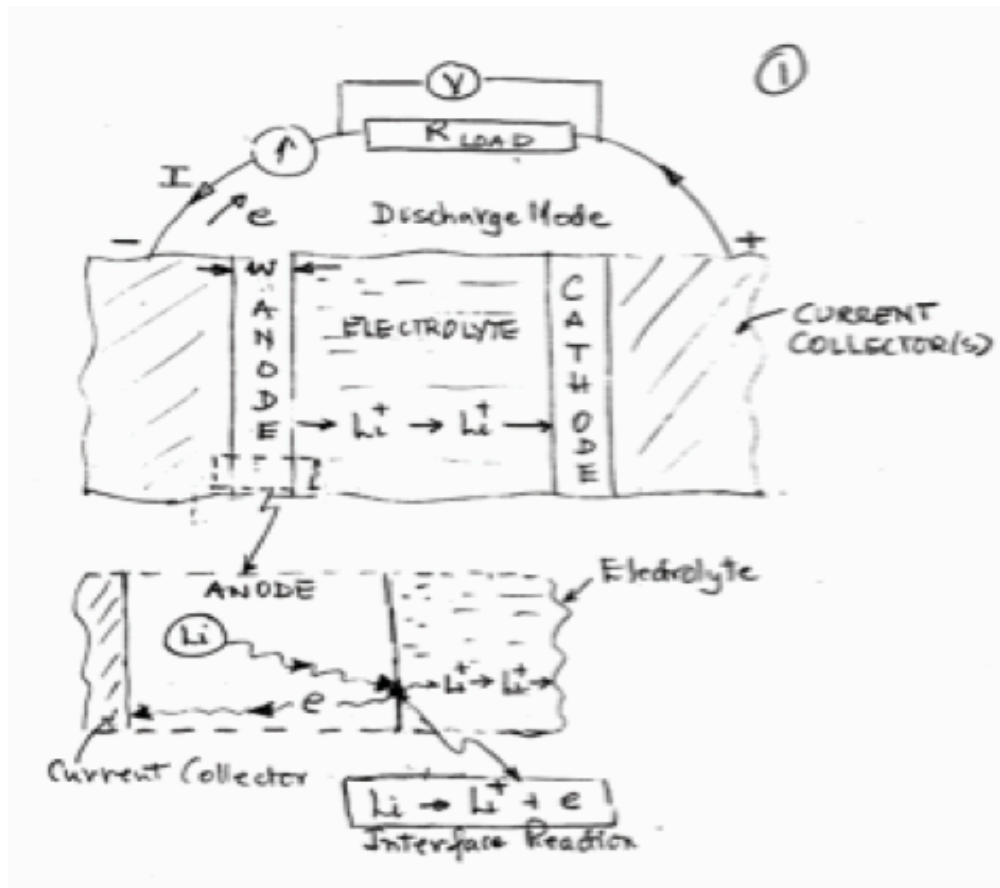# 4A_Li+ battery: the Nernst Equation

Topics

(i) Equivalence between chemical and electrical energy

(ii) Gibbs Free Energy

(iii) The Chemical Potential (species specific)

(iv) Anode, cathode and electrolyte in a Li+ battery

(v) Chemical potentials of Li, Li+ and electrons

(vi) Derivation of the Nernst Potential (a thermodynamic parameter)
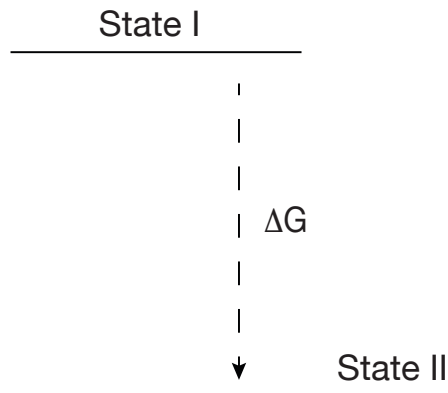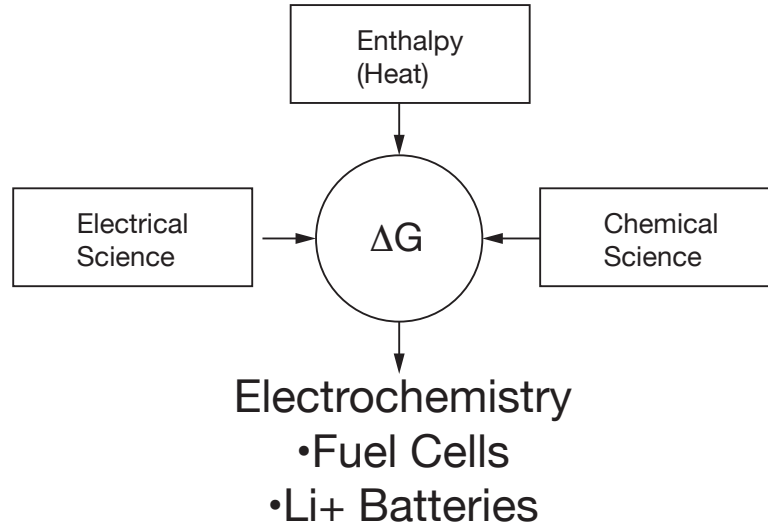
Schematic of a Li+ battery

Units: Amps, Volts, Coulombs (charge), watts (work)=A*V J s^{-1}, A=current is the flow of coulombs (C s^{-1}).

watts = Amp * V = C s^{-1}*V = CV s^{-1} = J s^{-1}; therefore C*V is energy in Joules. C=A*s (mAh)

The charge capacity of the battery is written as mAh/g when multiplied by the battery voltage gives the energy density.

Energy Density has units of kWh per kg.

Gibbs Free Energy

The generality of Gibbs Free Energy arises from the work done when a system changes from one state to another state. The total amount of work done on the system (Gibbs Free Energy is positive - it is an endothermic process) or by the system on the surroundings (Gibbs Free Energy is -ve means it is an exothermic process). Thus, the difference between the Gibbs Free Energy of the two states is equal the work exchanged with the surroundings. The pre-fix Δ arises because we are invariably interested in the change of state.

The units for ΔG are written as kJ mol^{-1}, or kJ atom^{-1}, their ratio being the Avogadro's Number.

For example $(N_A k_B)T = RT$ is a useful relationship.

Electrical Energy

The product of charge (C coulombs) moves between two electrodes at a potential difference of V volts is equal to

C*V J

This then leads to a simple unit for energy where the charge is equal one electron, and the voltage difference is 1 V.

Thus the definition of the electron volt is where C=charge on one electron= 1.6×10^{-19} C,

eV = 1.6×10^{-19} J

In order to calculate the work done by a battery, we must consider the relationship between the number of Li atoms (and ions) transported between the electrodes and the electrons that are thereby transported.

•One lithium atom can move one electron because it is Li(1+). Therefore the moles of electrons is equal to the moles of Li. So another unit of the charge on electrons is equal to C mol^{-1}, which is called one Faraday (F).

F = 1.6×10^{-19} *N_A = 96,500 Coulombs.

In terms of Gibbs Free Energy:

$$\Delta G_{mole} = nFV$$

the work done to move one mole electrons (ions) across a voltage difference of V

"n" is the charge number on the species in the electrochemical reaction. For example in the case of lithium the reaction is Li=Li$^+$ + e, that is one electron per ion therefore n=1.

In a solid oxide fuel cell the ionic species is O^{2-} and the reaction is O+2e=O^{2-}, therefore the charge number n =2.

Chemical Energy or Work

We now must translate the difference in the activity of the Li atoms at the anode and the cathode to work done.

Need a number in kJ mol^{-1} or eV from a chemical point of view.

The chemical work done is described by the difference between the chemical potential of the species at the two electrodes. The difference between the chemical potentials is equivalent to the electrical scenario of electrical potential difference.

The chemical potential is written as electro-chemical potential having the symbol eeta shown below,

$$\tilde{\eta}_{Li}^{A} = \tilde{\eta}_{Li}^{o} + k_B T \ell n(a_{Li}^{A})$$

Here the superscript implies Anode, the activity is written as a with a subscript Li which specifically refers to Li atoms present in the anode material. And $k_B T$ has units of energy per (lithium) atom. The electrochemical potential in the equation refers to one Li atom.. ....multiplying the equation by N_A will them change it to per mole (and $k_B T$ will be replaced by R).

We have a similar equation for the activity of Li at the cathode,

$$\tilde{\eta}_{Li}^{C} = \tilde{\eta}_{Li}^{o} + k_B T \ell n(a_{Li}^{C})$$

The significance of the electrochemical potential is that the work done in transporting on Li atom from the anode to the cathode is given by

$$\Delta G_{atom} = \tilde{\eta}_{Li}^{A} - \tilde{\eta}_{Li}^{C}$$

$$\Delta G_{atom} = k_B T \ell n \frac{a_{Li}^{A}}{a_{Li}^{C}}$$

Nernst Equation

The Nernst equation relates the electrical work done to the chemical work.

$$\Delta G_{mole} = nFV = RT \ell n \frac{a_{Li}^{A}}{a_{Li}^{C}}, \text{ where } k_B \text{ has been replaced by R since one mole, not one atom.}$$

$$V = \frac{RT}{nF} \ell n \frac{a_{Li}^{A}}{a_{Li}^{C}}$$

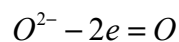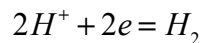This is the Nernst equation. In practice it is the open circuit voltage measured across the electrodes.

Relationship to the Heat of a Chemica Reaction

Consider the water splitting reaction

$$H_2O = H_2 + \frac{1}{2}O_2 \quad (\text{+240 kJ mol}^{-1}, \text{ per mole of H}_2\text{O})$$
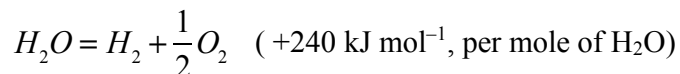
(this reaction is endothermic and therefore the heat of the reaction is +ve)

$$2H^+ + 2e = H_2$$
$$O^{2-} - 2e = O$$

Apply to water splitting with potential difference

charge on oxygen ion is 2

Voltage or splitting is 1.25 V

So the electrical work done to split one mole of H₂O

charge number x the voltage x work done to move F (one mole of electrons)

2 x 1.25 x 96500   J per mol^{-1}: 240 kJ mol^{-1}.