energy source is internal

# BATTERIES
# Discharge



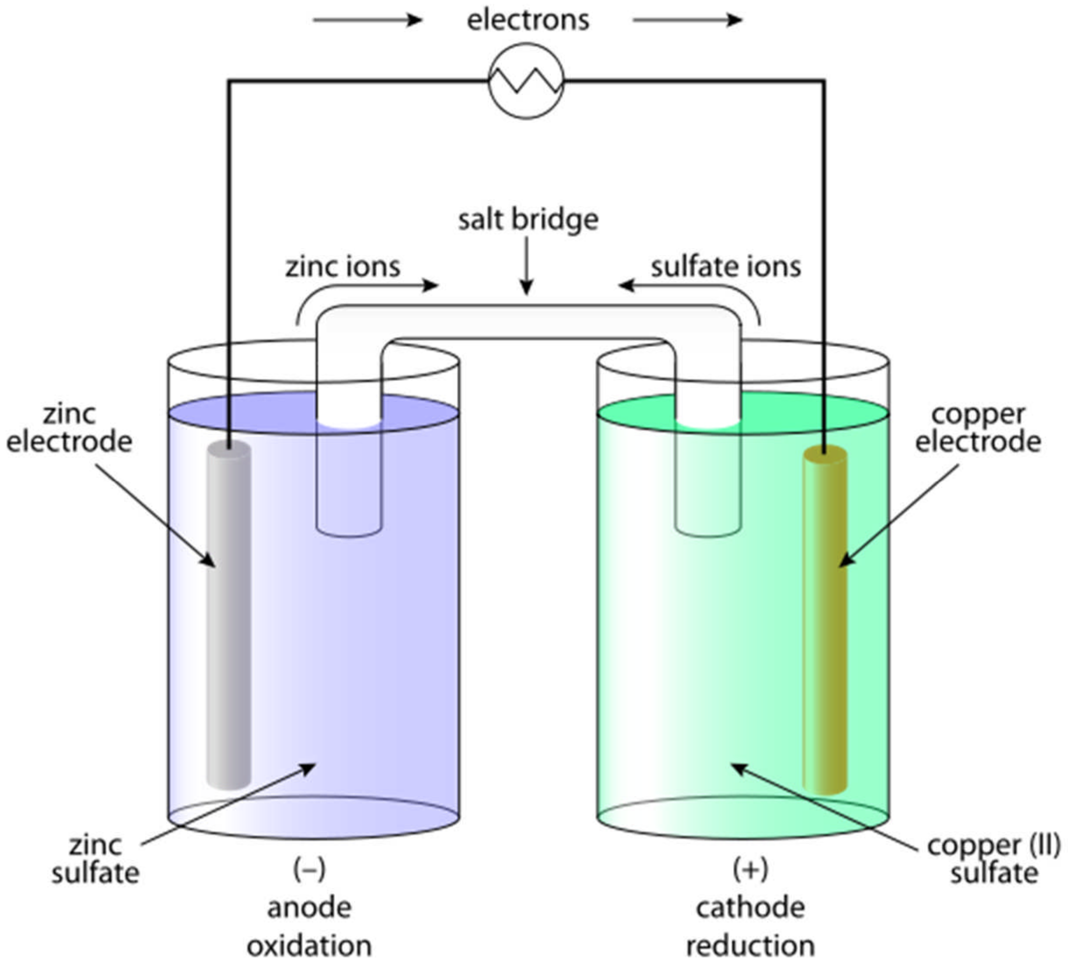
# BATTERIES
# Charge

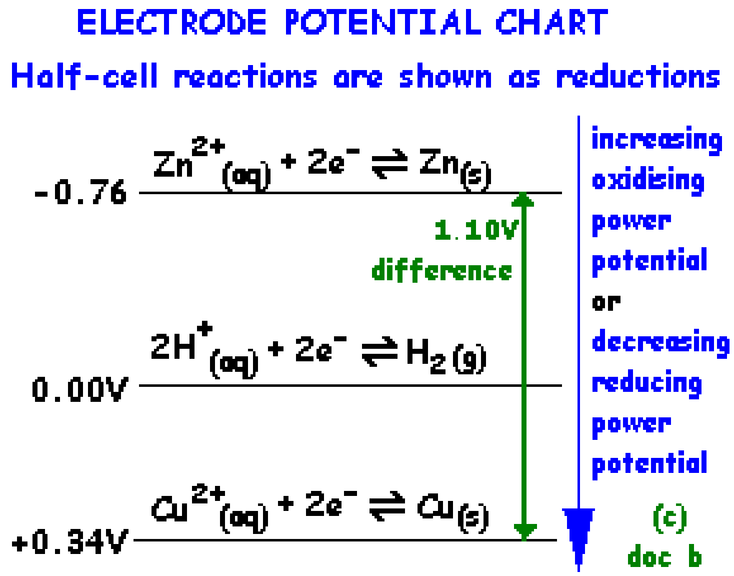


# Daniel Cell

$$Cu^{2+}_{(aq)} + Zn_{(s)} \Leftrightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$$

$$E^{\Theta} = 0.337-(-0.763) = 1.10\ V$$



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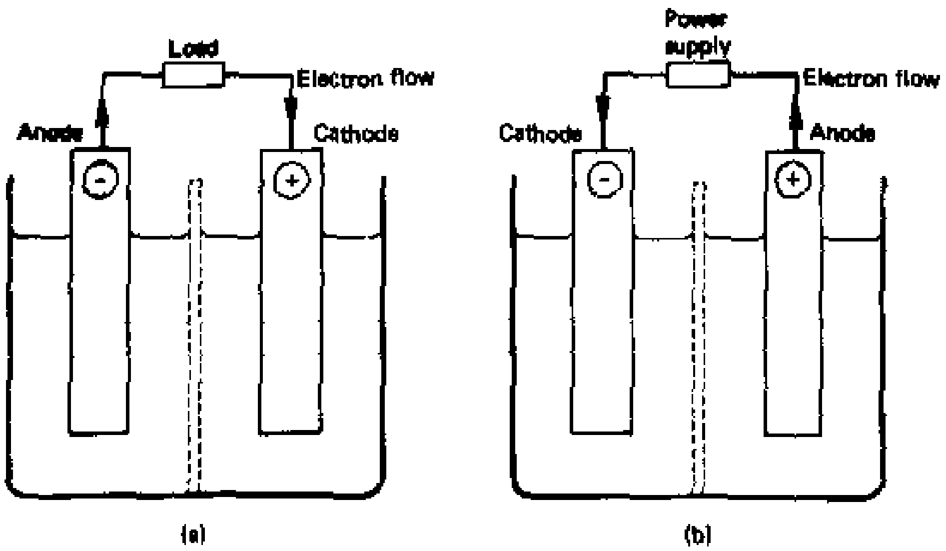



Anode and cathode in a cell during (a) spontaneous discharge and (b) during charge.

# Advanced Batteries

Batteries have been developed for utilisation in electric vehicles and consumer products

Primary or secondary - In primary, electrodes are consumed as a fuel, secondary are rechargeable

- High energy/power density required

Li, Na (-3.0, -2.7$V_H$) - large, negative redox potentials

Use Na or Li electrode as negative electrode
Need electrolyte that conducts Na or Li-ions

Counter electrode redox process must be compatible with Na or Li and ideally at as positive a potential as possible.

# Comparison of battery technologies

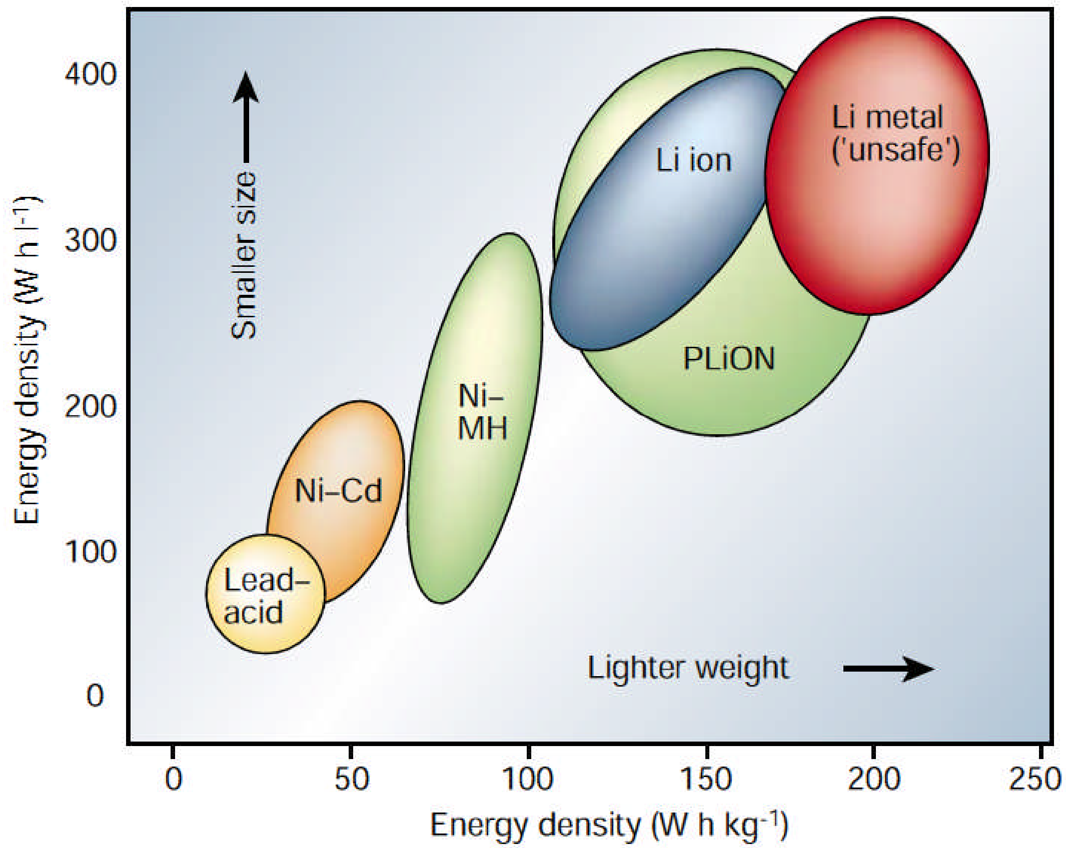



**Figure 1** Comparison of the different battery technologies in terms of volumetric and gravimetric energy density. The share of worldwide sales for Ni–Cd, Ni–MeH and Li-ion portable batteries is 23, 14 and 63%, respectively. The use of Pb–acid batteries is restricted mainly to SLI (starting, lighting, ignition) in automobiles or standby applications, whereas Ni–Cd batteries remain the most suitable technologies for high-power applications (for example, power tools). Now Li

# Nickel-metal hydride batteries

Positive electrode

Discharge

$$NiOOH + H_2O + e^- \Leftrightarrow Ni(OH)_2 + OH^-$$

charge

Negative electrode

Discharge

$$MH_x + OH^- \Leftrightarrow MH_{x-1} + H_2O + e^-$$

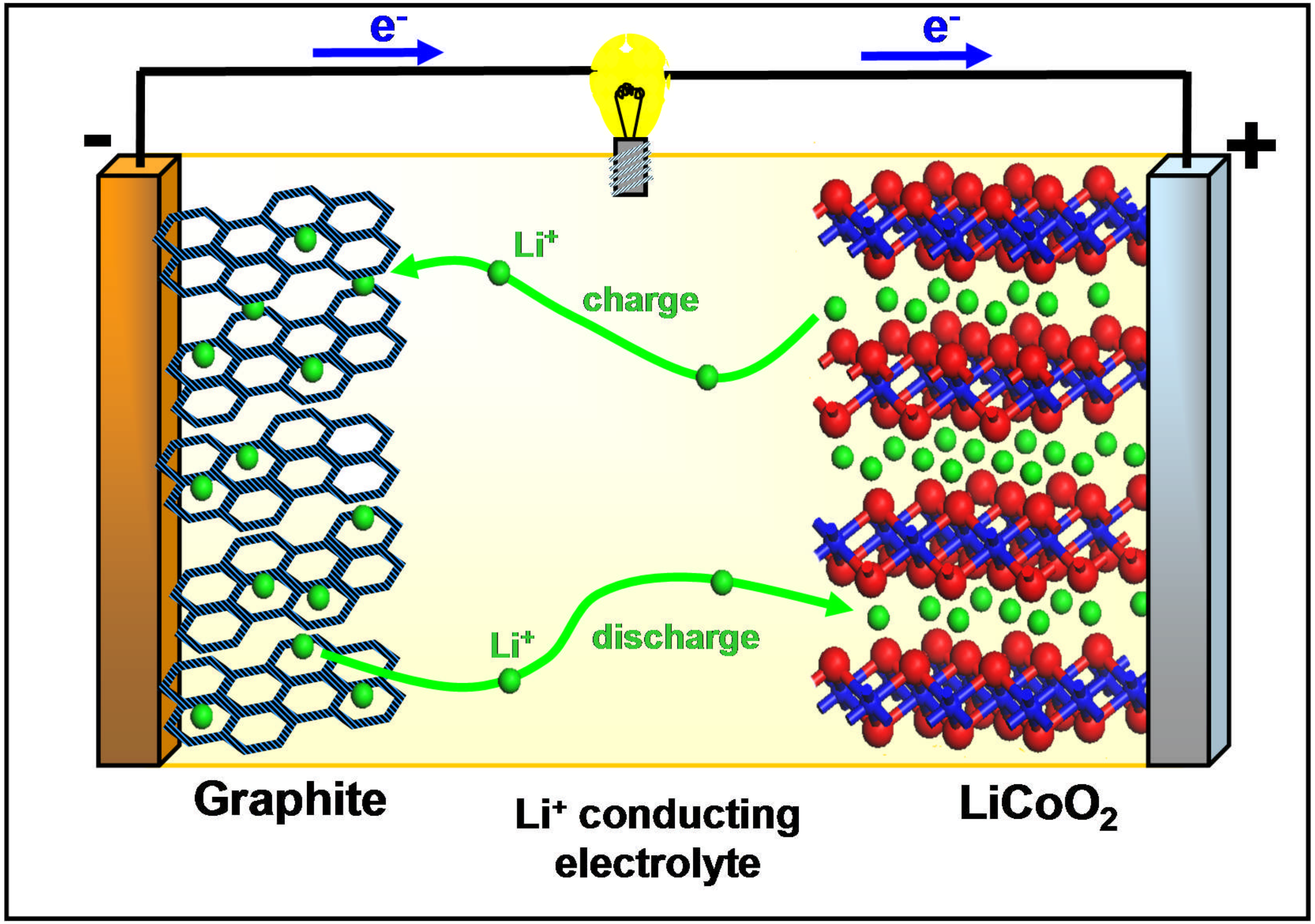
charge

$MH_x = LaNi_5H_6$ or $TiH_2$

Electric vehicle application possible

1.3V per cell

# Rechargeable Lithium Batteries

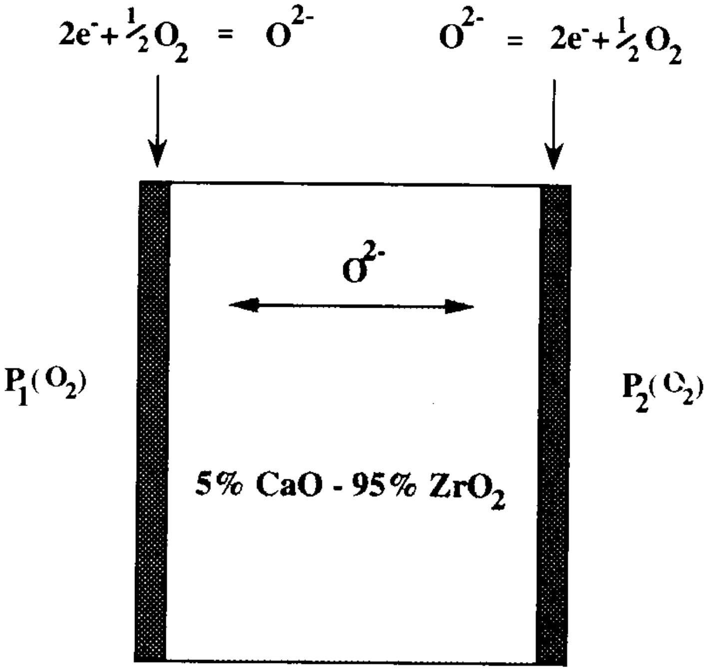


# Applications of Solid Electrolytes

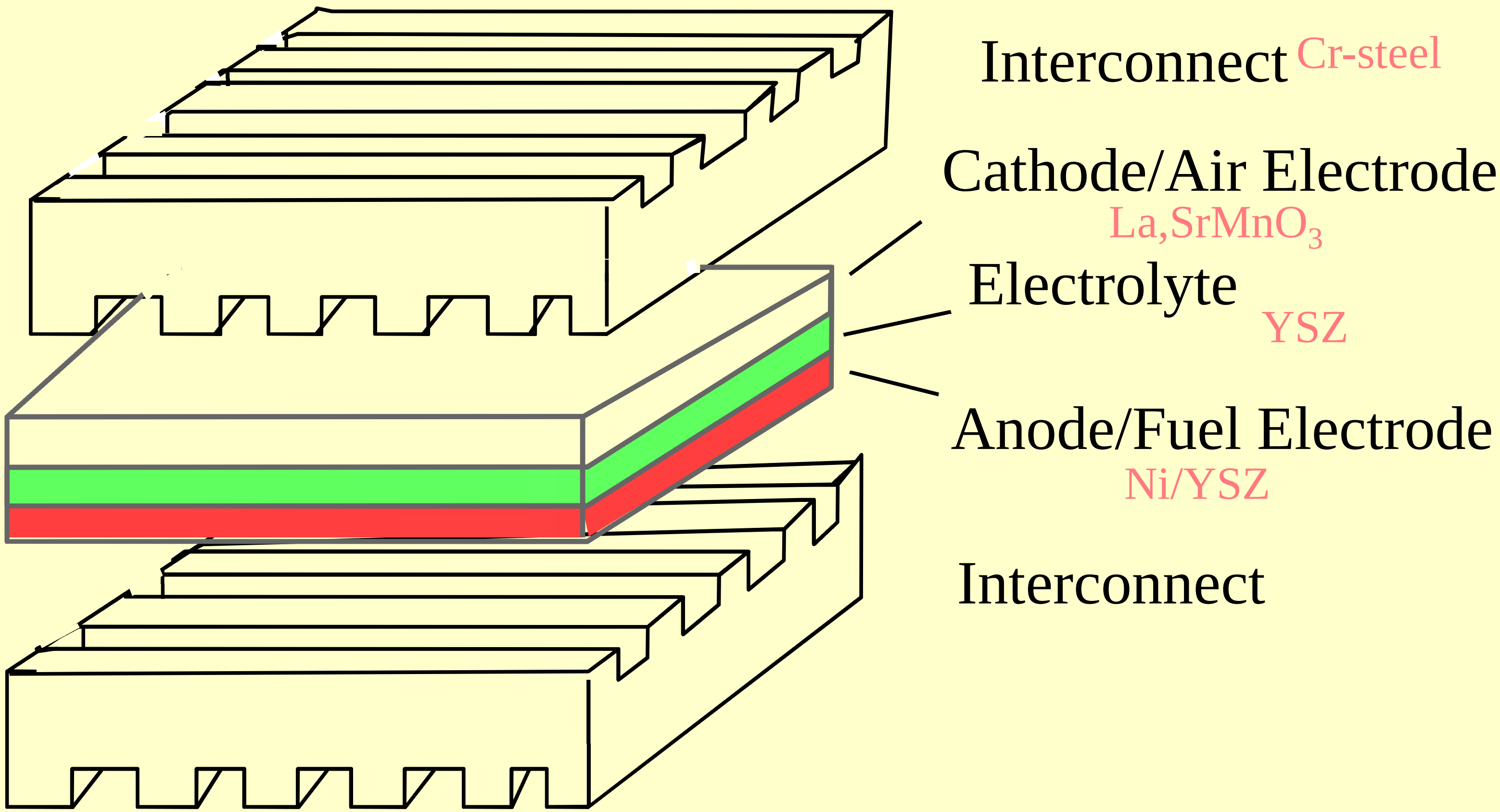
- Na/S batteries
- Li batteries
- Mixed conduction – Oxygen Transport Membranes
- Insertion chemistry - electrodes
- Solid oxide fuel cells
- Sensors

# Sensors

Also use solid electrolytes, oxygen sensor most widely used - eg exhaust emissions




$$E=(RT/4F)\log_e(P_1(O_2)/P_2(O_2))$$



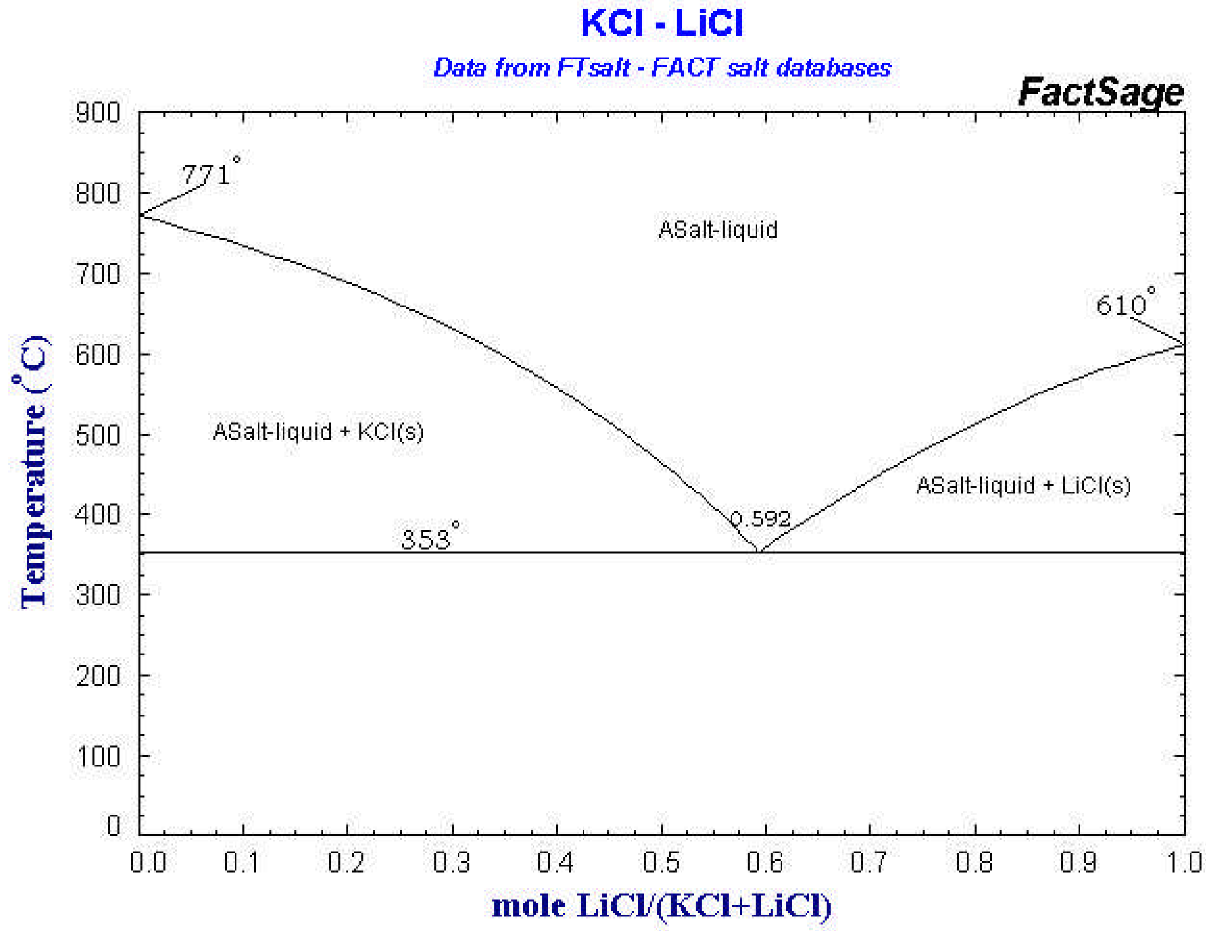

**Typical Planar SOFC Design**

# Thermal batteries

- High power primary
  - Watts, kW
- Li alloy anode (-ve)
- $FeS_2$ cathode
- Molten salt electrolyte, eg LiCl/KCl eutectic

# Molten Salt Electrolyte

- LiCl/KCl Eutectic
- LiCl-KCl (55.8 mol% - 44.2 mol%)



# Applications of a thermal battery

- **Ejector seats** for fighter aircraft
- **Emergency energy** sources for industrial purposes (safety systems etc.)
- Power supplies for **electronically operated** guidance systems in missiles, torpedoes etc.
- **Space launchers**, supplying power to electrical activation systems.

- High Power
- Long shelf life


Li(Si)/FeS2 SYSTEM BATTERIES
PULSE
fast rise
>40 amps
for >600 mst
SPIN
operates at
18,000 rpm
MULTIVOLTAGE
5 voltages
over a
5.1 current
density range
LONGLIFE
.35 amps
for 1 hour
in 400 cm³
volume
INSTRUMENTATION
3.2 amps
for 1½ hours
HIGH CURRENT
30 amps
for 30 minutes
Sandia National Laboratories

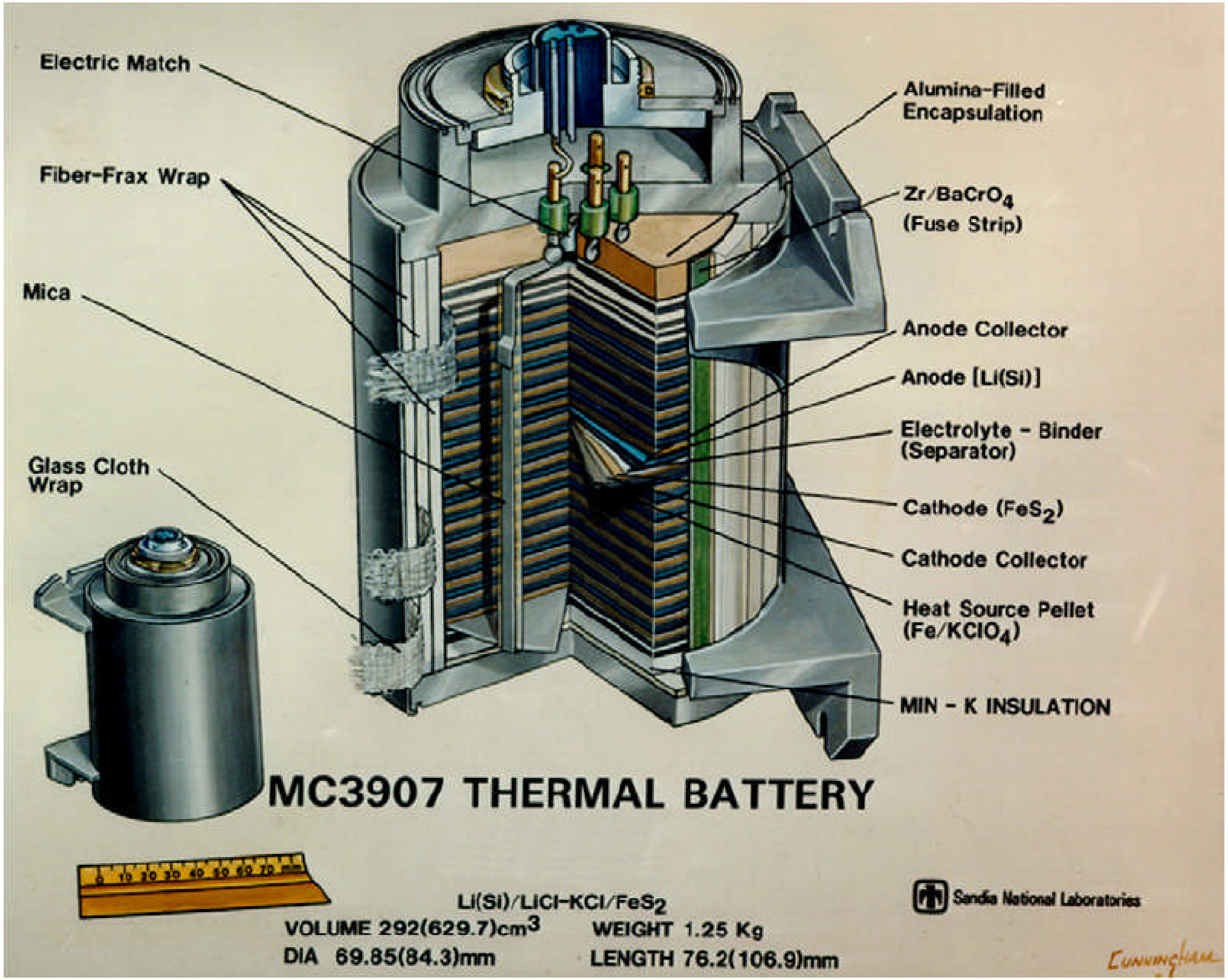
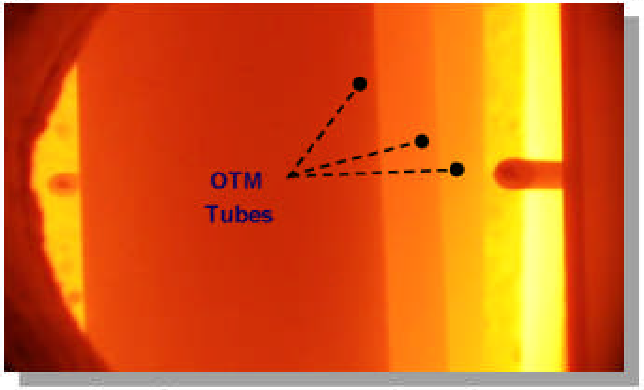



Fig. 2. Section view of a Li–Si/$FeS_2$ thermal battery.

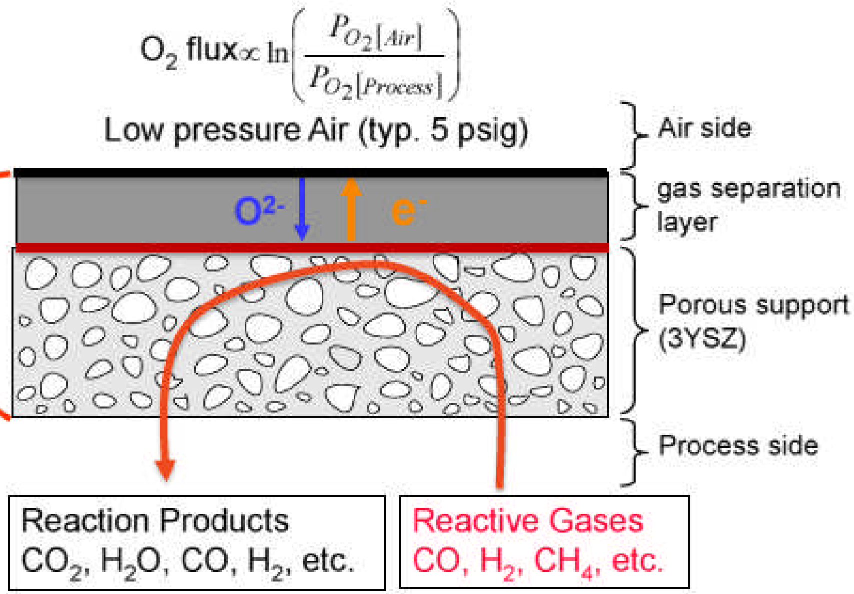
# Oxygen Separation Membranes

- Praxair

# Praxair Oxygen Transport Membranes (OTM)

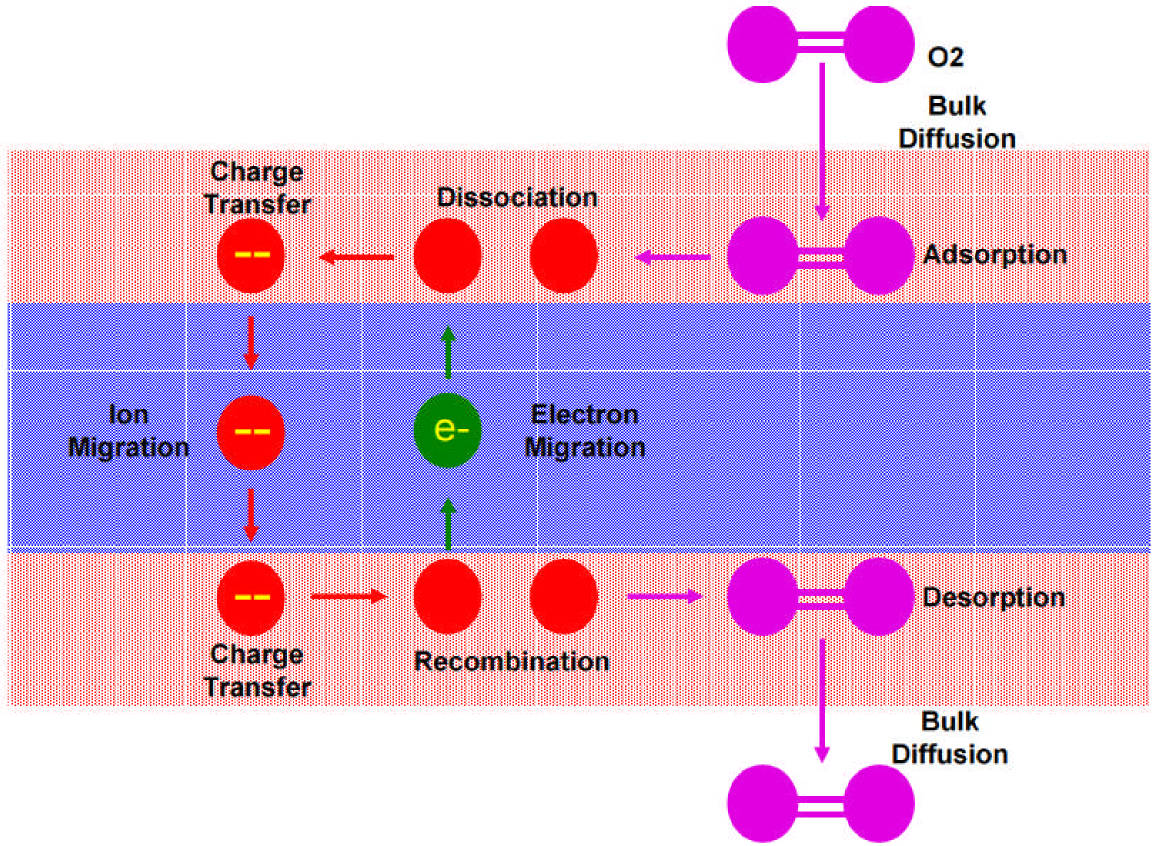

Oxy-Combustion on OTM Surface




Process pressure typ. 100 – 250 psig
Temperature range 900 – 1,025 °C

**Advanced architecture enables oxycombustion and syngas applications**

# OTM components



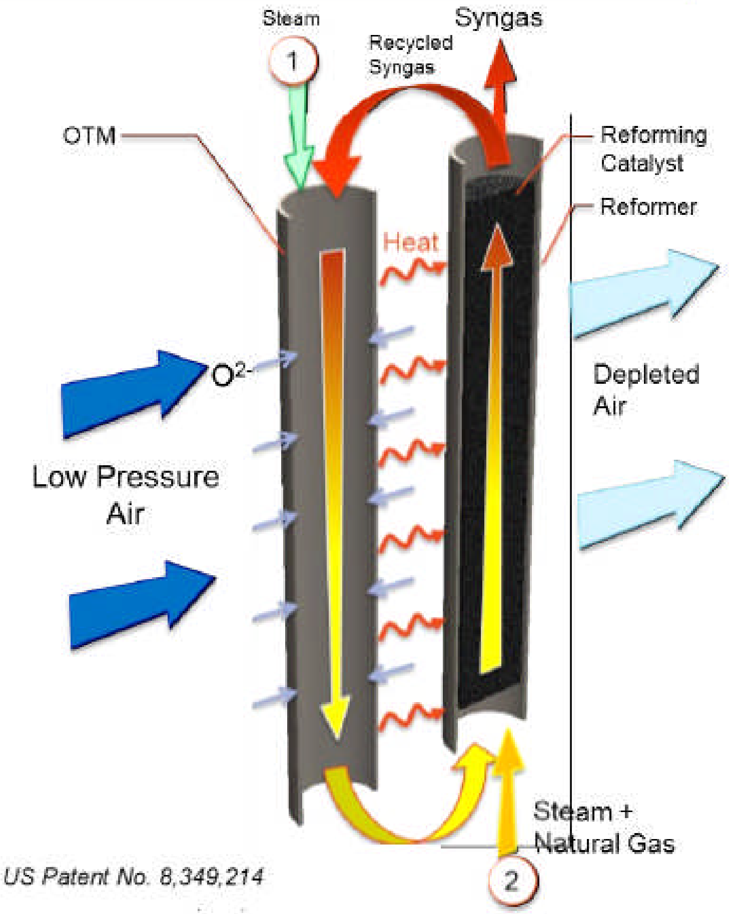

LSCoF (see SOFC cathode)

Composite O and e conductors eg ScSZ + LSCrF

LSCrF

Eg 1000$^{o}$C

# Improved OTM Syngas Process



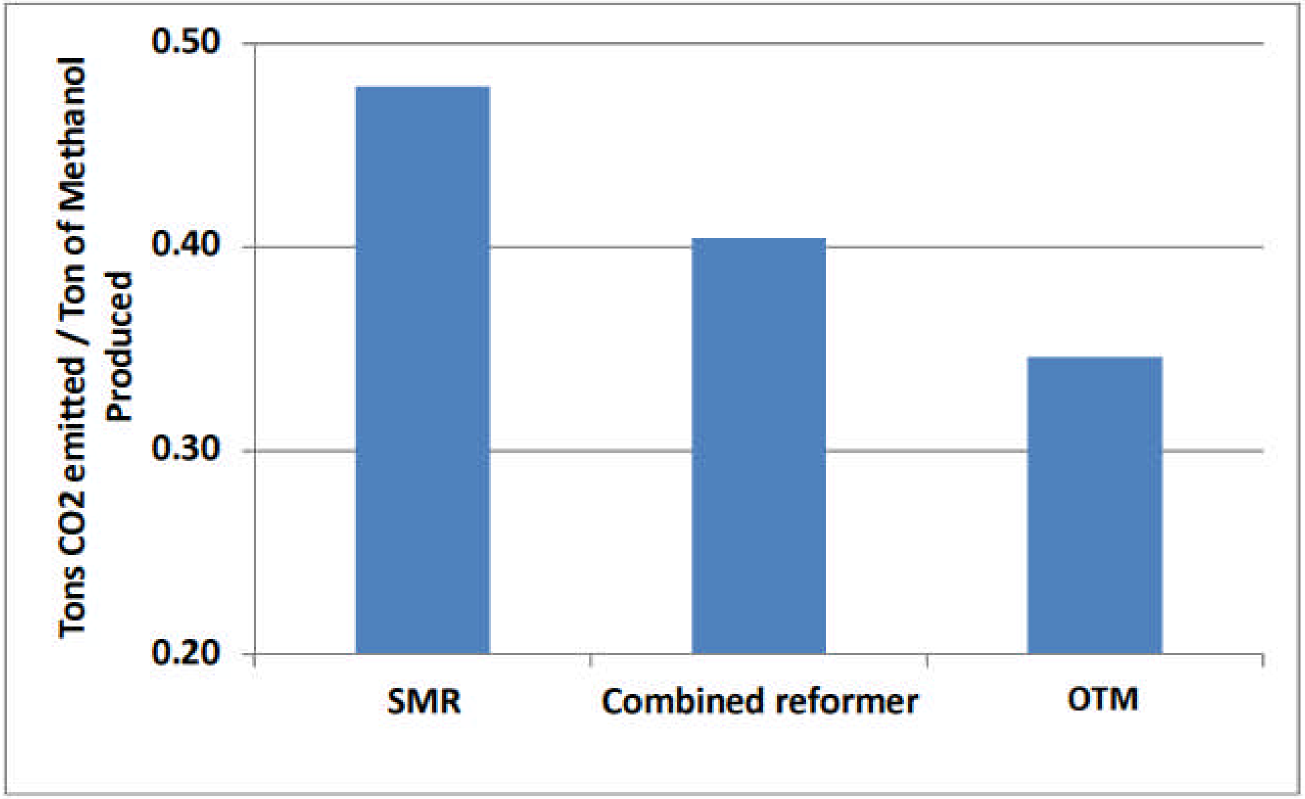

*US Patent No. 8,349,214*

- Use <u>recycled syngas as fuel</u>
- Steam and $CO_2$ reforming in separate reforming catalyst
- Reactive fuel drives high oxygen flux
- Inherent coking mitigation

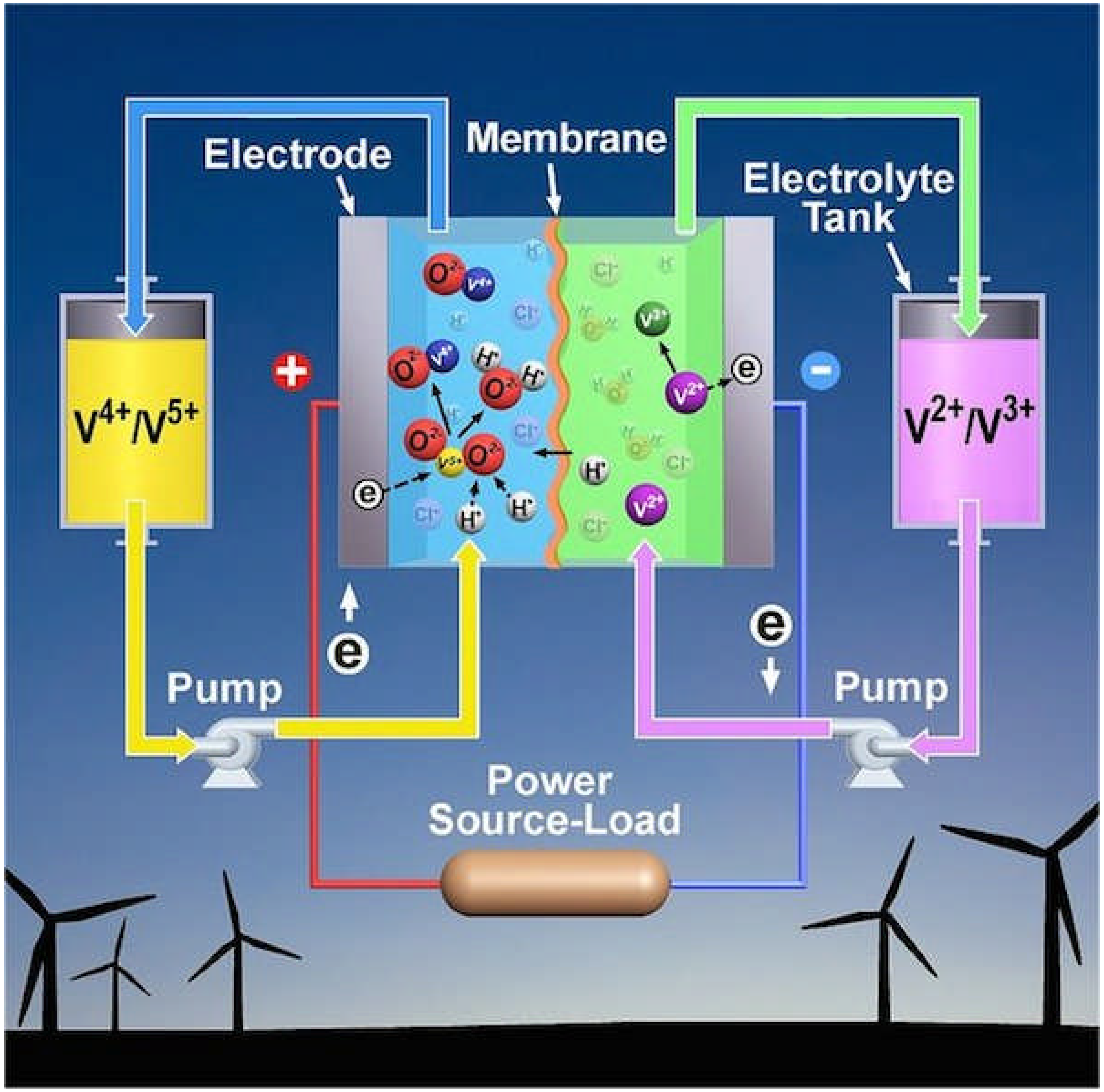
**Auto-thermal reformer with $O_2$ generation onboard**

# $CO_2$ emitted – MeOH example

PRAXAIR
Making our planet more productive




OTM reduces tons $CO_2$ emitted by 27% vs SMR and 13 % vs combined reformer




Flow cells for energy storage

*http://cleantechnica.com/2015/06/21/flow-battery-vs-tesla-battery-smackdown-looming/*

# Electrochemical Synthesis of Ammonia
# At protonic or oxide ion conducting electrolytes