

Lithium Air Battery

By Joshua Harris

Overview

- Background
- Discovery
- Science
- Conclusions
- References

Background: How are Batteries Green?

“A battery is a device that converts chemical energy into electrical energy by means of an electrochemical reduction-oxidation (redox) reaction”



Background: How are Batteries Green?

- There are two types of batteries: primary and secondary.
- In **primary batteries**, the electrode reactions are not reversible and the cells are therefore not rechargeable, *i.e.* after one discharge, they are discarded.



Background: How are Batteries Green?

- There are two types of batteries: primary and secondary.
- In **primary batteries**, the electrode reactions are not reversible and the cells are therefore not rechargeable, *i.e.* after one discharge, they are discarded.
- In **secondary batteries**, the electrode reactions are reversible and the cells are rechargeable.



Background: Electron Economy



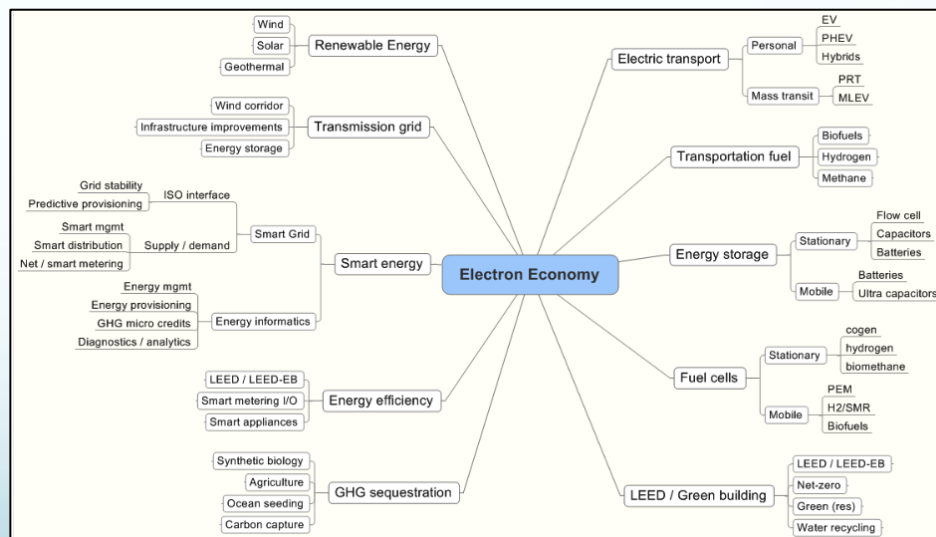
- The Goal is to replace fossil fuels as our main energy source
- The combustion of fossil fuels releases toxic and greenhouse gasses into the atmosphere

Background: Electron Economy



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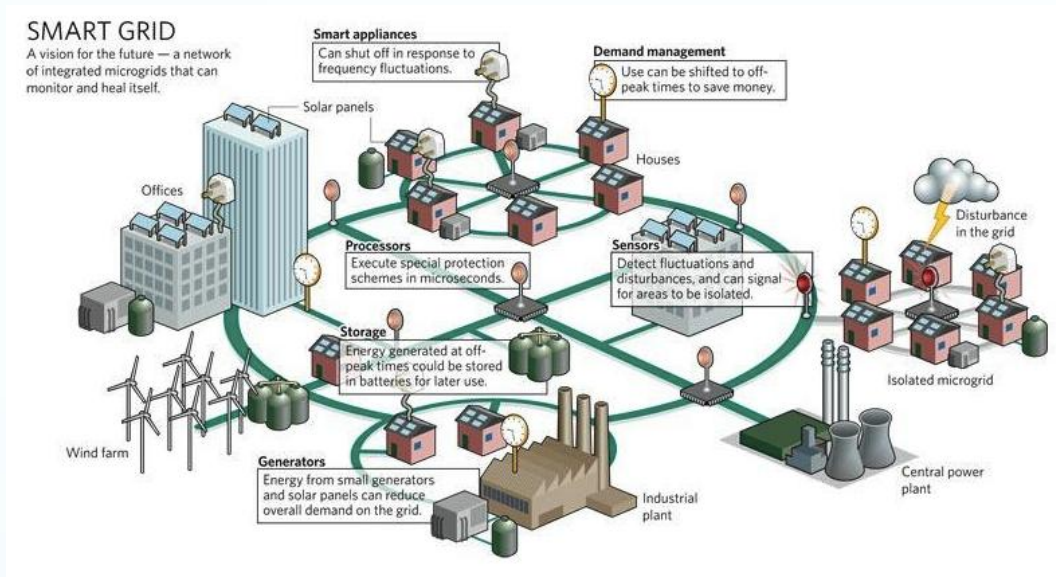
- This can be accomplished by creating an **Electron Economy**
- Electricity would be the main source of energy for all residential and commercial needs, with the goal of obtaining this electricity from renewable sources



Background: Electron Economy

Smart Grid

- Allows for the seamless integration of numerous of sources of electricity.



Background: Electron Economy

Smart Grid

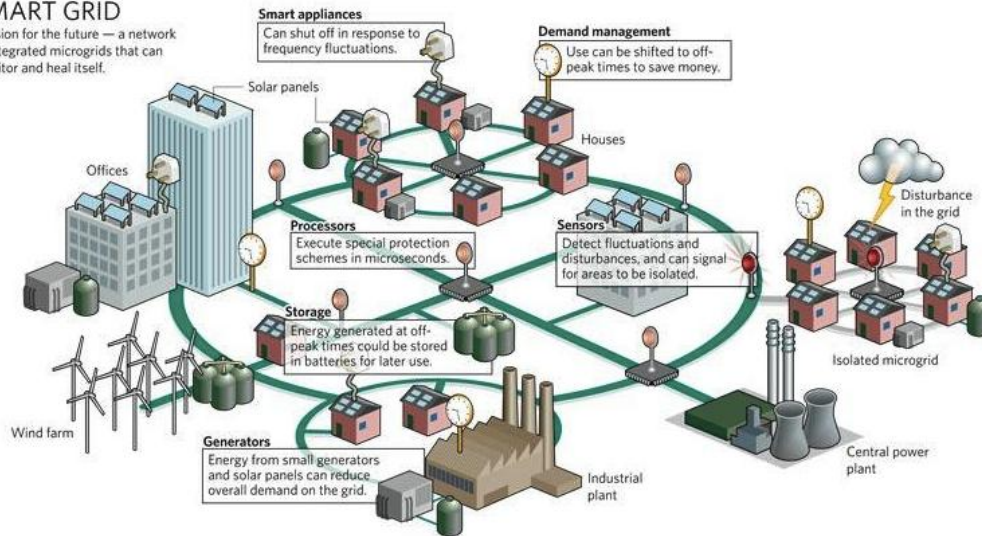
- Allows for the seamless integration of numerous of sources of electricity.

Electric Plug-in Cars

- Would constitute the largest portion of an individual's energy expense.

SMART GRID

A vision for the future — a network of integrated microgrids that can monitor and heal itself.



Background: Electron Economy

Smart Grid

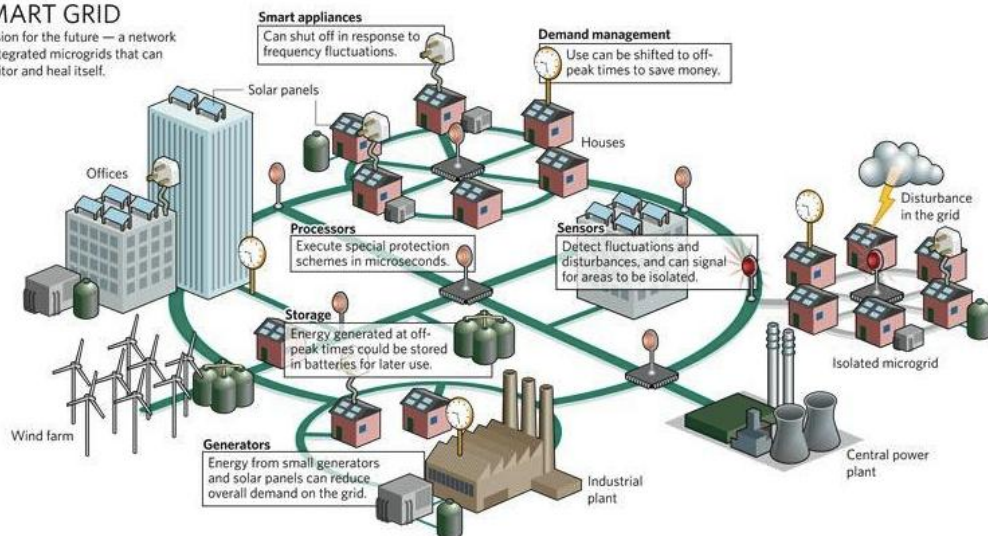
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Electric Plug-in Cars

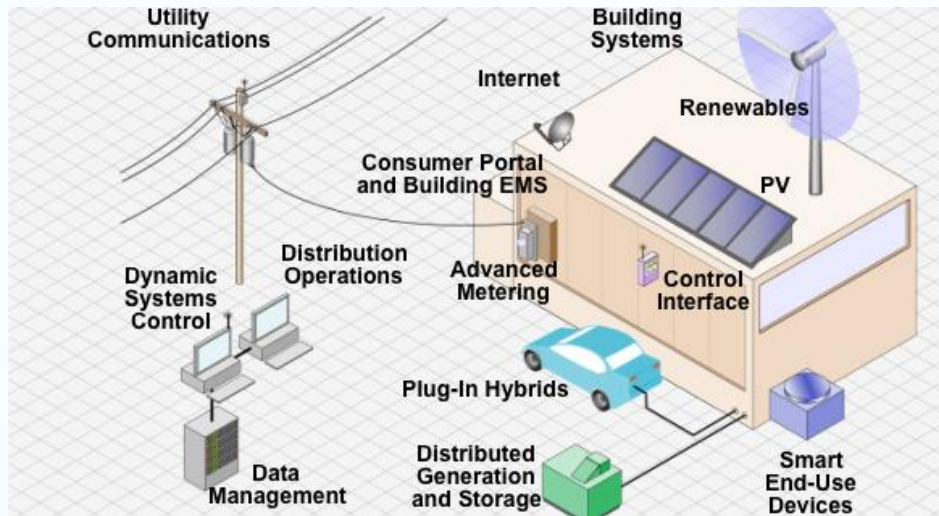
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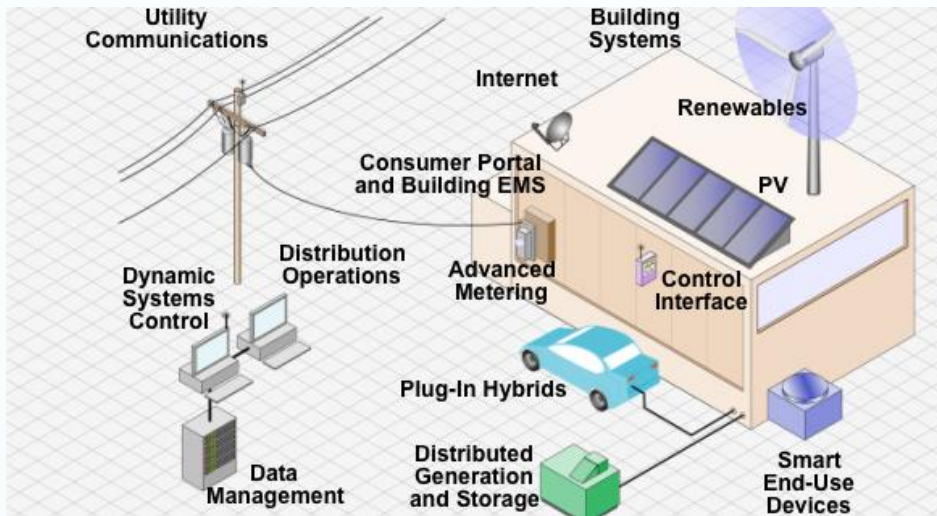
Background: Atom Economy



Home Storage

- Home running on energy from Solar or wind devices must be able to store energy, for use at night or cloudy days.

Background: Atom Economy



Home Storage

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Solar Farms

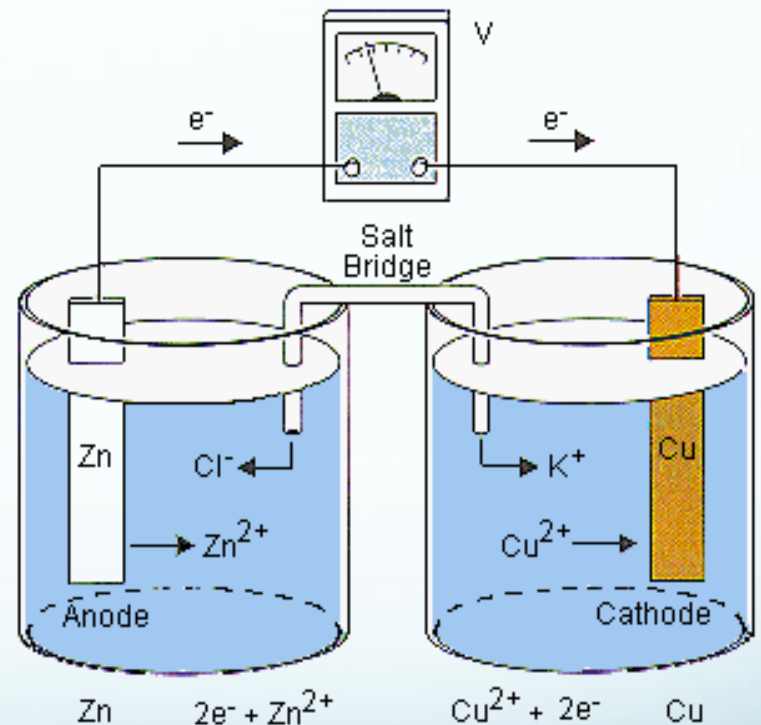
- Need to be able to store energy, to be able to deliver a constant steady output of energy.



Background: Battery Basics

Electrochemical Cell

- A battery is comprised of three main components: cathode, electrolyte and anode
- The cathode is characterized as the electrode where a reduction-reaction occurs (*i.e.* electrons are accepted from an outer circuit).
- An oxidation-reaction occurs at the anode (*i.e.* electrons are donated to an outer circuit).
- The electrolyte is an electronic insulator, but a good ionic conductor; it provides a transport-medium for ions to travel from one electrode to the other.
- The voltage and capacity of a cell are functions of the electrode materials used.



Background: Battery History

Battery Timeline

The historical battery development has gone from:

- 1800 - Copper/Zinc (Volta,)
- 1859 - Lead-Acid (Planté)
- 1866 - Zinc/Manganese-Oxide (Leclanché)
 - 1878 - over zinc-air
- 1899 - Ni-Cd (Jungner)
- 1966 - Sodium-Sulphur (Yao & Kummer)
- 1960 – Li Primary Cells
- 1980's - Ni-MH
- 1990's - Li-ion Secondary Cells
- 2008 – Lithium O₂ Cell (K. M. Abraham)

Background: Lithium Ion Electrochemical Devices

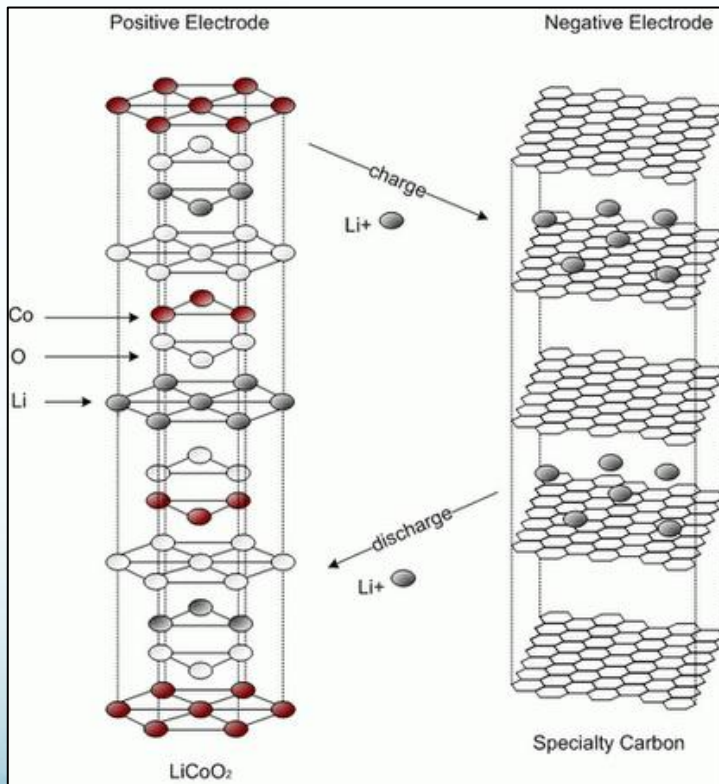
Lithium Ion Battery

- The most advanced batteries on the market today are the Li-ion and Li-ion-polymer batteries.
- High operating voltage: a single cell has an average operating potential of approx. 3.6 V, three times the operating voltage of both Ni-Cd and Ni-MH batteries and about twice that of sealed Pb-acid batteries.
- Compact, lightweight, and high energy density: the energy density is about 1.5 times high-capacity Ni-Cd batteries. Fast charging potential
- High discharge rate: up to 3C are attainable. Superior cycle life: service life of a battery exceeds 500 cycles.
- Non-polluting: does not use toxic heavy metals such as Pb, Cd or Hg.

Background: Lithium Ion Electrochemical Devices

Lithium Ion Battery

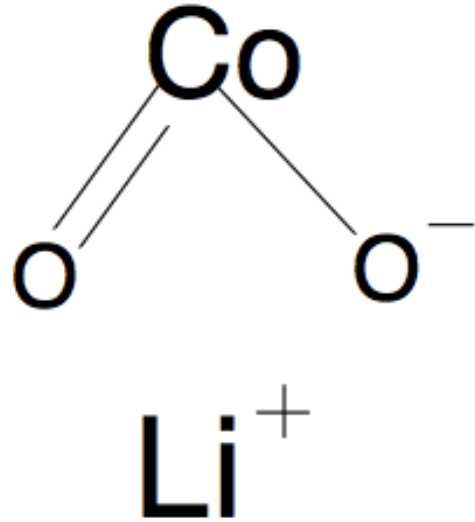
Lithium Ion Battery



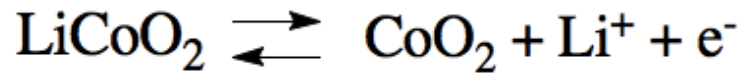
- The lithium travels from anode to cathode. Lithium (Li) is easily ionized to form Li^+ plus one electron
- Graphite (carbon) is most commonly used for the anode, and lithium cobalt oxide (LiCoO_2) is the most common cathode material.
- This combination gives an overall voltage of 3.6 Volts (V), more than twice that of a standard AA alkaline battery. This gives lithium-ion batteries a much better energy per volume ratio or energy density.

Background: Lithium Ion Electrochemical Devices

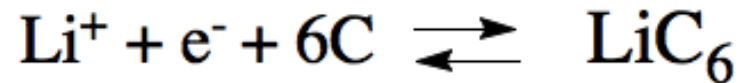
Lithium Cobalt Oxide



- Co is being oxidized from Co³⁺ to Co⁴⁺ during charging



- Co is being reduced from Co⁴⁺ to Co³⁺ during discharge



Background: Lithium Air Battery

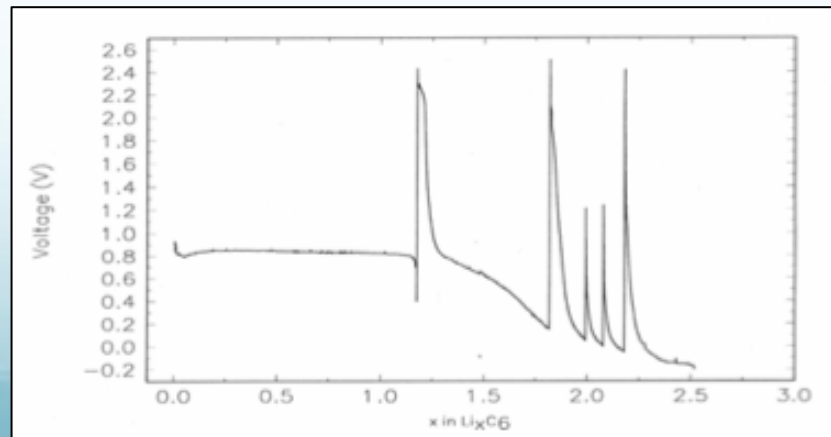
Lithium Ion Battery Issues

- A high temperature environment can lead to the rupture, ignition, and even explosion of liquid electrolyte-based lithium batteries.
- Some Li-ion cells are built with safety devices, which can prevent these hazards; however, separator defects and contaminants inside the cell can defeat those safety devices.
- The societal needs in the present energy scenario require the development of inexpensive, thermally stable, and safe lithium batteries with high energy and power densities.

Discovery: Lithium Air Battery

Lithium Air Battery

- Dr. K. M. Abraham while at Northeastern University was investigating the electrochemical properties of a Li/graphite cell with a polymer electrolyte.
- He was analyzing the gases produced in the cell as its discharge proceeded. He found that the discharge of this cell leads to the reduction of PC at about 0.9V with the generation of propylene.
- For the IR analysis they used a gas syringe to withdraw gases from the plastic-sealed Li/C cell at various stages in its discharge. When they resumed discharge after withdrawing the gases, each time the OCV of the cell increased to 2.5 V



Discovery: Lithium Air Battery

Lithium Air Battery

- Having repeatedly seen this behavior they recognized, supported by the thermodynamic calculations shown in equations 2- 4, that they were inadvertently introducing oxygen into the cell from the syringe.

$$\Delta G^{\circ} = -nFE^{\circ} \quad [1]$$



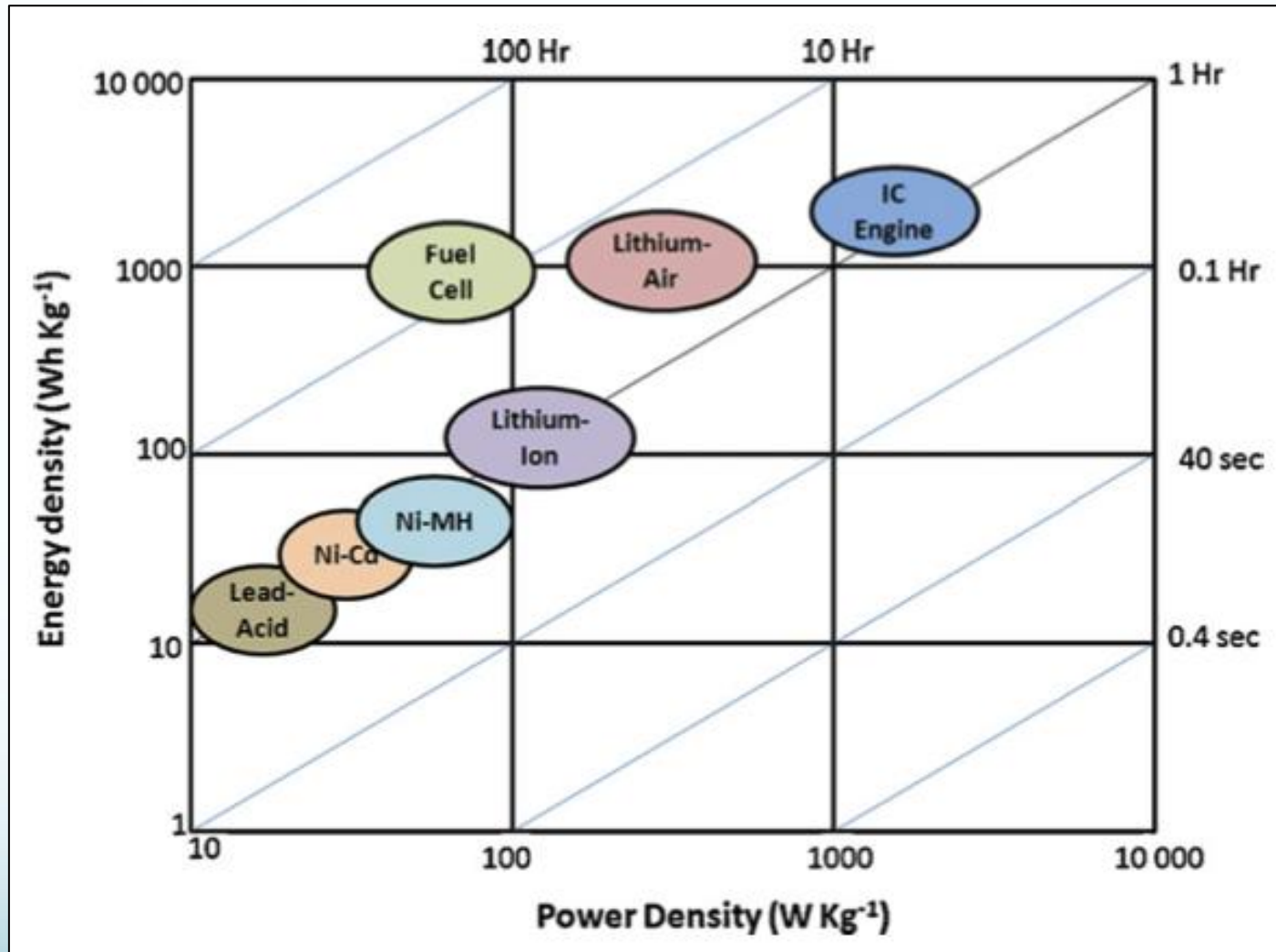
- Gibbs energy is the capacity of a system to do non-mechanical work and ΔG measures the non-mechanical work done on the system (negative sign equals work done by the system).
- When an amount of charge, Q , moves through a potential difference, ΔE , *the work equals* : $w = - Q \Delta E = -nFE$

Science: Lithium Air Battery

Lithium Air Battery

- A Li-O₂ cell provides an open-circuit voltage OCV of around 3.0 V and a theoretical specific energy of 5200 Wh/kg if oxygen is contained in the battery.
- The oxygen need not be contained in the battery because it can be accessed from the air, and if such is the case, the theoretical specific energy of the Li-O₂ battery is 11,140 Wh/kg.
- A well optimized Li-air battery should yield a specific energy of up to 3,000 Wh/kg, over a factor of 15 greater than the state-of-the-art lithium ion batteries.
- The Li-O₂ cell may be the ultimate power source among electrochemical energy conversion and storage cells derived from lithium chemistry.

Science: Lithium Air Battery



Science: Gas Diffusive Electrode

Gas Diffusive Electrode

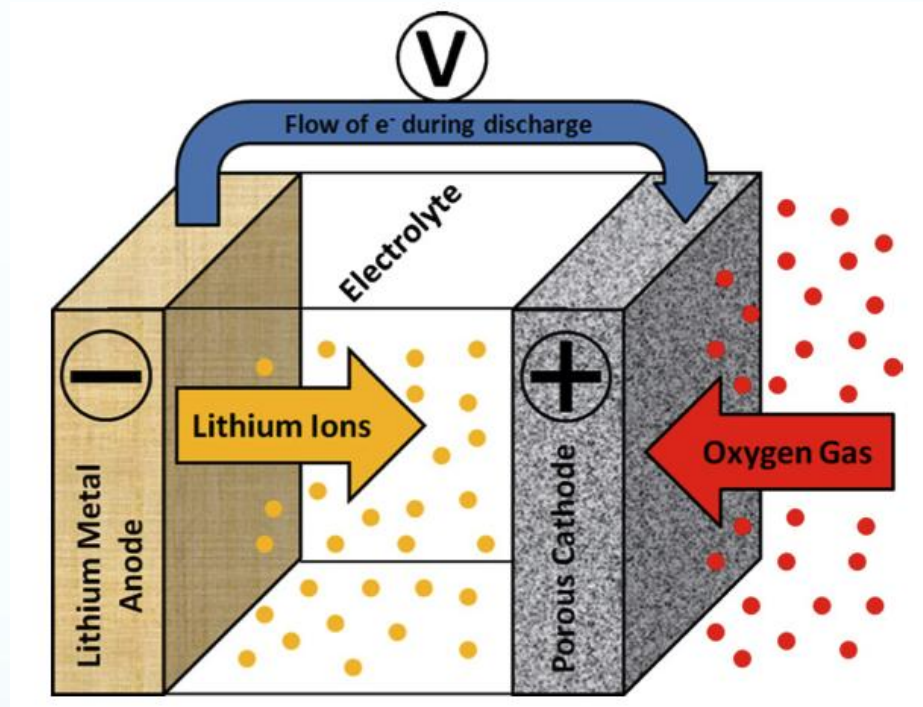
“Investigation of the gas-diffusion-electrode used as lithium/air cathode in non-aqueous electrolyte and the importance of carbon material porosity”

Journal of Power Sources, 13 October 2009

by, Chris Trana, Xiao-Qing Yangb, Deyang Qu
Department of Chemistry, Umass Boston

Science: Gas Diffusive Electrode

Gas Diffusive Electrode



- In the discharge of this cell, the oxygen is reduced on the carbon cathode and the products are stored inside the pores of the Teflon-bonded carbon electrode. As a result the cell capacity is expressed as ampere-hour per gram of the carbon in the cathode.

Science: Gas Diffusive Electrode

Gas Diffusive Electrode

- There are still several major obstacles before the commercialization of Li-air batteries becomes feasible.

Significant Barriers:

1. Development of a functional 3-dimensional 3-phase gas- diffusion-electrode (GDE) in non-aqueous electrolytes.
2. Avoidance of the GDE passivation caused by the deposition of reduction products.
3. Increase of O₂ solubility and diffusion rate in non-aqueous electrolytes (Future Work).

Science: Gas Diffusive Electrode

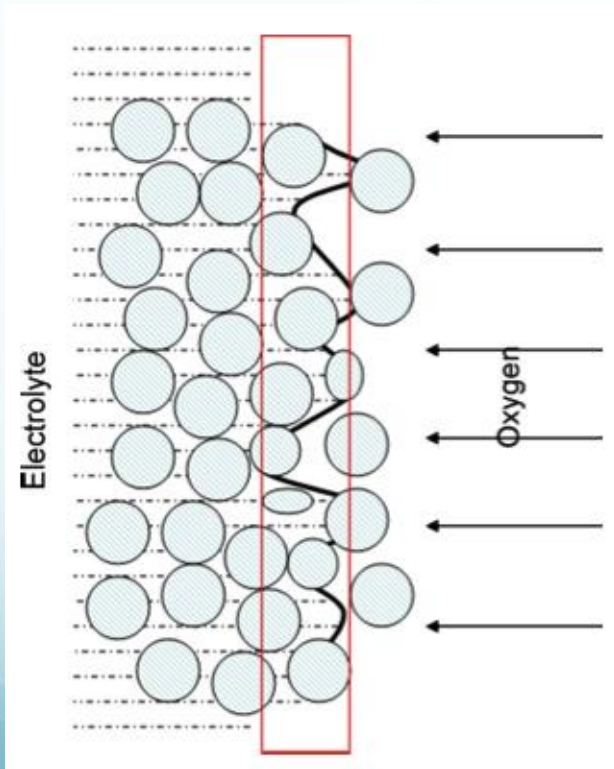
Experiment :

- A GDE was made with 90% wt of high surface area carbon and 10% wt of dry Teflon material (T-30).
- The carbon was first thoroughly mixed with T-30 and then hot-pressed onto a Ni-mesh current collector.
- the finished GDE was 0.008 in .thick and the weighed 10 mg.
- No catalyst was used.

Science: Gas Diffusive Electrode

Results

- An efficient porous electrode should not only have a large electrochemically accessible surface area, but also have a large diffusion path for the mass transfer.

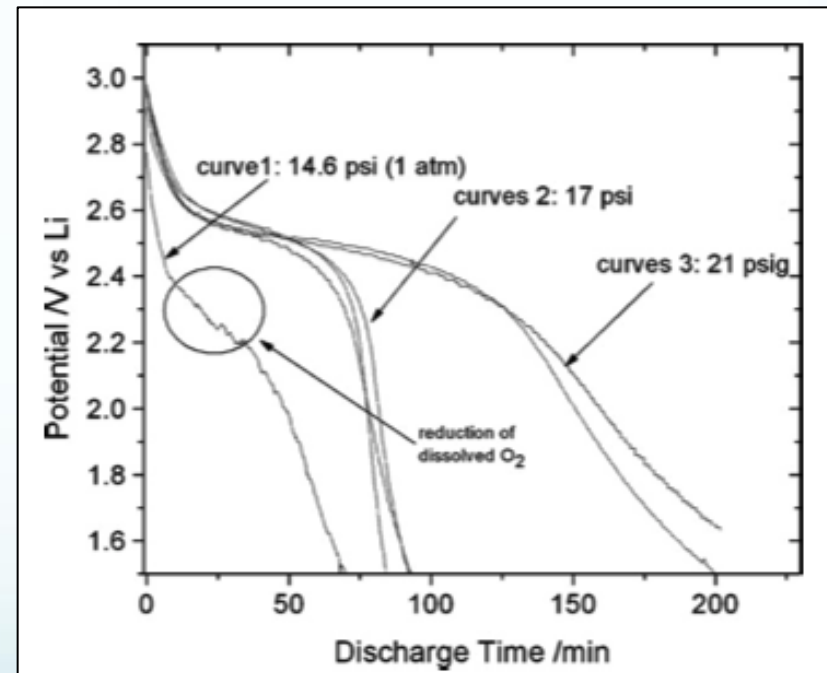


- The electrochemical interfacial reaction, takes place when electrolyte and gas molecules co-exist at the same solid electrode interface.
- A completely immersed electrode is limited by the mass transfer rate of gas molecules in the electrolyte. Thus, the current density for a completely immersed electrode is very low
- For a diffusive electrode a sufficient amount of reaction gas has to reach the thin electrolyte film dispersed on the surface of the porous electrode, which connects to the bulk electrolyte

Science: Gas Diffusive Electrode

Results

- The GDE function normally like a battery cathode when the pressure of O_2 increased slightly above 14 psi or 1 atm.
- When the O_2 pressure was higher than 1 atm, the electrolyte was forced back from the interface, and the complete wetting of the GDE was avoided.
- The reduction of O_2 took place at the GDE. Since higher O_2 pressure could create a larger interfacial area to accommodate more reduction products, the same GDE discharged at a higher O_2 pressure demonstrated a higher capacity than that at a lower O_2 pressure.



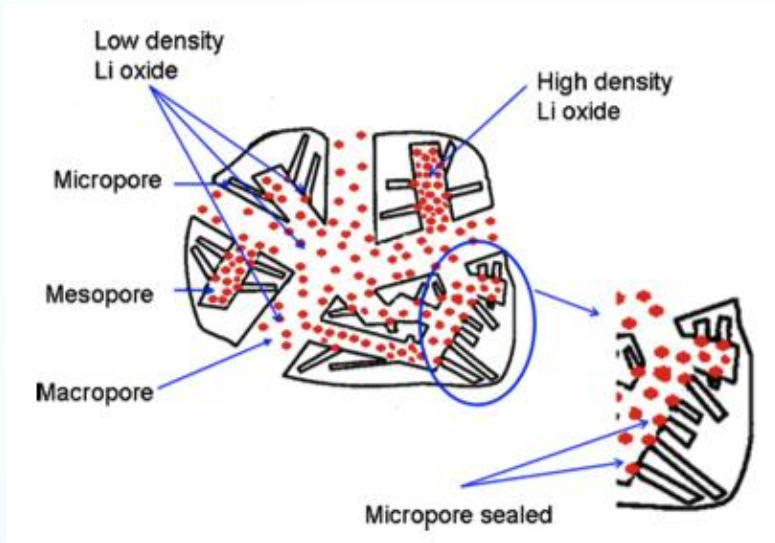
Science: Gas Diffusive Electrode

Results

- Oxygen reduction in a non-aqueous electrolyte is substantially different than that in an aqueous electrolyte
- It has been shown that the main discharge reaction in the absence of a catalyst in the porous carbon cathode is the reduction of oxygen to form insoluble Li_2O_2 and Li_2O
- Thus the Li_2O_2 and Li_2O will deposit at the location where the charge transfer occurs

Science: Gas Diffusive Electrode

Results

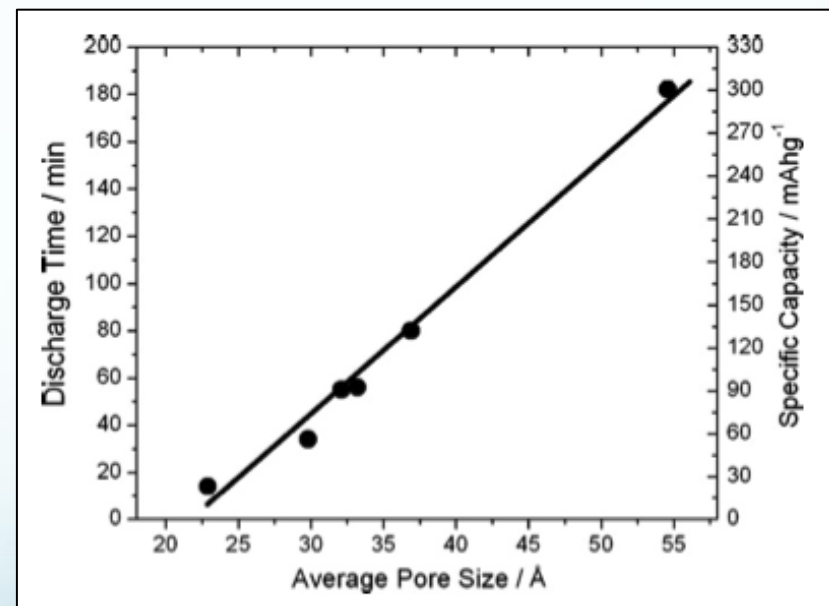


- In order for a GDE to function efficiently, both electrolyte and O_2 have to migrate to the reaction interface.
- When Li oxide particles are formed near the orifice of a micropore it would be sealed and mass transfer in and out of that pore would be blocked because the inside pore surface becomes inaccessible.
- Since micropores comprise most of the surface area for a carbon material with a very high total surface area, rendering them inaccessible substantially decreases O_2 reduction.
- Solid particles gradually cover the surface, sealing-off pores and eventually inactivating the GDE

Science: Gas Diffusive Electrode

Results

- Thus, the capacity of a GDE in a non-aqueous electrolyte is limited by the surface available for the deposition and the pore volume available for the storage of the solid reduction products.
- The discharge capacity increases almost linearly with the increase of average pore diameter.
- The large pores in the carbon could accommodate much more Li oxide precipitates than small pores. Thus, the utilization for the surface area in the large pores was much higher than that in the small pores.



Science: Gas Diffusive Electrode

Conclusion

- A 3-phase interface is essential for a GDE. Gas-diffusion paths and an air saturated portion need to be created. O_2 pressure which is slightly higher than ambient pressure is enough to force the electrolyte back and create the desirable 3-phase interface on the GDE.
- The majority of the solid Li oxides reside inside the large pores. The density of the oxides increases as the reduction proceeds until the density is high enough to completely block mass transfer. The capacity of the electrode is determined by the amount of Li oxides that the large pores can accommodate without jeopardizing mass transfer.
- The capacity of a GDE in a non-electrolyte was found to have an almost linear relationship with average pore diameter of carbon. Such a linear relationship could be used to estimate the capacity of a GDE in non-aqueous electrolyte quantitatively.

Conclusion

My Conclusion

- Li Air cells could be the battery of the future with continued research and funding.
- This technology is years (possibly decades) away from commercialization
- It is a very attractive research topic that will probably lead in the same direction as the current Lithium Ion Capacitors; manipulating nanotubes to make electrodes with a higher energy density and capacity.

References

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Thank You!