MSE 110

Materials for Energy and Sustainability

Min-Kyu Song

School of Mechanical and Materials Engineering

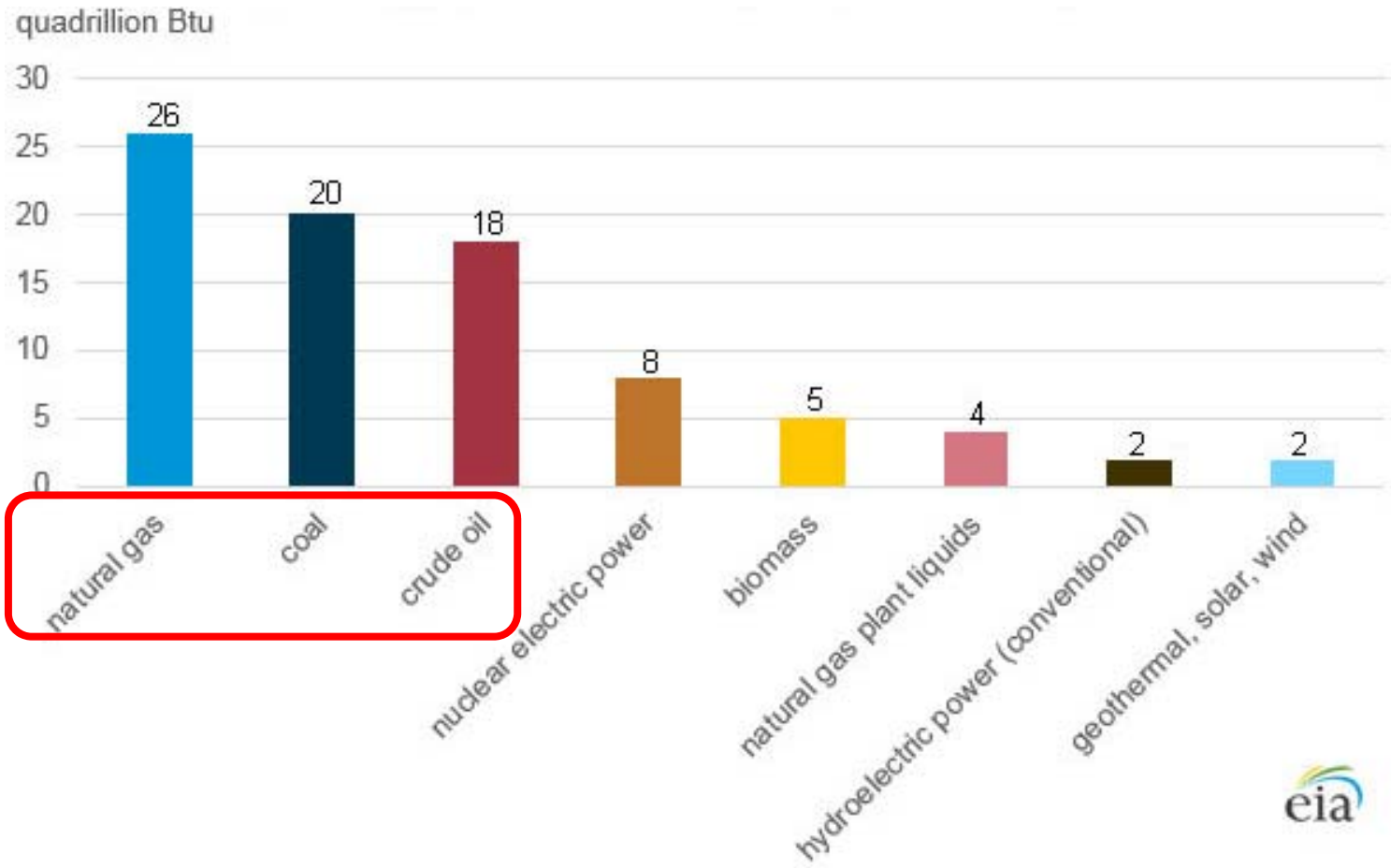
WASHINGTON STATE UNIVERSITY

World Class. Face to Face.

November 1, 2016

1. Critical Needs

1 Primary Energy Production in U.S. by Source, 2015

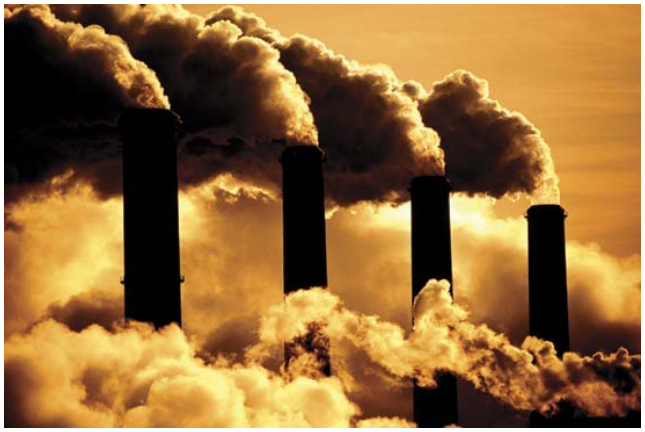


Source: U.S. Energy Information Administration, *Monthly Energy Review* (April 2016), preliminary data

1. Critical Needs

2 Conventional Energy and Limitation

(1) Fossil Fuels



- Pollutant Emission
- Limited Resources

(2) Nuclear Energy

- Wastes

➔ Unlimited and Clean Energy

1. Critical Needs

3 Alternative Energy and Limitation

Renewable and Clean!

- Solar
- Geothermal
- Wind
- Tides

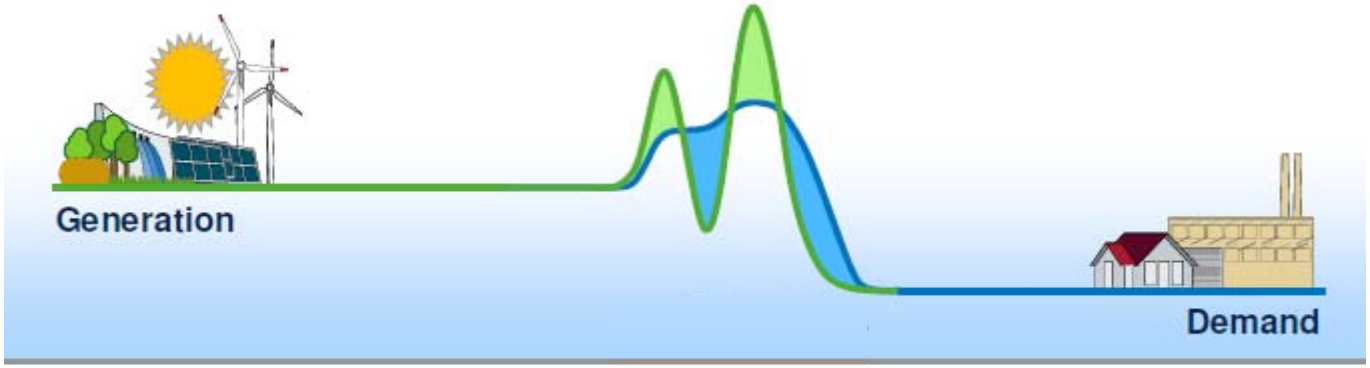
➔ **Intermittent (not continuous)**

Image Courtesy: Mother Earth News (http://www.motherearthnews.com/renewable-energy/free-online-class-zb01210zrob)

1. Critical Needs

4 Urgent Need for Energy Storage Systems

- **Renewable sources are intermittent in nature. (e.g., solar or wind-based electrical generation)**



➔ Electrical energy storage

2. Cutting Edge Technologies

1 Advanced Energy Storage Systems

1. Electrical Energy Storage

e.g. Batteries and Supercapacitors

2. Chemical Storage

e.g. Hydrogen Fuel Cells

2. Cutting Edge Technologies

2 Solar + Battery Systems

Image Courtesy: Tesla

2. Cutting Edge Technologies

2 Solar + Battery Systems

Image Courtesy: Tesla

2. Cutting Edge Technologies

4 Solar + Fuel Cells Systems

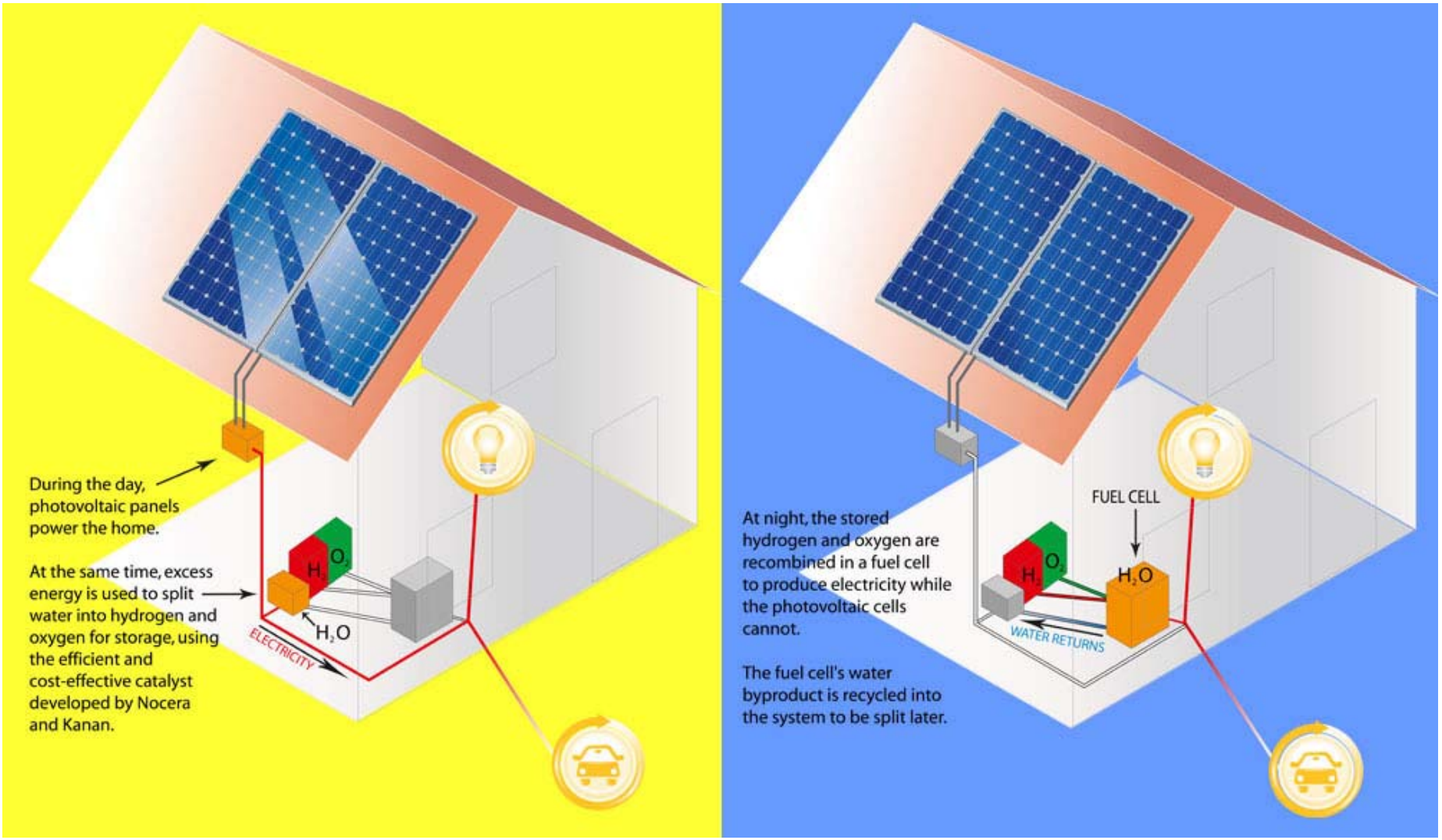


Image Courtesy: Sun Catalytix

2. Cutting Edge Technologies

5 Power Sources for Vehicles: Batteries vs. Fuel Cells

Tesla Model S EV

Hyundai Tucson FCEV

Image Courtesy: Tesla and Hyundai Motor

2. Cutting Edge Technologies

5 Power Sources for Vehicles: Batteries vs. Fuel Cells

Tesla Model S EV

Hyundai Tucson FCEV

Image Courtesy: Tesla and Hyundai Motor

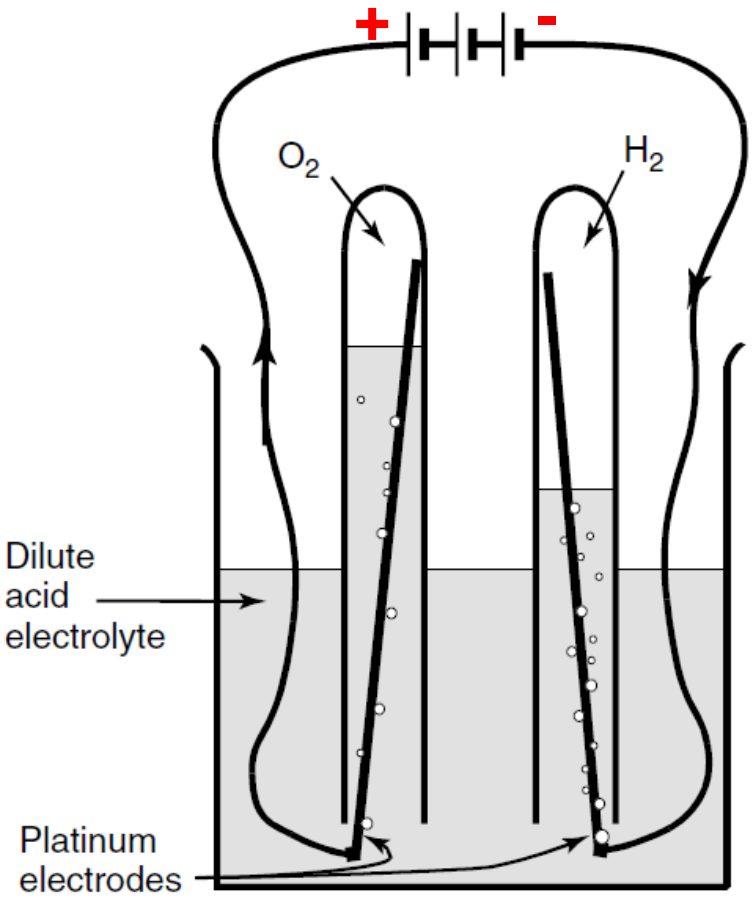
Principles and Materials of Fuel Cells

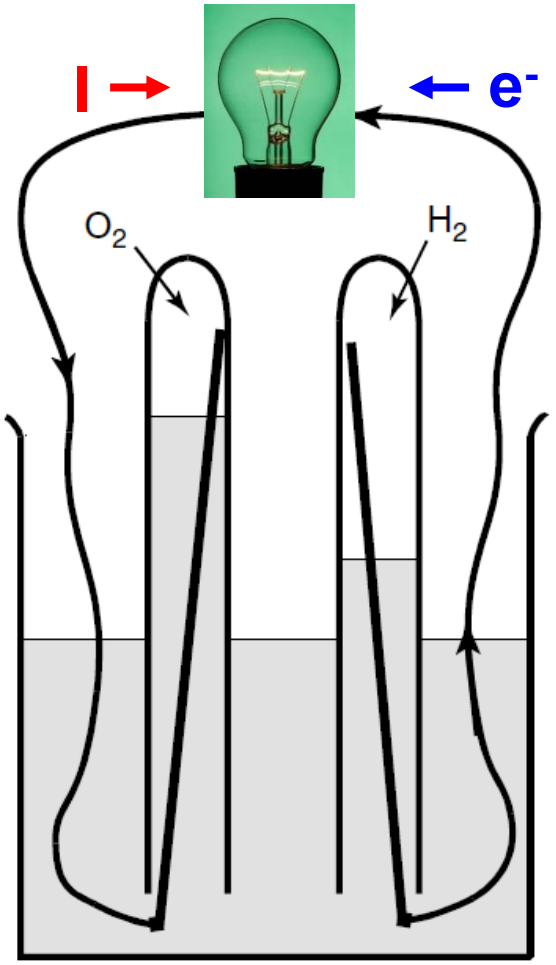
What is a Fuel Cell?

A device that transforms the chemical energy stored in a fuel into electrical energy, emitting only water.

- High energy efficiency
- Clean power sources

Basic principles



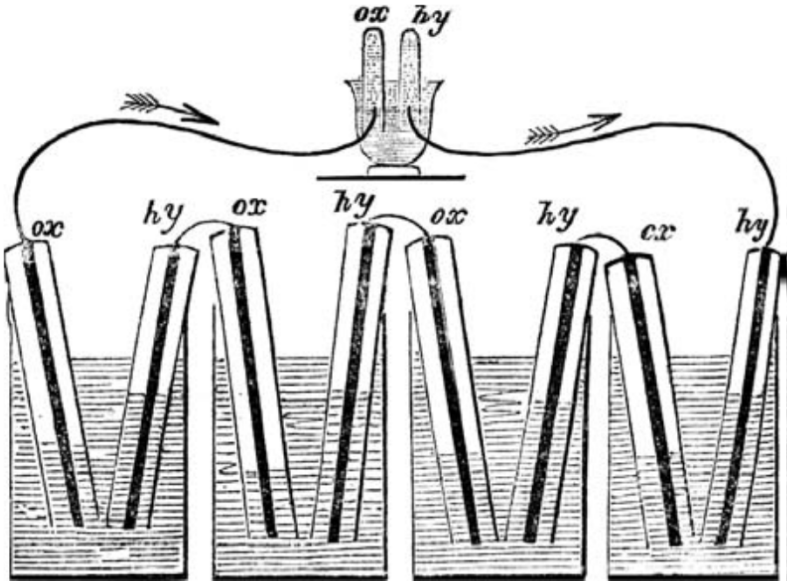


Water decomposition into H_2 & O_2 by passing current

Current generation by recombination of H_2 & O_2

A brief history

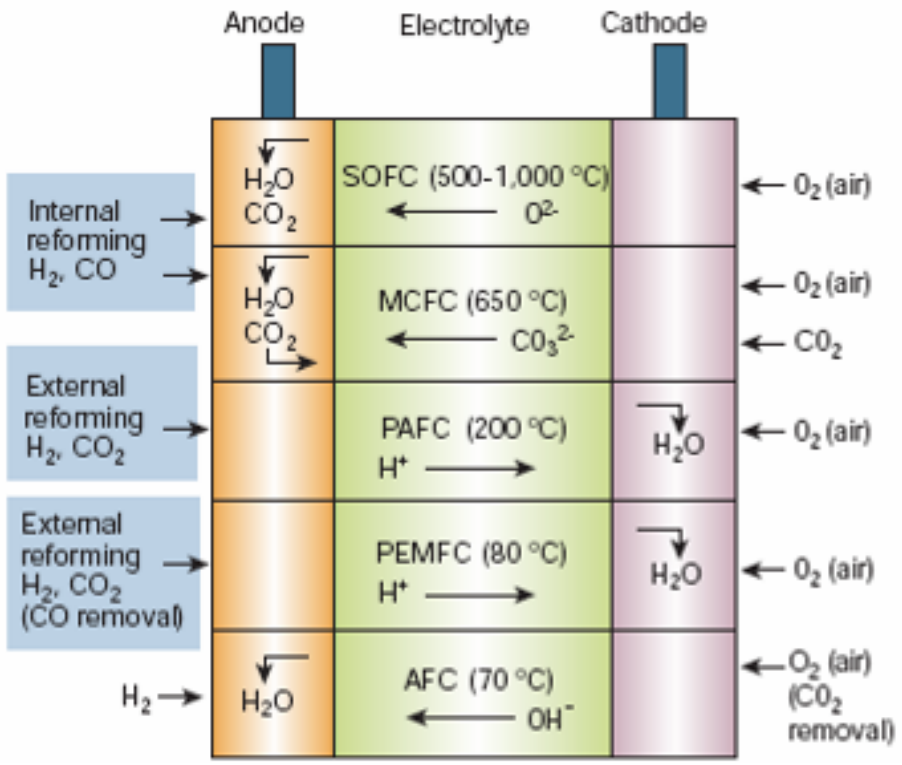
Since William R. Grove, a British lawyer and amateur physicist, discovered the principle of the fuel cell in 1839



The First laboratory demonstration in 1839

Gemini Spacecraft in 1965

Types of Fuel Cells



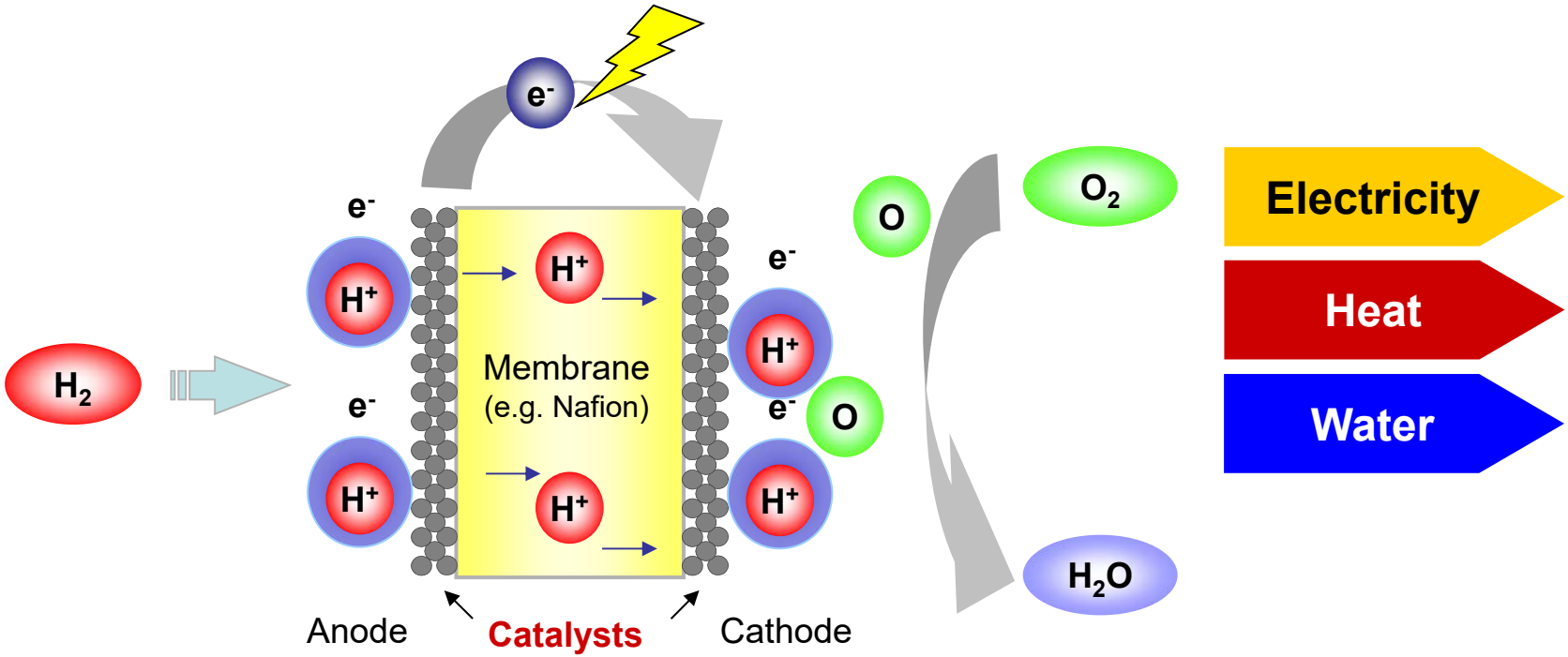
All fuel cells react a fuel and oxygen to generate electricity, **but differ in "electrolyte"** which determines the important features of fuel cells such as operating temperature, materials, the variety of fuels.

B.C.H. Steele et al., Nature, 414, 2001

Operation Principles of PEM Fuel Cells

What is PEM? Polymer Electrolyte Membrane
(or Proton Exchange Membrane)

Oxidation reaction at Anode	$2H^+ \rightarrow 4H^+ + 4e^-$
Reduction reaction at Cathode	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
Total cell reaction	$2H^+ + O_2 \rightarrow 2H_2O$



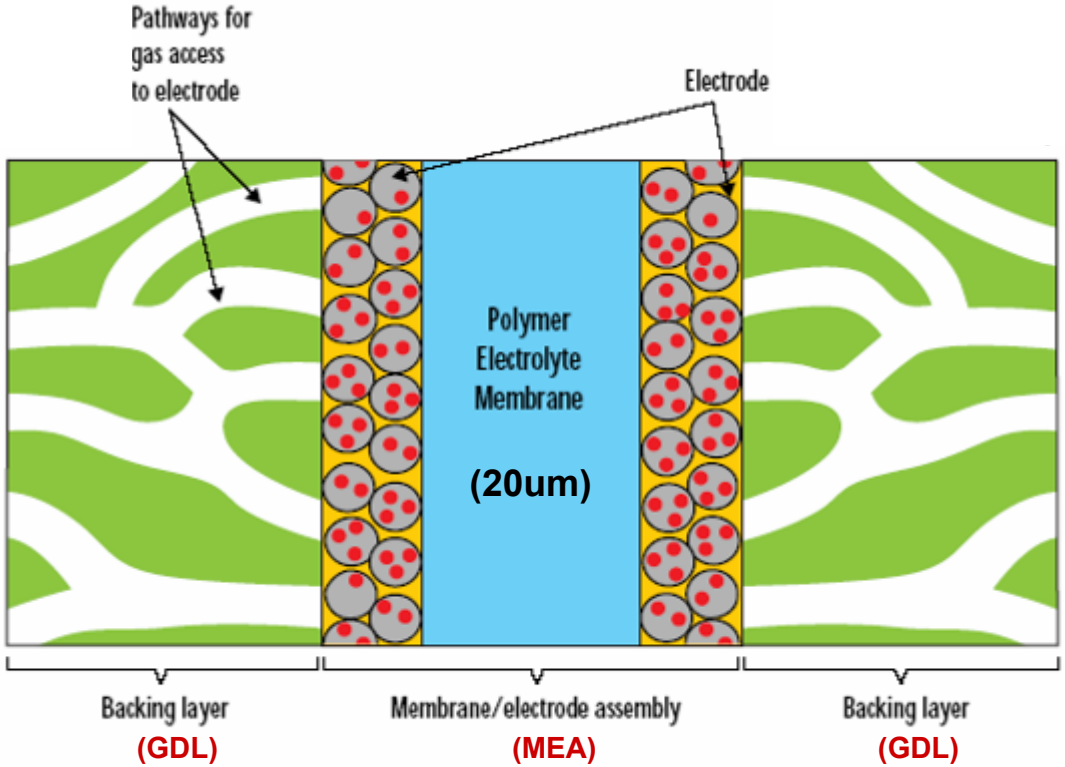
Components of PEM Fuel Cells

1 Proton Exchange Membrane

MEA : Membrane Electrode Assembly

3L-MEA : Electrode + Membrane + Electrode

5L-MEA : GDL + 3L-MEA + GDL



Enlarged cross-section of a membrane/electrode assembly showing structural details.

Thomas, *Fuel Cells: Green Power* from Los Alsmos National Lab.

Components of PEM Fuel Cells

2 Electrode : Platinum catalysts + Carbon supports

Why Platinum?

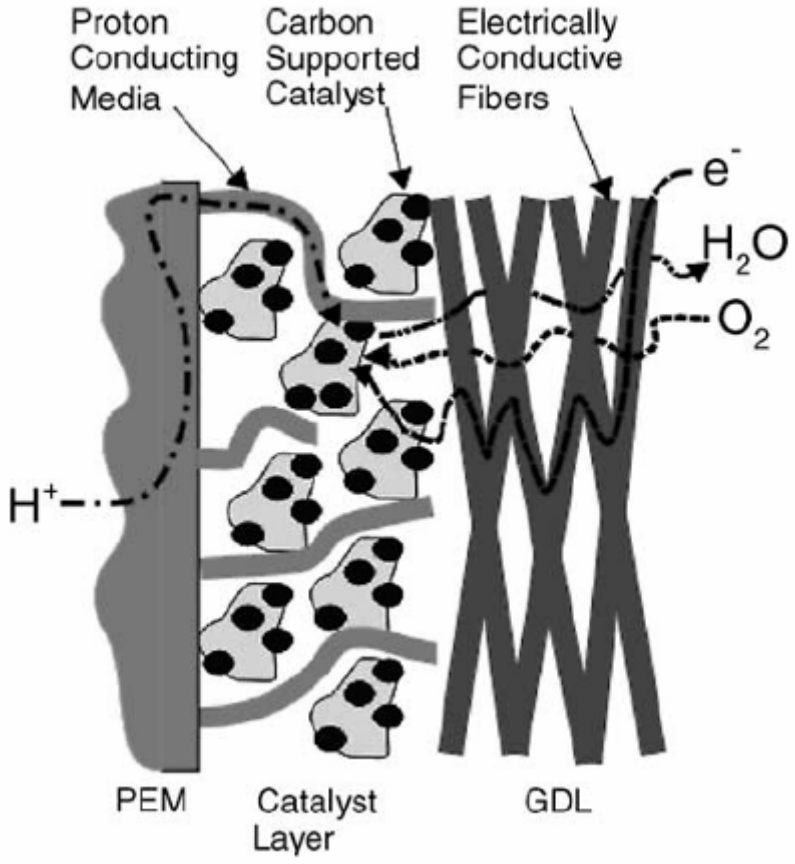
- Sufficiently reactive in bonding H and O intermediates as required to facilitate the electrode process
- Capable of effectively releasing the intermediate to form the final product

e.g., $H_2 + 2Pt \rightarrow 2\ Pt\text{-}H$

$2\ Pt\text{-}H \rightarrow 2Pt + 2H^+ + 2e^-$

Why Carbon supports?

- Low cost compared to others such as alumina, silica
- Superior mechanical, thermal and chemical stability
- Various structural forms: planar, porous etc.



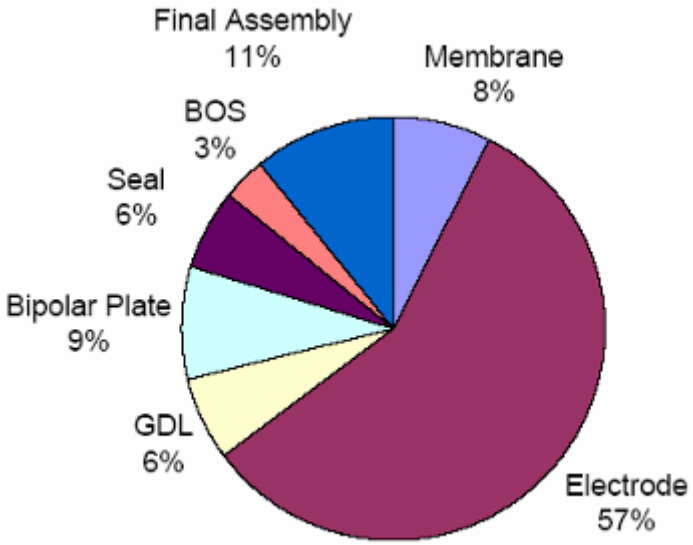
Transport of gases, protons, and electrons in a PEMFC electrode

(Litster et al., *Journal of Power Sources, 130,* 2004)

Remaining Challenges

1 Current challenging issues of electrodes

1) Cost : Precious metal requirement and loadings



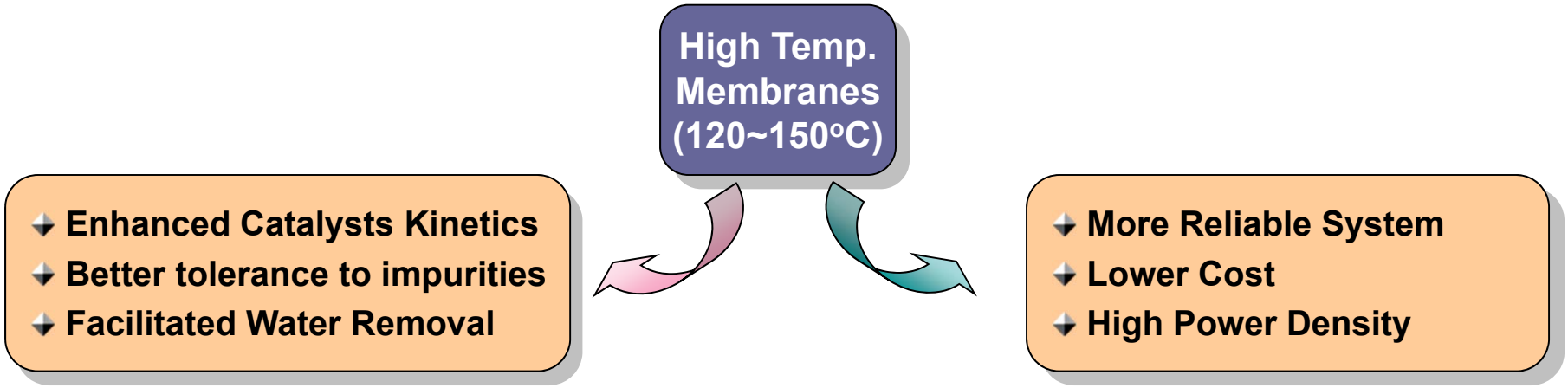
Source: http://www.hydrogen.energy.gov/annual_review07_fuelcells.html

2) Electrode efficiency : Cathode voltage loss

Remaining Challenges

2 Current challenging issues of polymer membranes

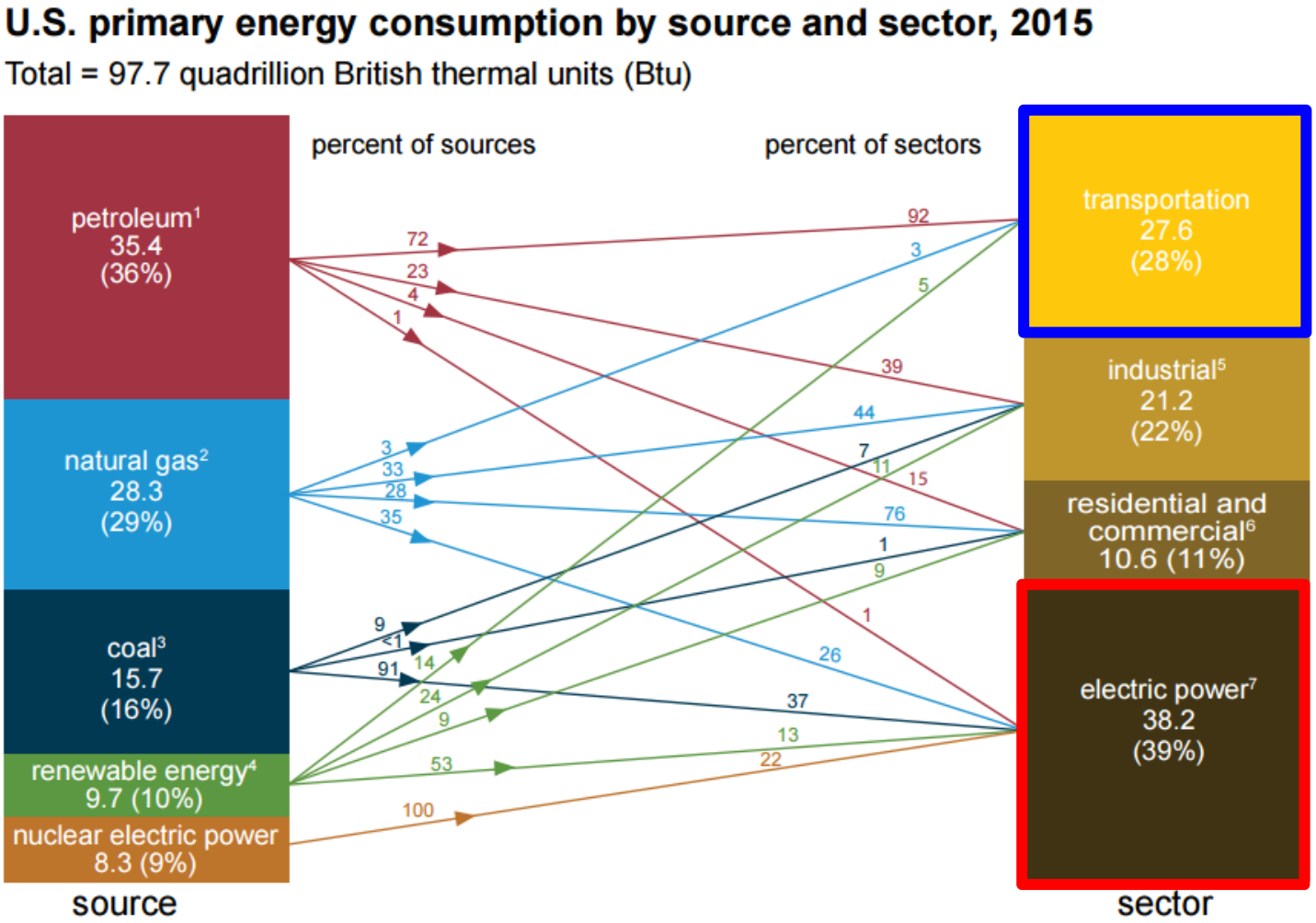
- ✓ Degradation due to freeze/thaw cycling
- ✓ Requires difficult water and thermal management
- ✓ Not functional in low humidity (<10% RH)



Advanced Batteries based on Earth-abundant Materials

1. Motivation

1 Two largest energy sectors: Grid & Transportation

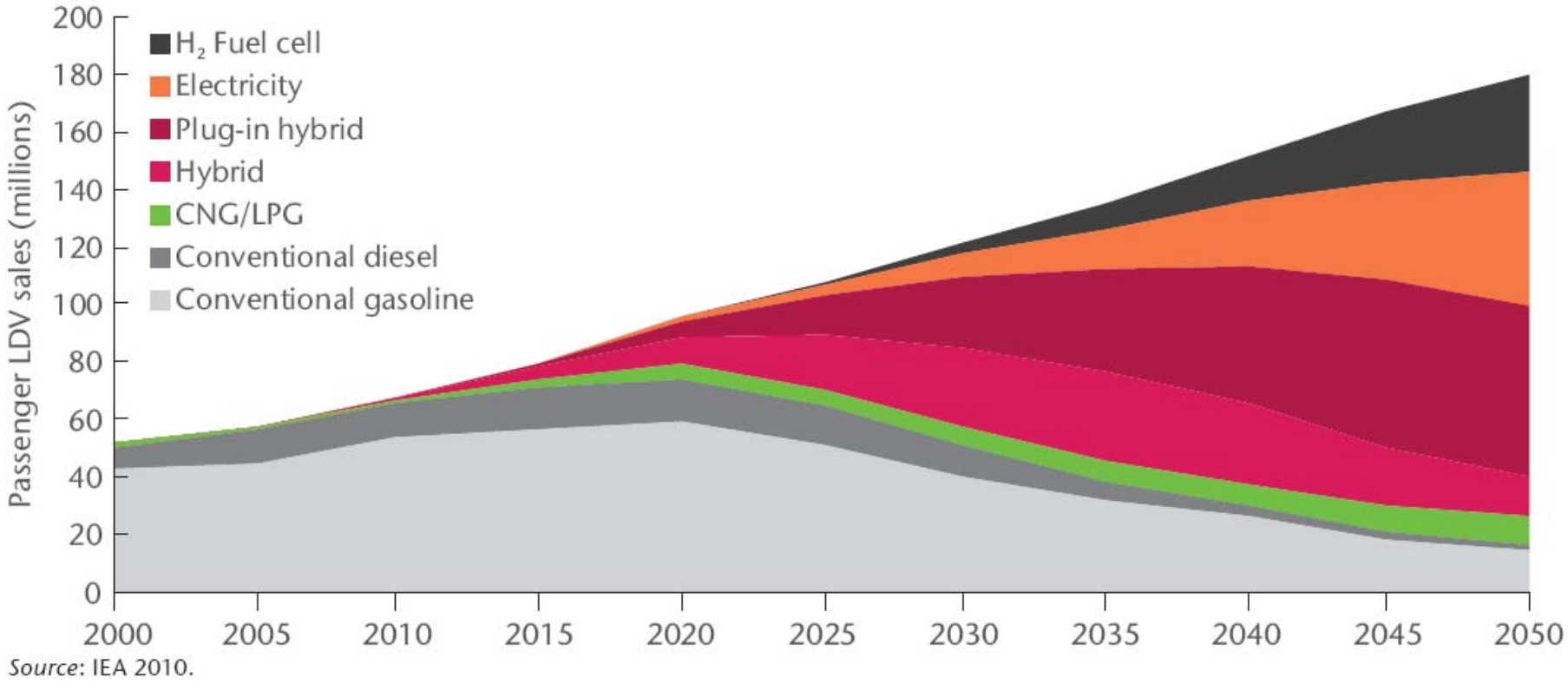


Sources: U.S. Energy Information Administration

1. Motivation

2 Vision 2050: "Green" Transportation

IEA Vision: To achieve by 2050 the widespread adoption and use of EVs and PHEVs, which together represent more than 50% of annual light duty vehicle sales worldwide.



Source: IEA 2010.

2. Background

1 Key Challenge of Current Li-ion Batteries

Not able to meet the ever-increasing demands of advanced technology at affordable cost

http://tia.ucsb.edu/range-anxiety-electric-vehicles-use-new-battery-technology-to-travel-farther/

2. Background

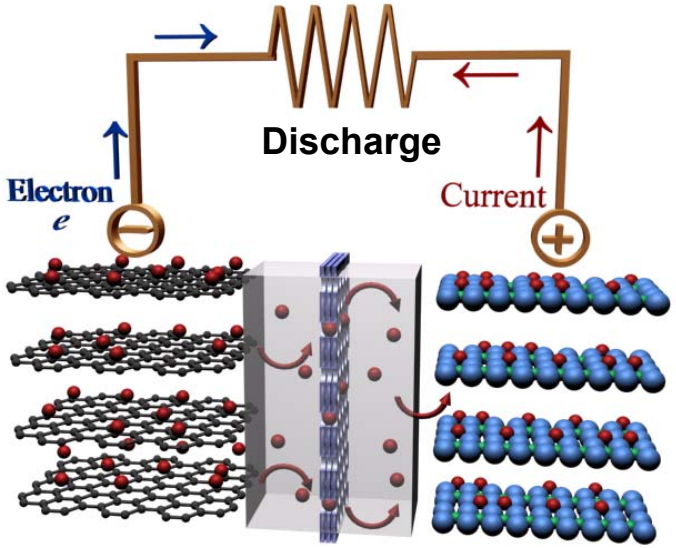
2 Principle of Li-ion Batteries: Intercalation Chemistry

Future anodes

Silicon

Hard Carbon

Lithium metal



Future cathodes

O_2 (Air)

Sulfur

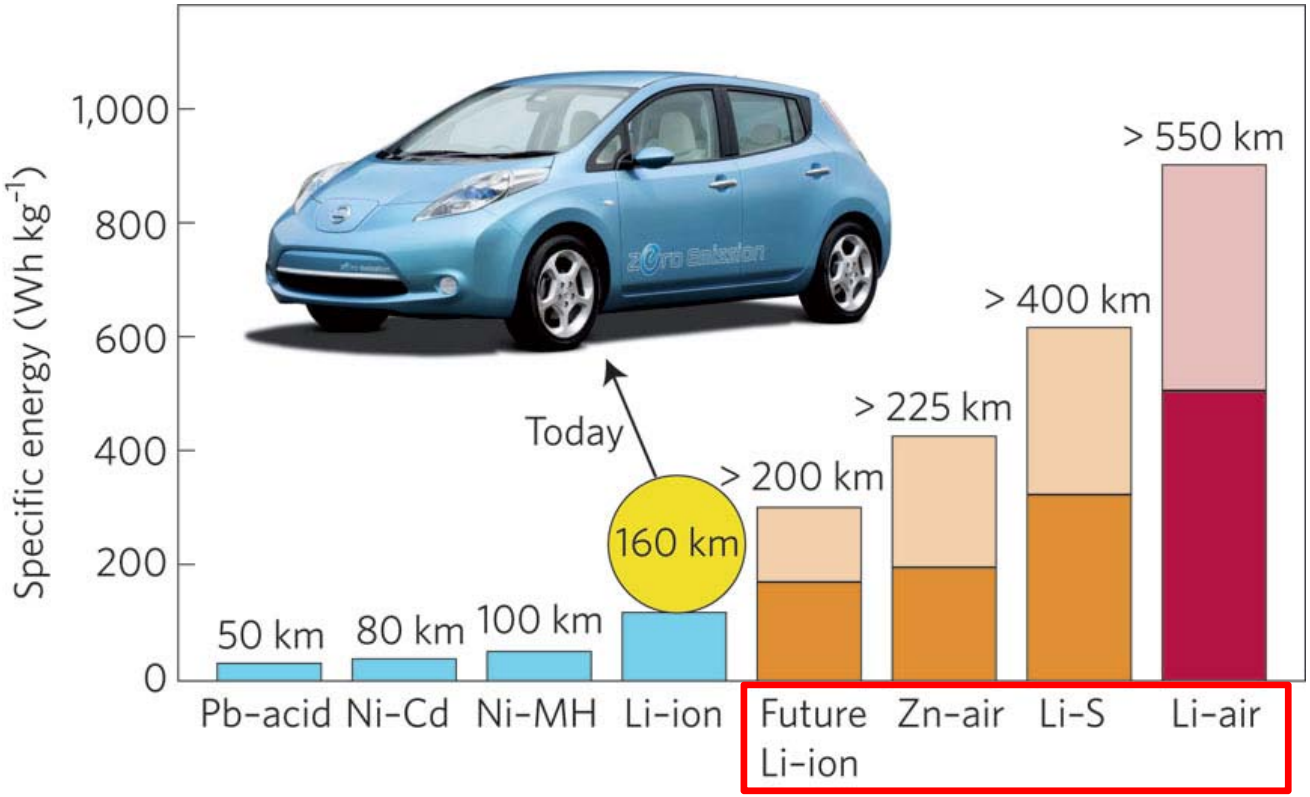
$$\tfrac{1}{2}\, C_6Li + Li_{0.5}CoO_2 \leftrightarrow 3C + LiCoO_2$$

- **Major limiting factor: low intrinsic capacities of current electrode materials**

2. Background

3 Next-Generation Batteries for Electric Vehicles

1 km = 0.62 mi (1 mi = 1.61 km)



e.g. Silicon anode

P. G. Bruce et al., Nature Materials, 11, 2012

2. Background

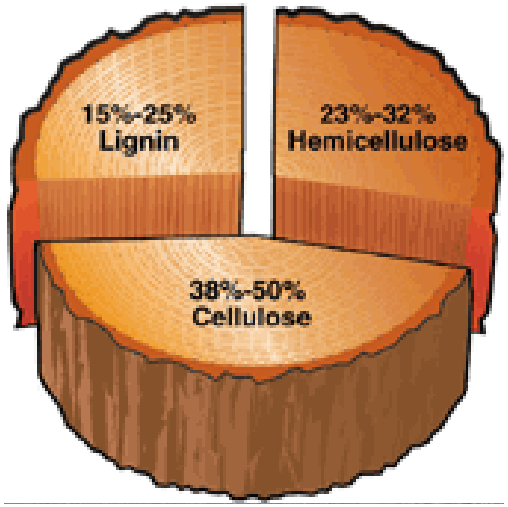
4 Key Elements for Advanced Batteries

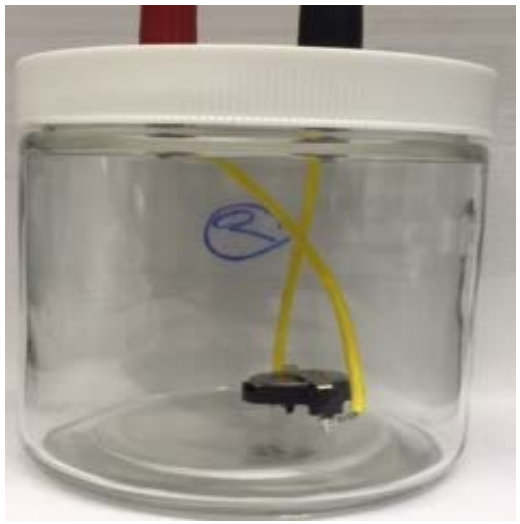
2. Background

5 Sustainable Resources for Clean Energy Storage

2. Background

5 Sustainable Resources for Clean Energy Storage





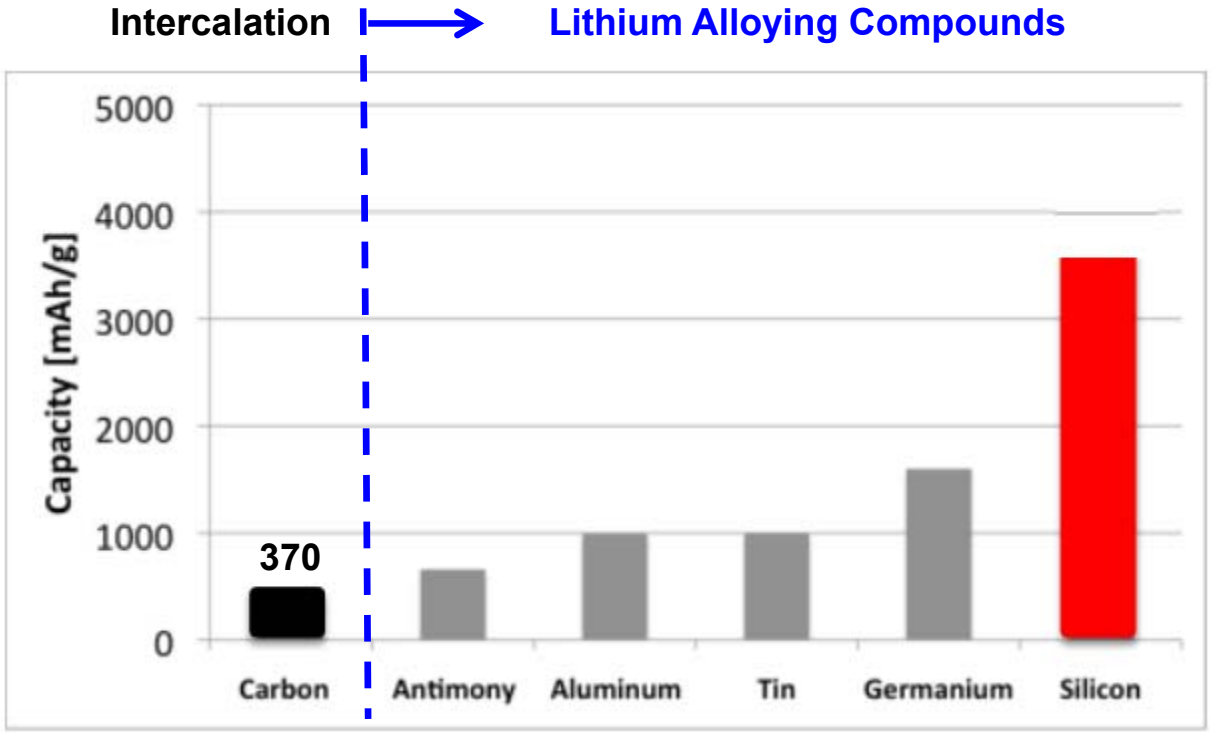
3. Electrodes for Next-Generation Batteries

3.1. Silicon Anodes for Advanced Batteries

3.2. Sulfur Cathodes for Advanced Batteries

3-1. Silicon Anodes for Advanced Batteries

1 Why Silicon to replace Graphite Anodes?



Silicon can offer 10 times higher capacity (specific energy) than current graphite anodes

3-1. Silicon Anodes for Advanced Batteries

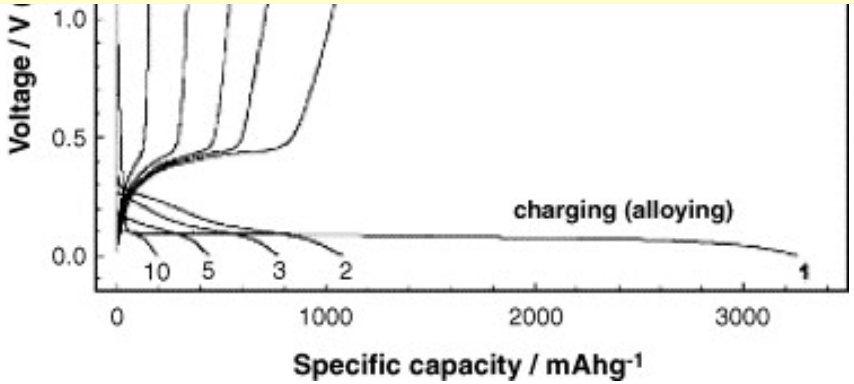
2 Critical Challenge of Silicon Anodes

Large volume expansion (~300%)

→ Cracking and disintegration of the electrodes

→ Poor electronic contacts between Si particles

→ Severe capacity fade & low columbic efficiency



Typical charge–discharge profiles for Silicon powder (10 μm) anodes

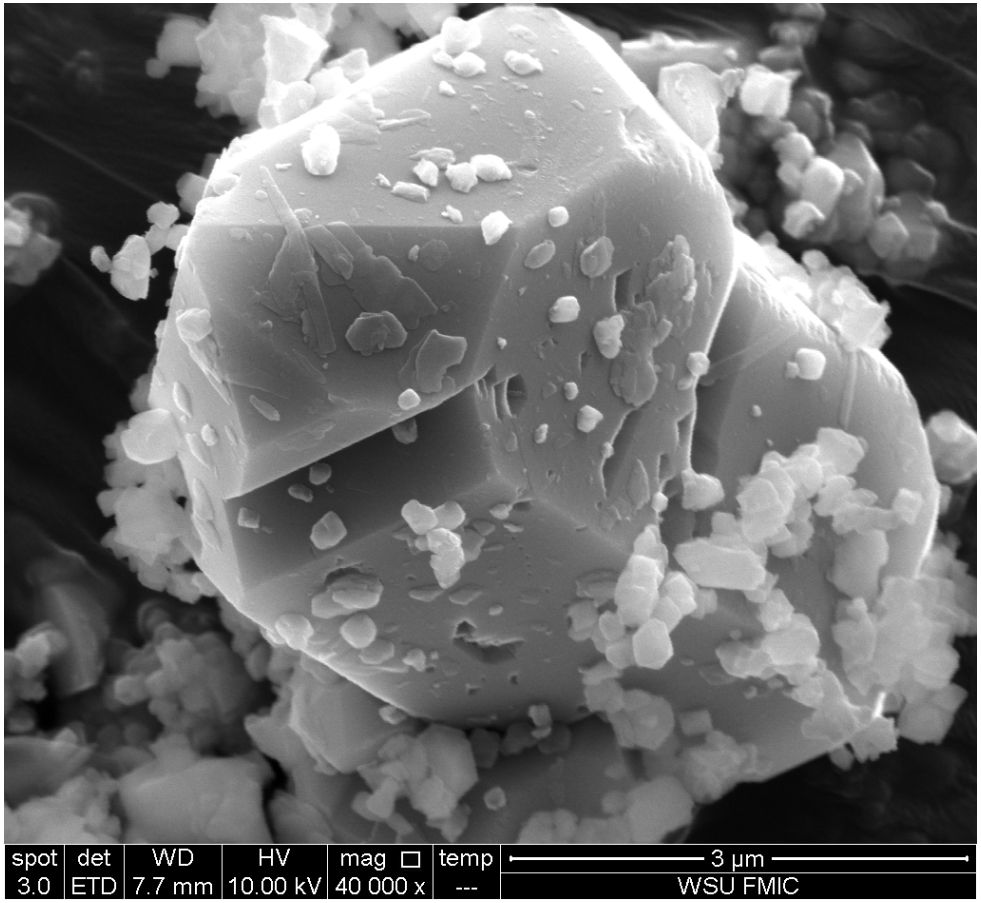
Irreversibility: Rapid fading in capacity during cycling

J. Appleby et al, Journal of Power Source, 163, 2007

3-1. Silicon Anodes for Advanced Batteries

3 Synthesis of Porous Silicon from Commercial SiO_2

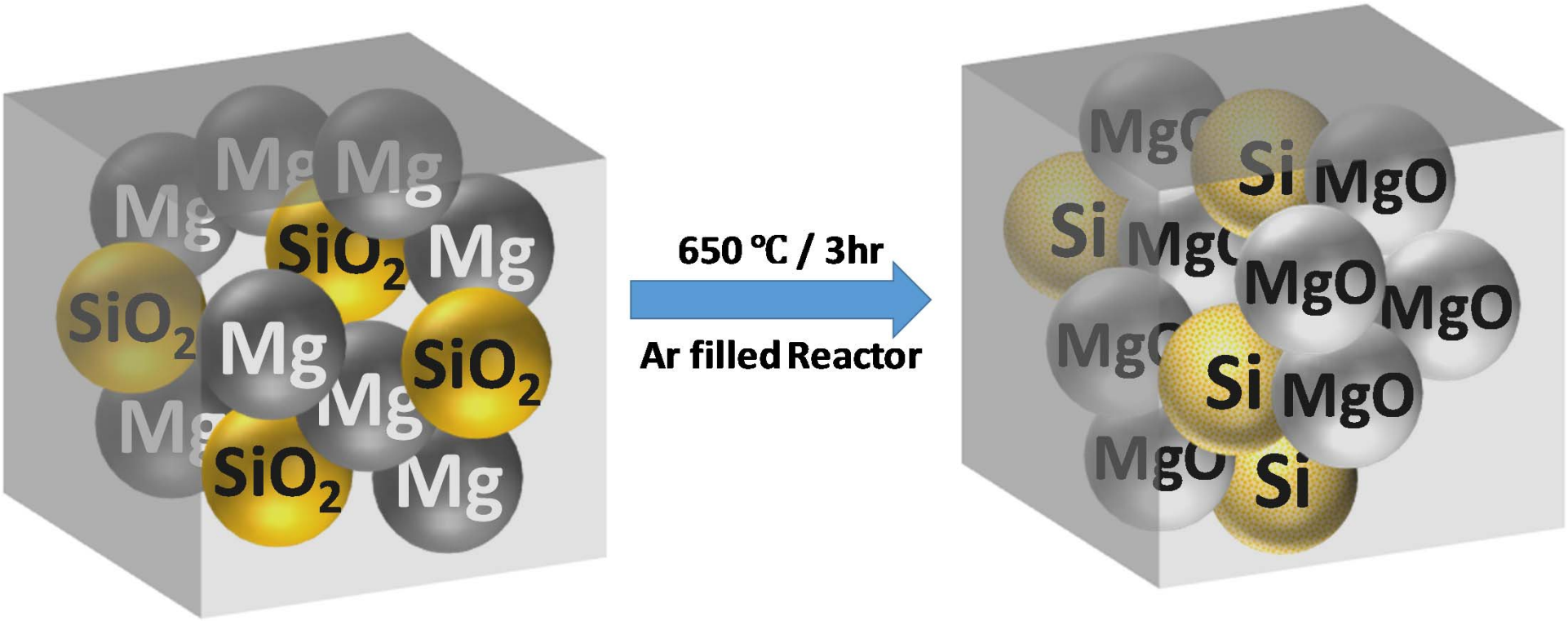
Commercial Silica (quartz, < 10um)



$$2Mg(g) + SiO_2(s) \rightarrow 2MgO(s) + Si(s)$$

3-1. Silicon Anodes for Advanced Batteries

4 Magnesiothermal Reduction Route

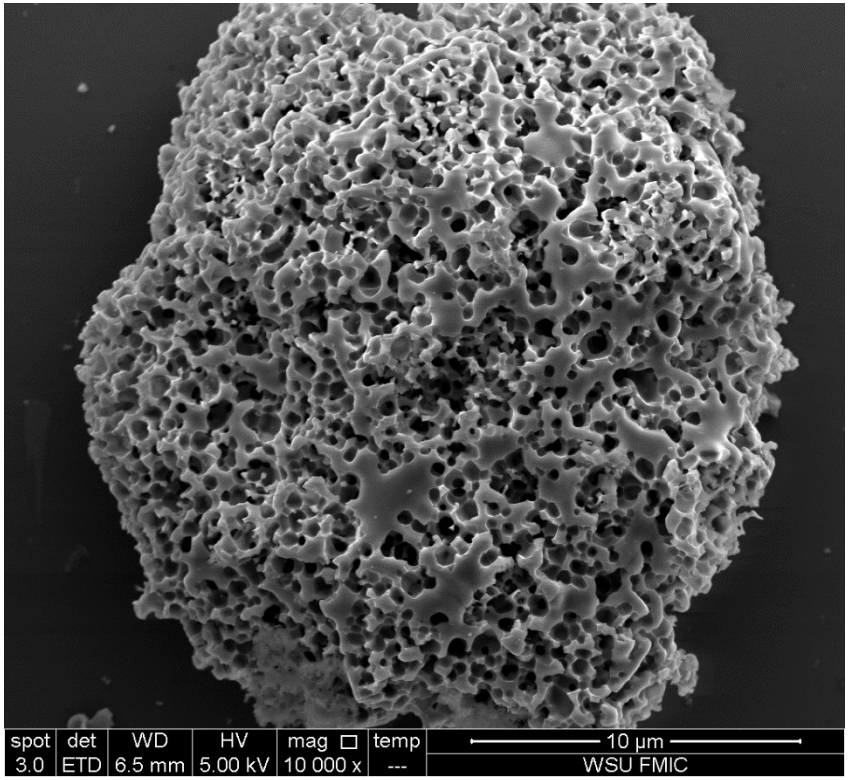


$$2Mg(g) + SiO_2(s) \rightarrow 2MgO(s) + Si(s)$$

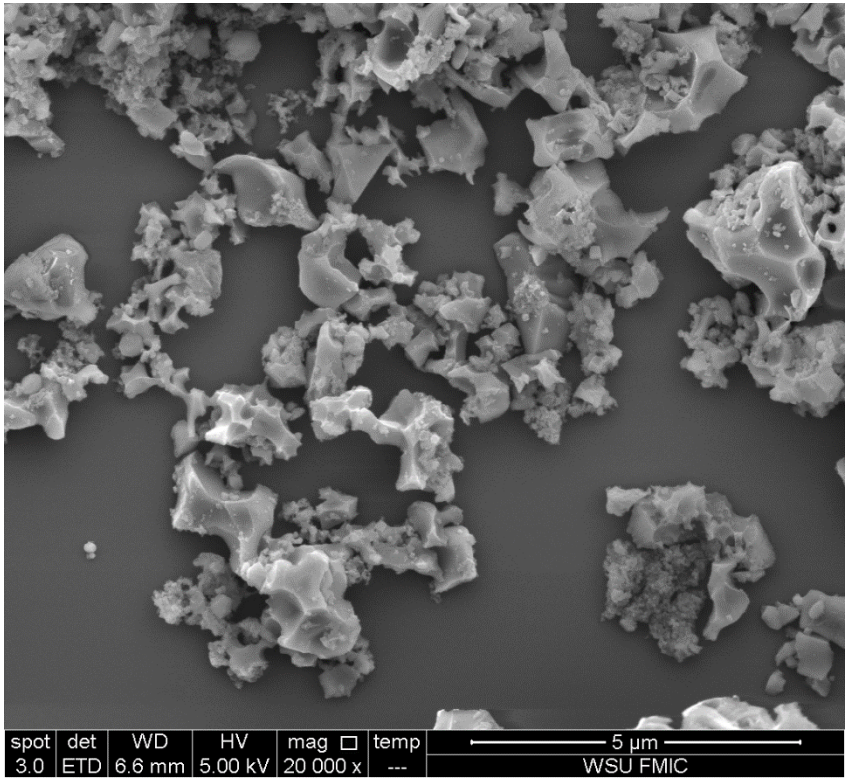
3-1. Silicon Anodes for Advanced Batteries

5 Processing-Structure Relationship

1℃/min



5℃/min

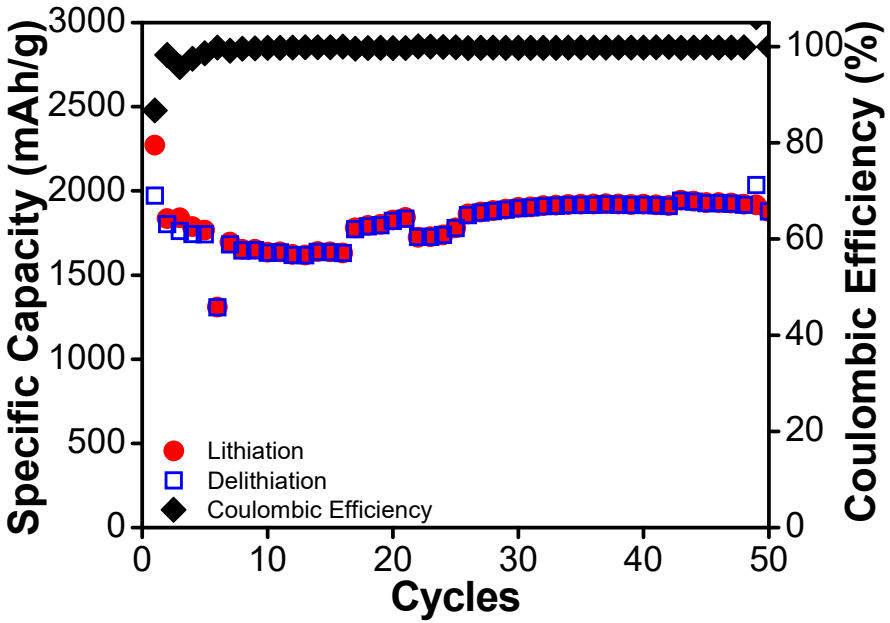


$$2Mg(g) + SiO_2(s) \rightarrow 2MgO(s) + Si(s)$$

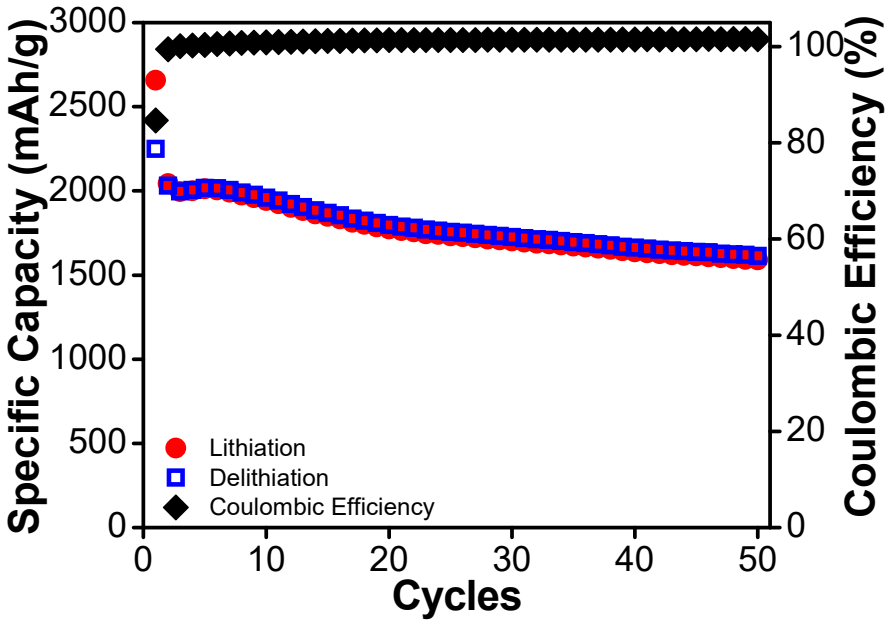
3-1. Silicon Anodes for Advanced Batteries

6 Structure-Performance Relationship

1℃/min



5℃/min



3. Electrodes for Next-Generation Batteries

3.1. Silicon Anodes for Advanced Batteries

3.2. Sulfur Cathodes for Advanced Batteries

3-2. Sulfur Cathodes for Advanced Batteries

1 Why Li/S Batteries?

High Theoretical energy density

: Advanced Li/S batteries could provide >300 mile range for electric vehicles.

Light Weight

$LiMO_2$:4.8g/cm³ vs. α-Sulfur:2.07g/cm³

Environmentally benign

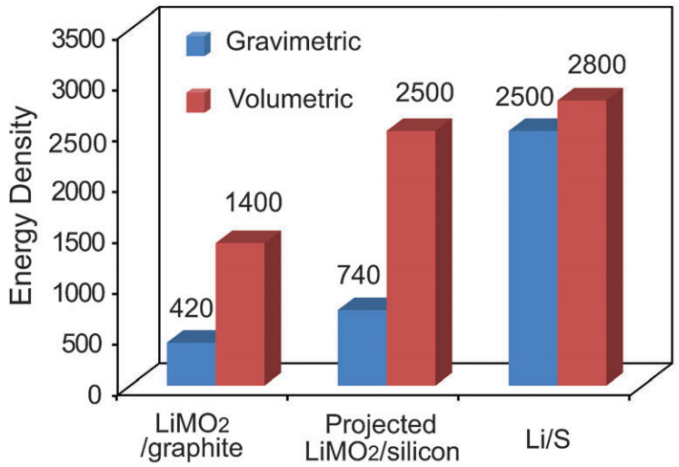
Sulfur is a non-toxic material while $LiCoO_2$ is harmful to environment.

$$S + 2Li^+ + 2e^- \leftrightarrow Li_2S$$

(2 electron reaction)

Theoretical specific capacity: 1,672 mAh/g

Capacities of current cathodes: 130 ~200 mAh/g (e.g. $LiCoO_2$)



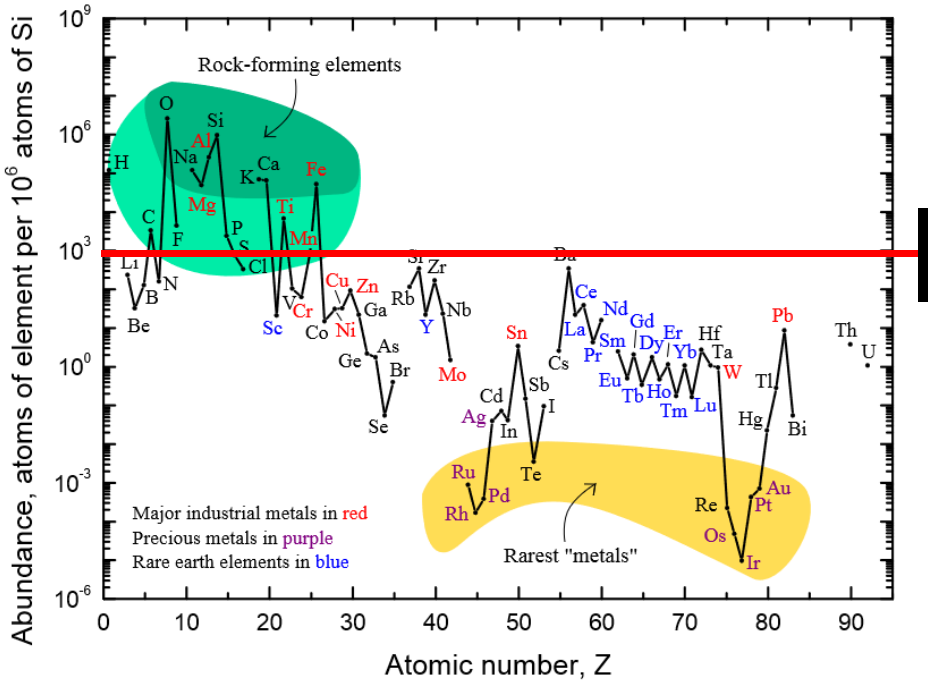
(M = $Ni_{1/3}Mn_{1/3}Co_{1/3}$)

Y Yang, et al. Chemical Society Reviews, 2013, 42 (7), 3018

3-2. Sulfur Cathodes for Advanced Batteries

1 Why Li/S Batteries? (continued)

Earth-abundant source → Lost cost

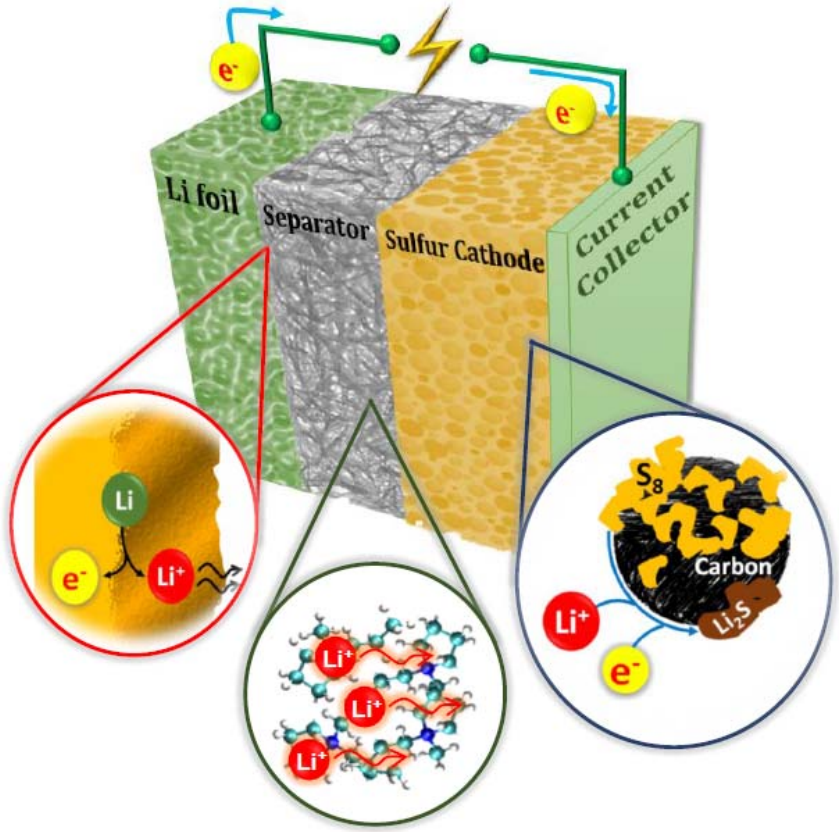


- **350 mg / 1kg of Earth Crust**
- **880 mg / 1kg of Sea Water**

Direct Utilization of Industrial waste

3-2. Sulfur Cathodes for Advanced Batteries

2 Structure and Chemical Reactions in Li/S Batteries



Chemical Reaction Formular

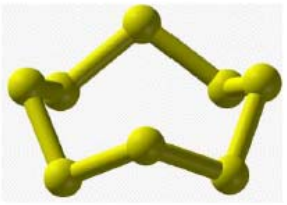
Anode: $Li \rightarrow Li^+ + e^-$

Cathode : $2Li^+ + 2e^- + S \rightarrow Li_2S$

Overall Reaction: $2Li + S \rightarrow Li_2S$

Overall Reaction (real)

$16Li + S_8 \rightarrow 8Li_2S$?



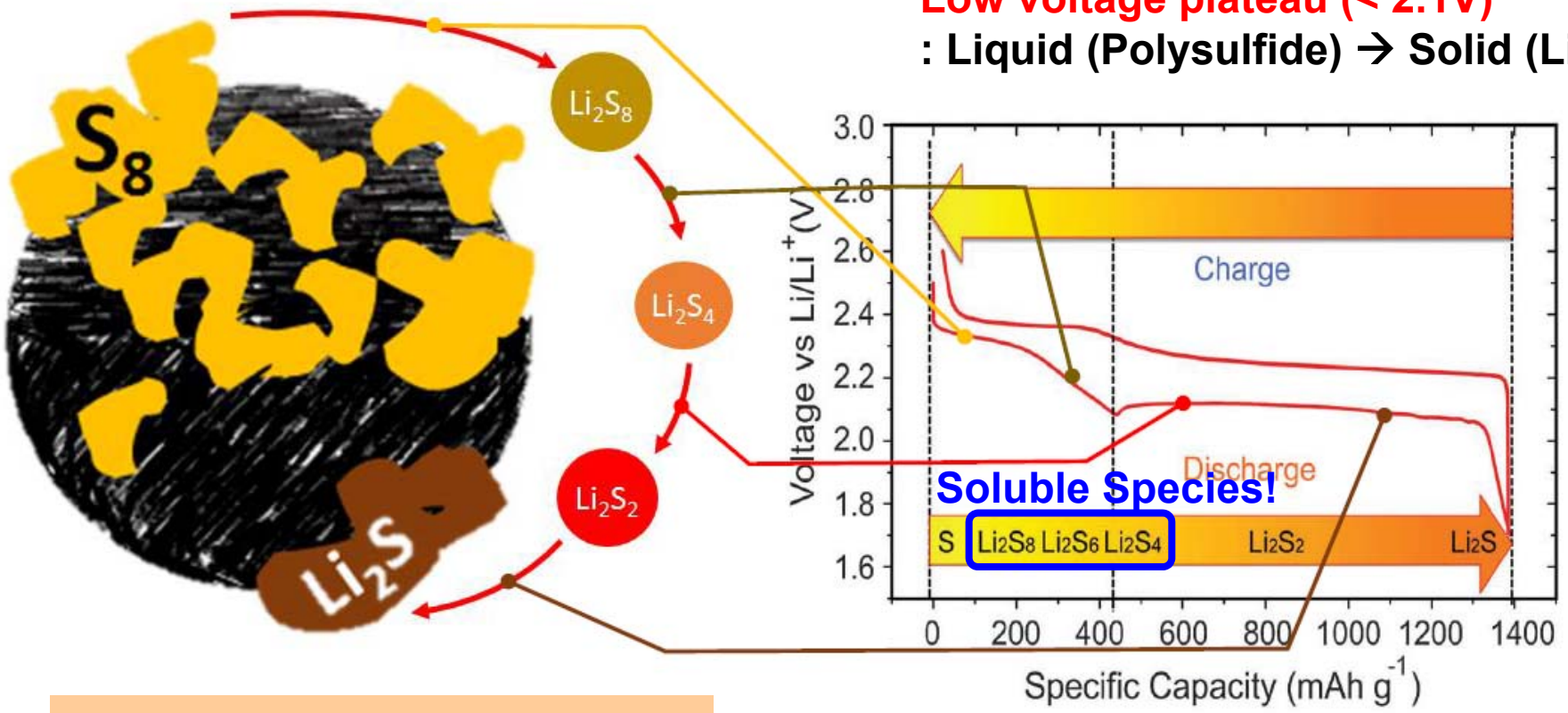
Under normal condition, sulfur atoms form cyclic octatomic molecules with chemical formula S_8.

$S_8 \rightarrow 8S$: How the order reduces ?

3-2. Sulfur Cathodes for Advanced Batteries

3 Discharge/Charge Characteristics of Li/S Batteries

High voltage plateau (2.4-2.1V)
: Solid (S_8) → Liquid (Polysulfide)
Low voltage plateau (< 2.1V)
: Liquid (Polysulfide) → Solid (Li_2S)



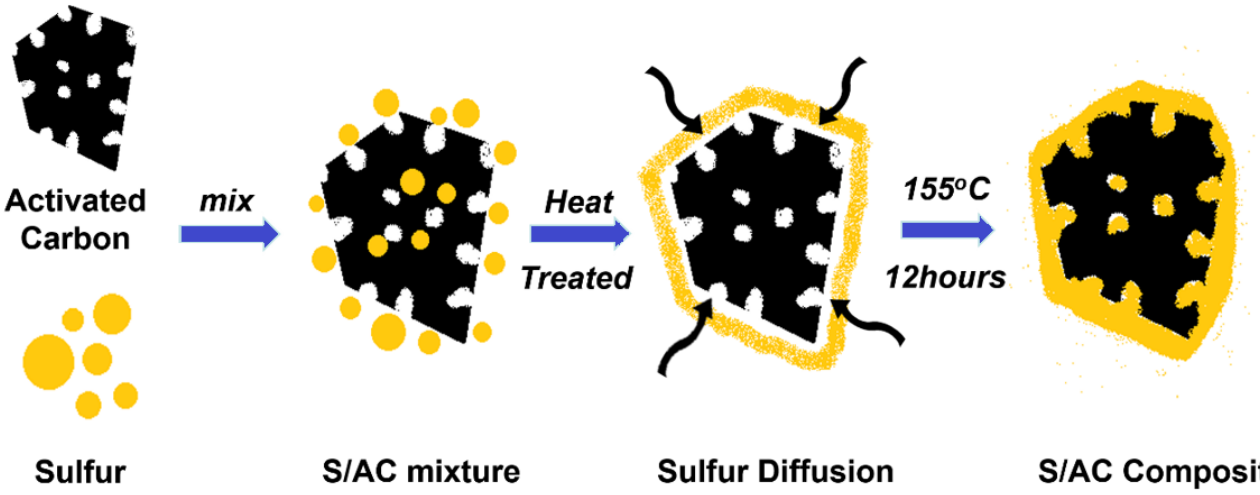
Solid → Liquid → Solid

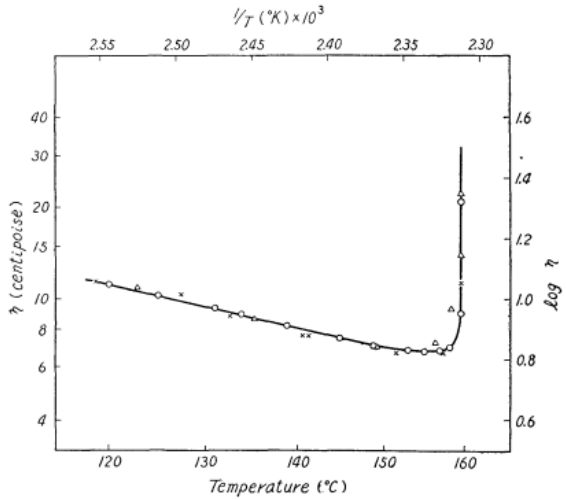
Y Yang, et al. Chemical Society Reviews, 2013, 42 (7), 3018

3-2. Sulfur Cathodes for Advanced Batteries

4 Design Criteria for Sulfur Electrodes

Requirements of an ideal Sulfur electrode for Li/S cells

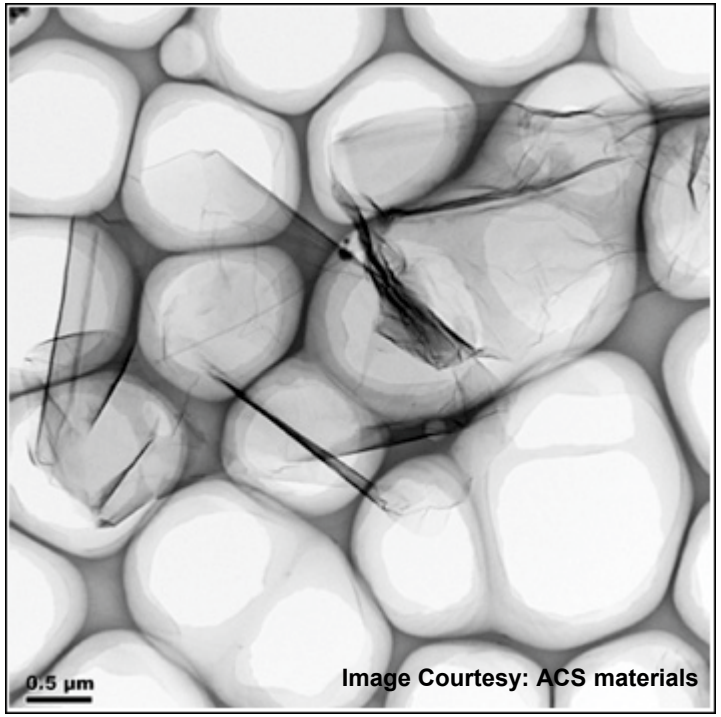




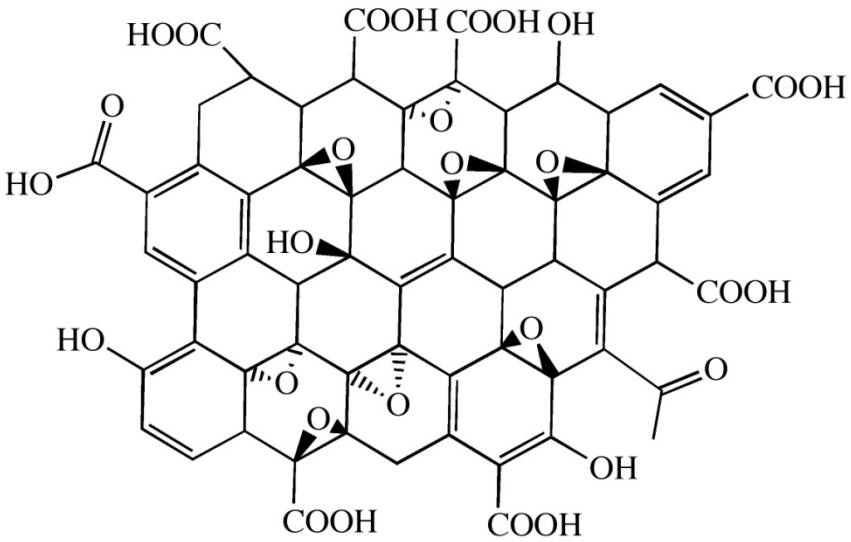
(3) Use chemical interaction to immobilize sulfur/polysulfides.

3-2. Sulfur Cathodes for Advanced Batteries

5 Oxygen Functional Groups as Sulfur Immobilizer



Chemical Approach

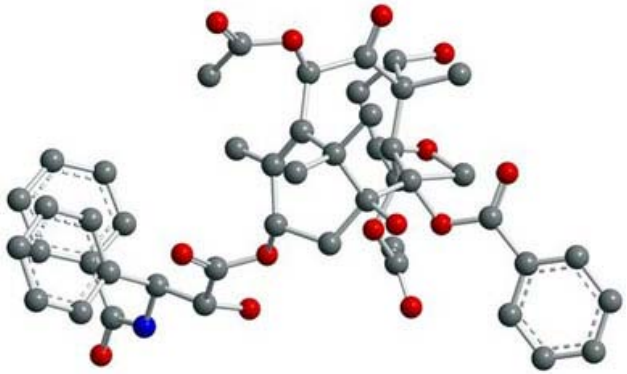


There are functional groups such as sp^2 carbon (C=C), hydroxyl (C-OH), epoxide (C-O-C), carbonyl (> C=O) and carboxyl (HO-C=O) on the surface.

3-2. Sulfur Cathodes for Advanced Batteries

6 Polymeric sulfur materials

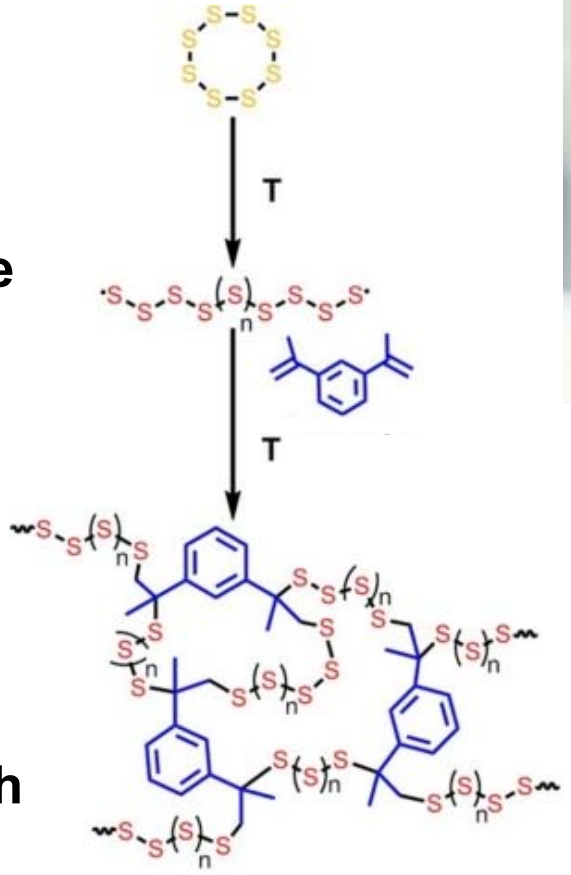
Sulfur-byproduct during the refining of petrol



Polymer-chain structure with functional groups

W. Chung et al, Nature Chemistry, 5, 2013

Inverse vulcanization



Inverse vulcanized polymeric sulfur

Long-Lasting, High Capacity Batteries

4. Outlook: *Beyond 2020*

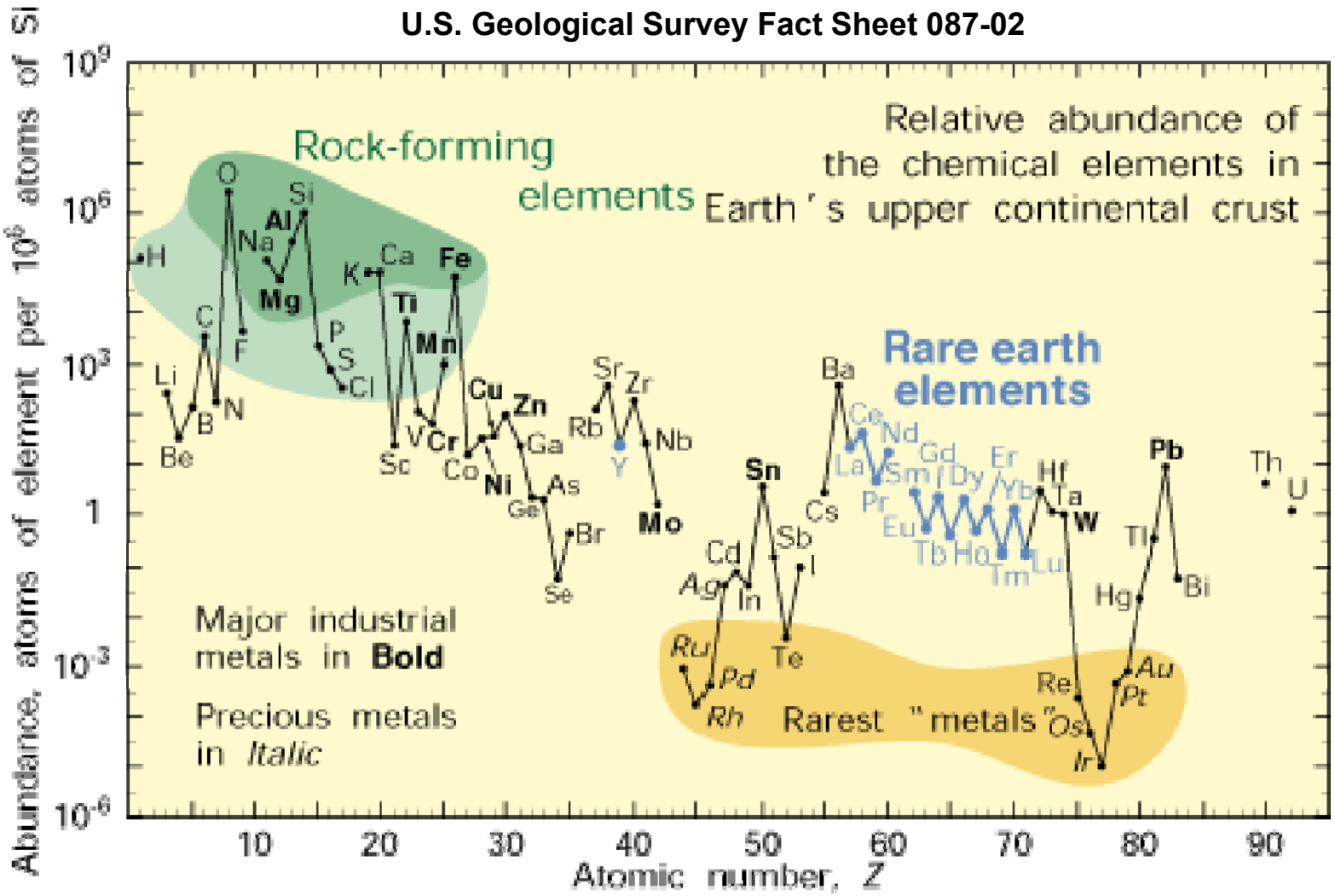
1 Who will drive Electric Vehicles?

Cost, Cost, Cost!

Image courtesy: Fraunhofer ISI

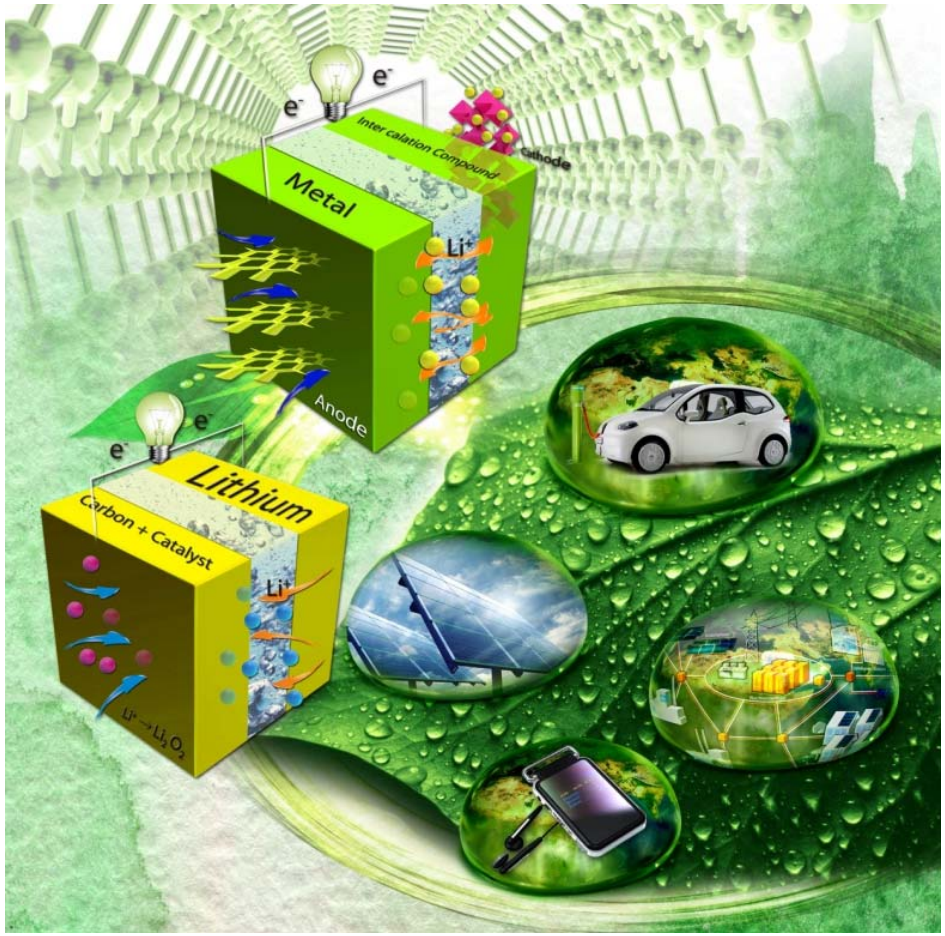
4. Outlook: *Beyond 2020*

2 Abundance matters!



http://pubs.usgs.gov/fs/2002/fs087-02/

Q & A


e⁻
e⁻
Inter calation Compound
Cathode
Metal
Li⁺
Anode
e⁻
e⁻
Lithium
Carbon + Catalyst
Li⁺
Li⁺ → Li₂O₂