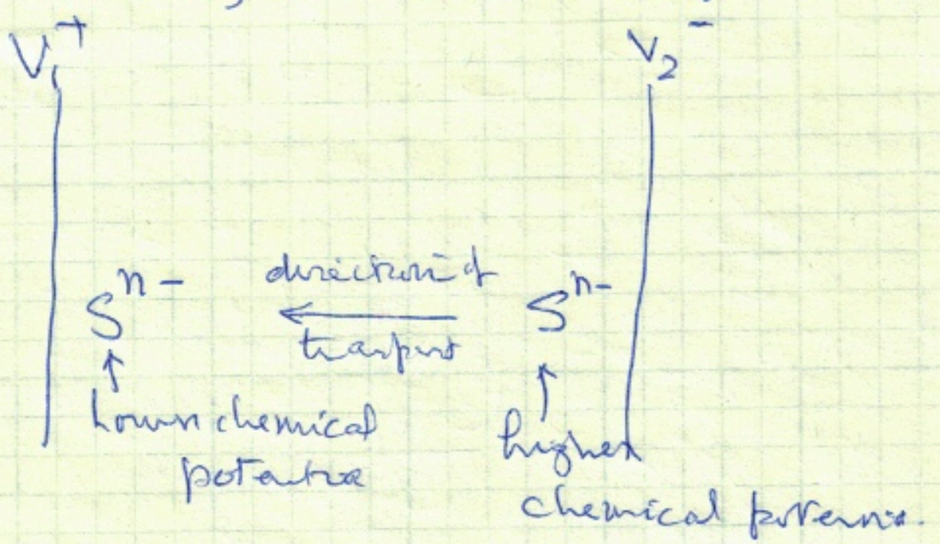
Notes on Fuel Cell and Batteries

Thermodynamics (Chemical potential of charged species)

The chemical potential difference between $\Delta V = V_1 - V_2$ (voltage difference) at two electrodes for a charged species S^{n+} or S^{n-} meaning the ions have either a positive charge of $+n$ or a negative charge of $-n$. For example O^{2-} has a charge of $2-$; n is called the charge number



$$\Delta\mu_{S^{n-}} = \underbrace{(V_1 - V_2)}_{\text{volts}} \times n F$$

$\Delta\mu_{S^{n-}}$ per mol

F: Faraday const 96,500 Coulomb/mol

Note that units of

Volts * Coulombs = Joules

$F = |e| N_{AVO}$

$$\Delta\mu_{S^{n-}} = \Delta V \times n|e| .$$

$\Delta\mu_{S^{n-}}$ per atom

See next page

Thermodynamics (Equilibrium between charge neutral and charges species of the ~~like~~ same atom)

For example consider

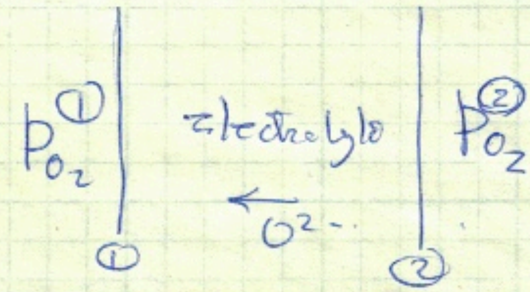
$$4e + O_2 = 2O^{2-}$$

(note the charge balance. e has a unit charge of −1)

Equilibrium equation:

$$4\mu_e + \mu_{O_2} = 2\mu_{O^{2-}}$$

Now consider



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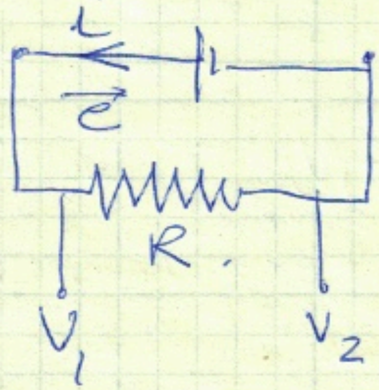
Chemical potential of electrons



$$\Delta V = (V_1 - V_2) = i \times R.$$

$$\Delta \underset{\uparrow \text{electron}}{\mu_e} = \Delta V |e|$$

Consider the difference between the chemical potential of the ~~star~~ species.

for example $\Delta\mu_e = \mu_e^{②} - \mu_e^{①}$

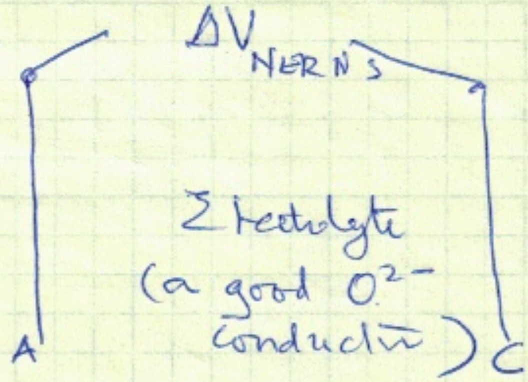
$$4\Delta\mu_e + \Delta\mu_{O_2} = 2\Delta\mu_{O^{2-}}$$

$$\Delta V|e| + k_B T \ln \frac{p_{O_2}^{②}}{p_{O_2}^{①}} = 2\Delta\mu_{O^{2-}}$$

Note how the chemical potentials create a relationship between $p_{O_2}^{②}/p_{O_2}^{①}$ and ΔV, the voltage expressed between the electrodes.

<u>thermodynamics (the Nernst Potential)</u>

$p_{O_2}^{An}$ determined by the reaction



$p_{O_2}^{Cath}$ (air)

$2H_2 + O_2 = 2H_2O$

$$\Delta G_{Janaf} + k_B T \ln\left[\frac{1}{p_{O_2}^{AN}} \times \left(\frac{p_{H_2O}}{p_{H_2}}\right)^2\right] = 0.$$

$\Delta(\ldots) = \text{Cathode} - \text{Anode}.$

$$\Delta\mu_{p_{O_2}} + 4\Delta\mu_e = 2\Delta\mu_{O^{2-}}.$$

$$k_B T \ln \frac{p_{O_2}^{cat}}{p_{O_2}^{an}} + \Delta V_{Nern.} \times 4|e| = 2\Delta\mu_{O^{2-}}$$

Now → If the electrolyte is a good conductor of O^{2-} and there is no current flow. (open circuit) then

$$2\Delta\mu_{O^{2-}} = 0$$

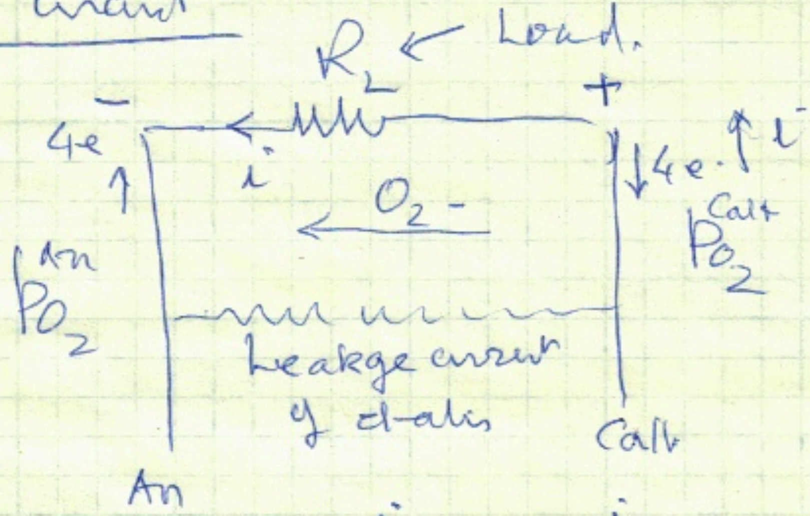
(diffusion would occur to equalize the potential)

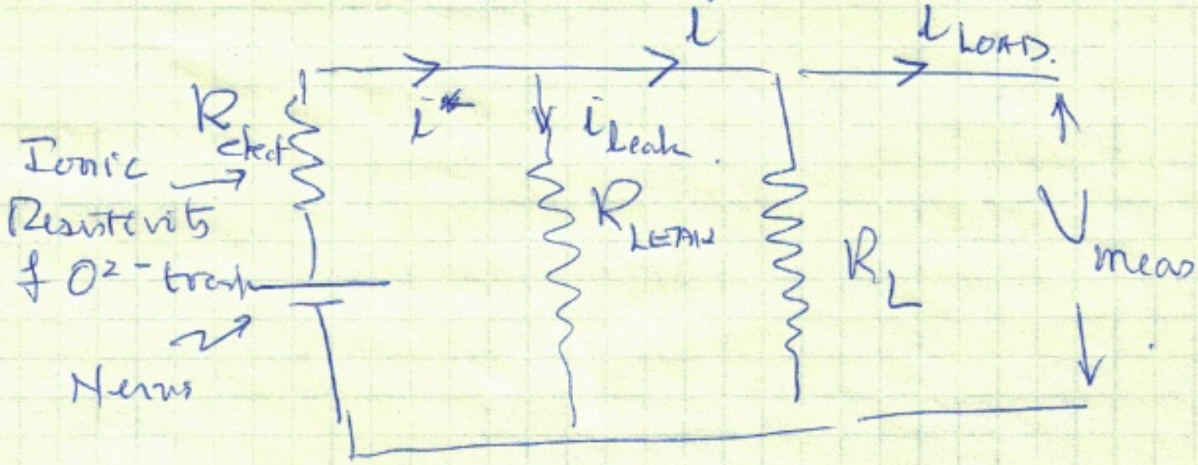
$$\therefore \Delta V_{Nern} = \frac{k_B T}{4|e|} \ln \frac{p_{O_2}^{cat}}{p_{O_2}^{an}}$$

charge number of $O_2 \rightarrow 2O^{2-}$

$$\text{or} \quad \Delta V_{Nernst} = \frac{RT}{4F} \ln (\quad)$$

Equivalent Circuit :





$$i^* = \frac{\Delta V_{NERNS}}{R_{TOTAL}}$$

$$R_{TOTAL} = R_{elect} + \frac{R_{LEAK} * R_L}{R_{LEAK} + R_L}.$$

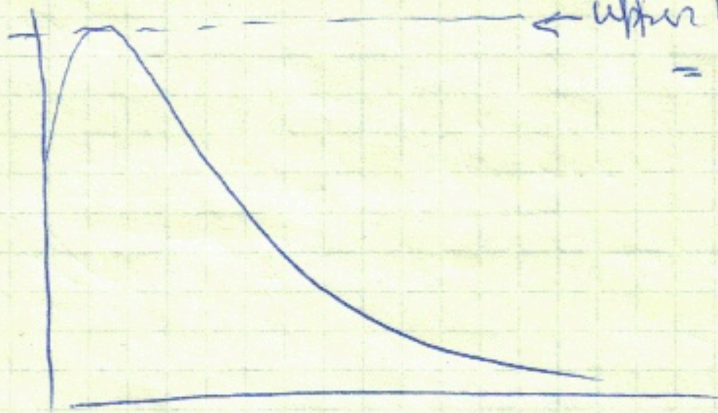
$$V_{meas} = i^* \times \frac{R_{LEAK} * R_L}{R_{LEAK} + R_L}.$$

$$= \cancel{\left(\Delta V_{NERNS.} \times \frac{1}{R_{ELECT} + \frac{R_{LEAK} * R_L}{R_{LEAK} + R_L}} \right)}$$

i^*

Performance $\quad P_W \rightarrow$ delivered to R_L

$$P_W = i_{LOAD}^{2} R_L$$



← upper bound

$$= i_{LOAD} = \frac{\Delta V_{Nernst}}{R_L}$$

P_W

i_{LOAD}

Show this plot!

$R_{electrolyte}$

(A) — σ_{elect} (conduc) $= \left(R_{ELECT} \times \dfrac{A}{h}\right)^{-1}$ ← surface area of the electrolyte

h ← thickness of the electrolyte

$$I = \sigma_{ela} \times E_e$$

(current density A/cm²) ↳ $\dfrac{\Delta V_{meas.}}{h}$

$$= \frac{h}{R_{elect} \times A} \times \frac{\Delta V_{me}}{h}$$

$$\Delta V = \left(R_{elect} \times A\right) \times \underbrace{\frac{i}{A}}_{I \Rightarrow \text{current Density}}$$

i ← total current

$\left(R_{elect} \times A\right)$ → called Area Specific Resistance. (~~ARS~~) ASR.

ASR → units of $\Omega\,cm^2$.

$$\underset{\text{(current Density)}}{I} = \frac{\Delta V}{ASR}$$

$$ASR = \frac{\Delta V}{I} \quad I \leftarrow \text{current Density}.$$

<u>Kinetics</u> Relate $D_{O^{2-}}$ (diffusion through the electrolyte) to ASR

use Eqn (A)

$$\sigma_{elect} = \frac{h}{ASR}$$

$$\cancel{\boxed{\sigma_{elect} = I \times \mathcal{E}_e}}$$

current Density

$\frac{\Delta V}{h}$.

$$I = \sigma_{elect} \times \mathcal{E}_e \quad \text{———} \quad (B)$$

$$I = J \times 4|e| \quad \text{—} \; Ⓒ$$

coulombs/sec. flux of O^{2-} per unit area per unit time

$$J = \frac{C_{O^{2-}} D_{O^{2-}}}{k_B T} \times \frac{\Delta\mu}{h}$$

$$\Delta\mu = \Delta V \times 4|e|$$

$$J = \frac{C_{O^{2-}} D_{O^{2-}}}{k_B T} \times \frac{\Delta V}{h} \times 4|e|$$

$$\therefore I = J \times 4|e| \quad (\text{from } Ⓒ)$$

$$= \frac{(4|e|)^2 C_{O^{2-}} D_{O^{2-}}}{k_B T} \times \mathcal{E}_e \quad \text{—} \; Ⓓ$$

comparing Ⓑ & Ⓓ

$$\boxed{\sigma_{elec} = \frac{(4|e|)^2 C_{O^{2-}} D_{O^{2-}}}{k_B T}}$$

the conductivity is related to the Diffusivity of O_2- through the electrolyte