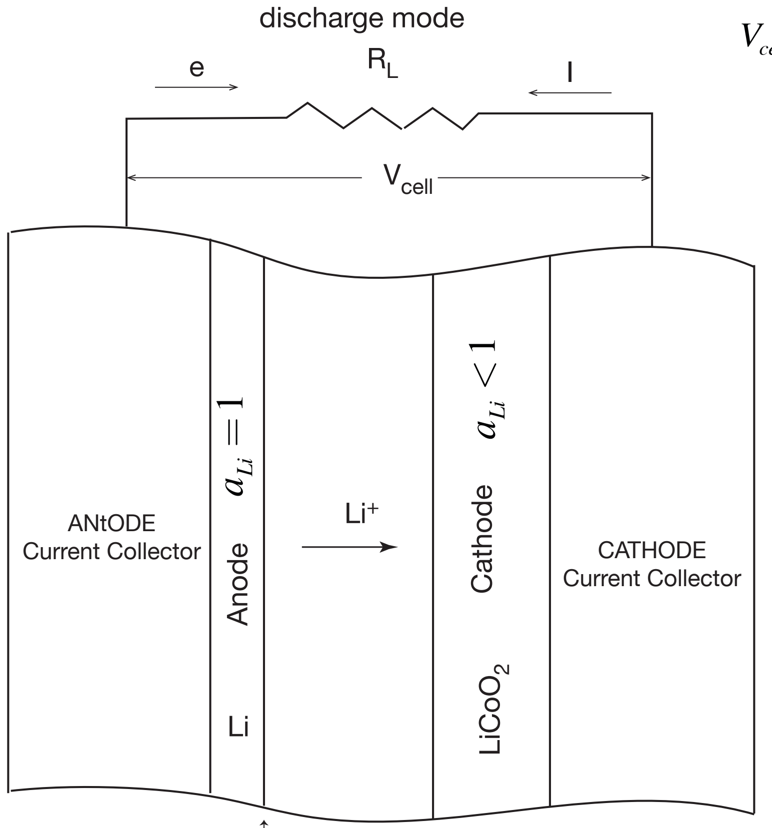
# 02E_Lithium Ion Batteries




$$V_{cell} = \frac{RT}{F} \ln \frac{a_{Li}^{A}}{a_{Li}^{C}}$$

$$Li \to Li^+ + e$$

oxidation

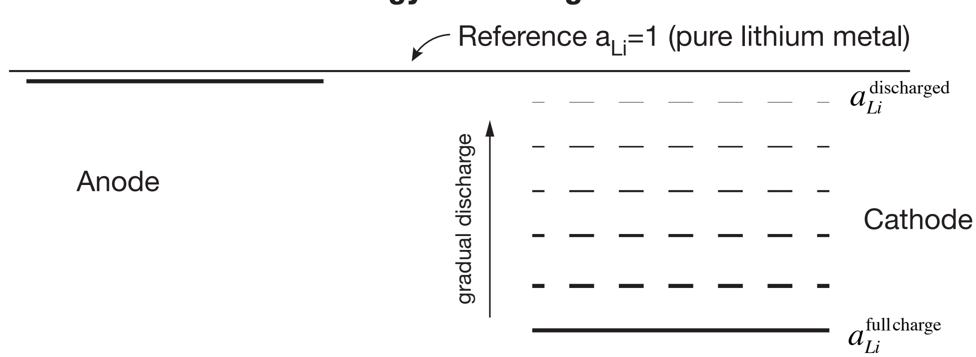
$$Li \to Li^+ + e$$

reduction

$$ASR_{cell} = ASR_A + ASR_E + ASR_C$$

$$J = \frac{V_{cell}}{ASR_{cell}}$$

**Energy Level Diagram**




## Topics

•Difference between Fuel Cells and Li+ Batteries

•Nernst Potential

•Materials Selection

•Microstructural Features

# What are the similarities and differences with SOFC

## Similarities

•The electrolyte is a pure ion conductor (no electronic conduction). The higher the conductivity the better.

•The Nernst potential is derived in the same manner by considering the chemical potential of Li, Li+ and electrons.

•At the Anode the oxidation reaction is $Li \rightarrow Li^{+}(\text{to the electrolyte}) + e(\text{to the circuit})$

•At the Cathode the reduction reaction is $Li^{+}(\text{from the electrolyte}) + e(\text{from the circuit}) \rightarrow Li$

## Differences

•Activities in the solid state, not in the gas phase

| | Activity of species the anode | Activity of species the cathode | Nernst Potential |
|---|---|---|---|
| SOFCs | $p_{O_2}^{A}$ | $p_{O_2}^{C}$ | $\frac{RT}{4F}\ln\frac{p_{O_2}^{C}}{p_{O_2}^{A}}$ |
| Li+ Battery | $a_{Li}^{A}$ | $a_{Li}^{C}$ | $\frac{RT}{F}\ln\frac{a_{Li}^{A}}{a_{Li}^{C}}$ |

•Activities in the electrode materials change with time (the energy level diagram on the previous page) causing the battery to discharge

# Materials Selection

•Cathode/anode must have high capacity for Li:  mAh/g of the electrode material. Volumetric and gravimetric capacity.

Cathodes and anodes are solids.. Cathode $LiCoO_2$. Anode can be pure Li metal but graphite is used now because pure lithium metal reacts with the current electrolyte (liquid) can causes fires. Search is on for next generation batteries where the electrolyte is a ceramic and the anode can be Li metal which does not react.

Present day anode is graphite: insert one Li atom for six carbon atoms..

Other consideration is the Li uptake leads to expansion which when cycled causes failure due to expansion/contraction fatigue.

•Current electrolyte is an organic liquid (a solution of a Li salt in a organic liquid). It is inflammable, and it limits the highest voltage of the battery to its breakdown voltage. One great asset (it is a big deal) is that the liquid enables to establish contact between the current collector, the Li storage material and the electrolyte. The liquid p(lermeates through the cell making the reaction possible and greatly reducing manufacturing complexity.

•Solid ion conductors like ceramic LLZO (lithium, lanthanum, zirconium oxygen) have good conductivity but are very difficult to assemble in a way that creates the junctions between the current collector, the electrode material and the electrolyte.

# How many "computer batteries" would be needed to construct a car battery with a capacity of 50 kWh.

## The unit kWh

$$kWh = Volts*(Amps = C\ s^{-1})*one\ hour\ (=3600\ )/10^3$$

Multiplying by 3600 coverts W=Js to Wh, and then dividing by 1000 into kWh

## My computer

My computer battery is specified to have

a capacity of 7850 mAh delivered at 12 volts

In units of kWh it is equal to $7850*10^{-3}$ (converts mAh into Ah) *12 V (converts Ah into Wh)

multiply by $10^{-3}$ to convert Wh into kWh (1)

Therefore the computer battery has a capacity of $7850*10^{-3}*12*10^{-3} = 0.094$ kWh

How many batteries for a car battery,

=50/0.094, i. e. approximately 500 batteries.

# Gravimetric (and Volumetric) Capacity

Graphite is used as an anode in current batteries. For simplicity let us assume that anode constituted one third of the total weight of the battery (the remainder, two thirds, being the weight of the cathode, the electrolyte, and the current collectors).

The properties of anode (or the cathode) are specified in terms of mAh $g^{-1}$. The values for a few candidate materials for anodes and cathodes are given at the top of the next page. Remember these are "ideal" values. The practical values may be half of them perhaps even less. Note that the capacity for pure lithium metal is 3868 mAh $g^{-1}$ (needs to be checked), and its theoretical value can be immediately realized in application since it is simply pure lithium not an alloy of lithium and other elements such as carbon.

| Materials | Specific capacity, $mAhg^{-1}$ |
|---|---|
| **Anode Materials** | |
| Lithium Titanate | 140 |
| Hard carbon | 527 |
| Sphere graphite | 364 |
| MCMB (special carbon) | 340 |
| Silicon | 3200 |
| Tin | 638 |
| Tin Oxide | 850 |
| **Cathode Materials** | |
| LiCoO2 | 170 |
| LiNi0.8Co0.15Al0.05O2 | 160 |
| LiFePO4 | 160 |
| LiCo0.3Ni0.7O2 | 165 |
| LiMn0.67Ni0.33O2 | 250 |

Now to obtain the gravimetric capacity of the battery we need to calculate the capacity, that is, kWh per kg. You can then convert the capacity as given above into the weight of a battery for a EV-car.

To convert mAh $g^{-1}$, as given in the above table in to kWh $kg^{-1}$ we do the following,

$$\frac{mAh}{g} * \frac{10^{-3}}{10^{-3}} (Ahkg^{-1}) * 12(volts - converts\, to Whkg^{-1}) * (\frac{1}{1000} to\, kWhkg^{-1}) \quad (2)$$

which gives that

$$\text{gravimetric capacity} = \frac{mAh}{g} 12x10^{-3} \text{ kWh kg}^{-1} \quad (3)$$

Let us apply to graphite which has practical capacity of about 150 mAh $g^{-1}$ which then gives that the gravimetric capacity is of graphite is 1.8 kWh $kg^{-1}$.

Assuming that the anode is one third of the battery weight we obtain the gravimetric capacity to be 0.6 kWh $kg^{-1}$.

Therefore a 50 kWh battery would weigh about 100 kg.

The volumetric capacity can be calculated in the same way by dividing by the density of graphite and so on.

Actually the anode is a porous body therefore the volumetric capacity will be lower than (perhaps two-thirds) what is calculated above.

# Figure of Merit of the anode

As in the case of SOFCs the technical development of batteries is characterized by the capacity per unit surface area of the electrodes.

So, if the thickness of the electrodes is *w* cm, and the area (we assume) is 1 $cm^2$, then the volume of the anode per unit surface area of the battery is *w* $cm^3$. Thus the weight of the battery per unit surface area of the battery will be $w\rho$ where $\rho$ is the density of graphite in g $cm^{-3}$ , or 2.3 in g $cm^{-3}$.

Therefore the area specific capacity will be $\frac{mAh}{g}\rho(mAh\,cm^{-3})*w(cm), gives\frac{mAh}{cm^2}$

Assuming the anode to have a thickness of 50 μm, the area specific capacity of an anode made with graphite will b

$150*2.3*0.05$ mAh $cm^{-2}$

of ~17 mAh $cm^{-2}$.

In reality the capacity would be less because the graphite anode contains about 50% porosity; also the thickness may be overestimated. Thus a realistic value is:

about 5 mAh $cm^{-2}$.

You can calculate the value for lithium metal, which will be much, much larger.

# The Future

The calculate for lithium metal as an anode highlights the great advantage of batteries made with ceramic electrolytes. The present electrolytes (a liquid organic) is inflammable if it comes into contact with lithium metal (which can be precipitated by overcharging for example).

The ceramic electrolyte (LLZO or $Li_7La_3Zr_2O_{12}$) is therefore being intensely studied for next generation batteries. You can imagine why.