

Charge transfer at metal electrodes (Quantum effects)

Notes by MIT Student (and MZB)

1. Review on Marcus Theory

Let's consider a redox reaction shown on the following reaction coordinate:

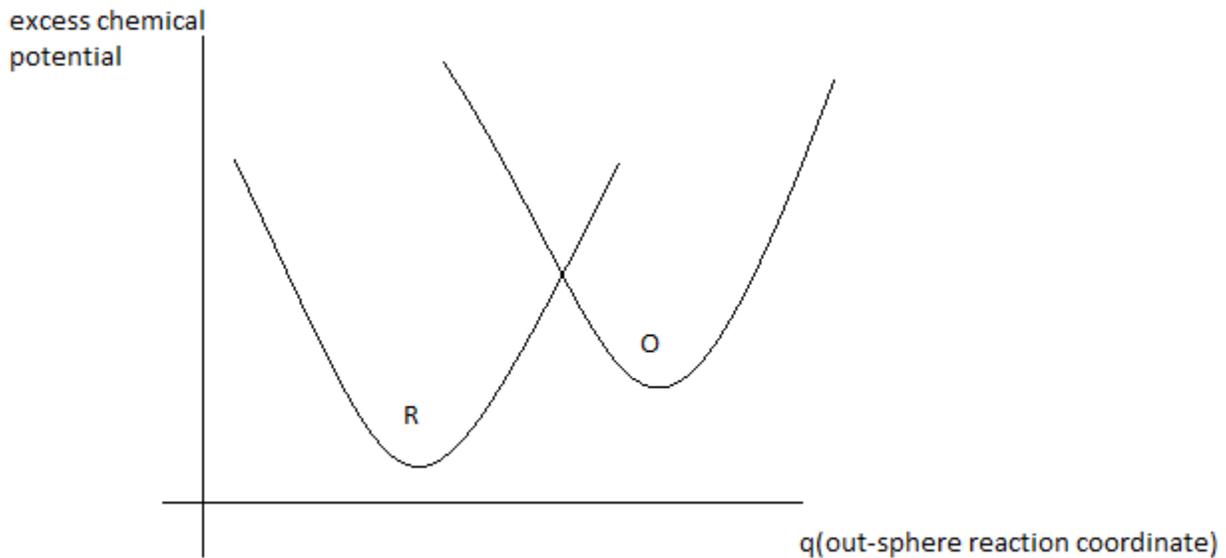


Figure 1 Reaction coordinate of reaction $R - ne^- \rightarrow O$

The reaction happens on the intersection of two parabolas which are used to approximate energy-coordination relationship of species.

Last time we already derived the Marcus theory (assume one electron transferred)

$$k_{red} = k_0 e^{-\frac{(\tilde{\eta} + \tilde{\lambda})^2}{4\tilde{\lambda}}} = k_0 e^{-\frac{(e\eta + \lambda)^2}{4\lambda k_B T}}$$

$$k_{ox} = k_0 e^{-\frac{(\tilde{\eta} - \tilde{\lambda})^2}{4\tilde{\lambda}}} = k_0 e^{-\frac{(e\eta - \lambda)^2}{4\lambda k_B T}}$$

λ is the reorganization energy, which is the difference in μ^{ex} when reactants and products are both reactants' coordinate position or products' coordinate position and the reactants and products have the same ground state energy.

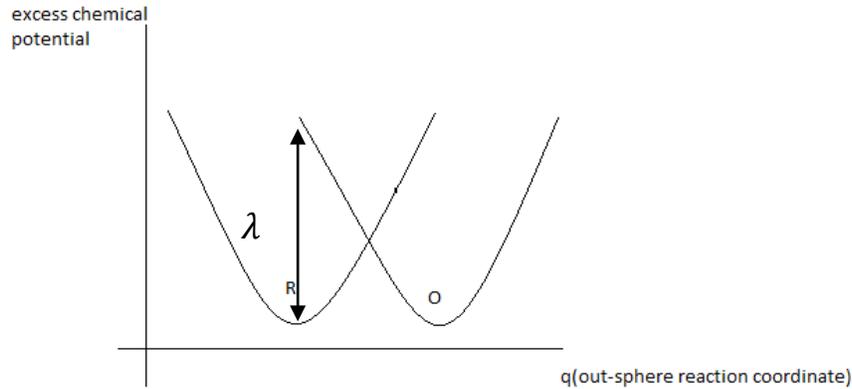


Figure 2 A illustration of reorganization energy

2. Quantum effects at the electrode

There are two main quantum effects at the electrode:

- (1) Electron energy levels are quantized. Two states per energy level and only one electron per state (Pauli Exclusion Principle). There exists a distribution of electron energy so the using $e\Phi_e$ as an approximation of electron energy is too rough.
- (2) Quantum tunneling (We will not discuss about it in this lecture).

Fermi-Dirac distribution:

Because of the Pauli Exclusion Principle, electrons cannot stay all in the same state. It is distributed on a variety of different states with different energy. For a fermion (electron is fermion), the energy distribution of electrons obeys Fermi-Dirac distribution. The filling fraction at each state is determined by the state's energy:

$$n_e^{FD} = \frac{1}{1 + e^{\frac{\varepsilon - \mu_e}{k_B T}}}$$

Where n_e^{FD} is the filling fraction of that state (A decimal number of n_e doesn't mean electrons are split. It can be viewed as the probability that an electron will occupy this state). μ_e is usually called Fermi-level, which is the chemical potential of electrons. ε is the electron energy at that state.

At $T = 0K$, all electrons occupy all states with energy levels just below μ_e . For higher temperature, the filling fraction as a function of state's energy is showed below:

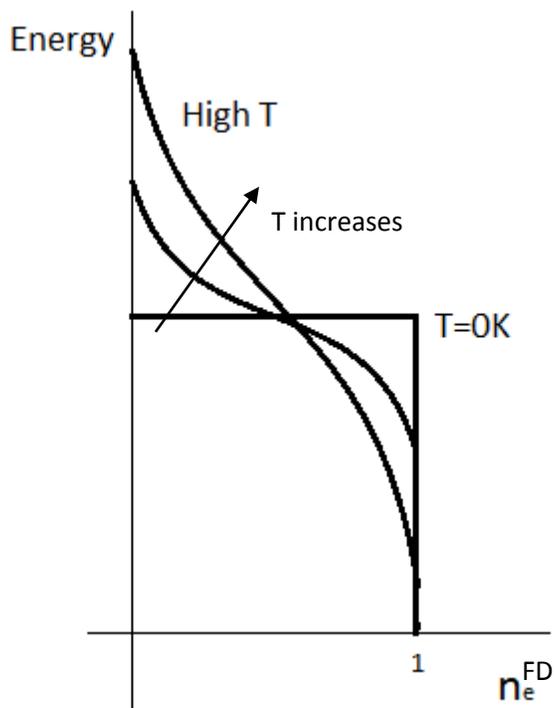


Figure 3 Fermi-Dirac distribution

Another thing that needs to be mentioned is that states are not evenly distributed among different energy levels. n_e^{FD} must time another variable, the number of states per energy interval, to represent the probability density distribution of electrons as a function of energy. The number of states per energy interval is termed density of state (DOS), which is a function of energy. Strictly speaking, DOS of electrode should be both a function of energy and μ_e . In an electrode reaction, the energy distribution of electrons are mainly shifted up and down equally with μ_e because of an applied potential. Thus DOS will only be a function of $\varepsilon - \mu_e$. Later in this lecture, we will non-dimensionalize electron energy using a new variable $x = \frac{\varepsilon - \mu_e}{k_B T}$ and then DOS will only be a function of x . (For details, see textbook: Bard, Allen J *Electrochemical methods: fundamentals and applications* 2nd ed, page 125) The multiplication of DOS with n_e^{FD} is number of electrons occupying a certain energy level.

$$n_e(\varepsilon - \mu_e) = \frac{g(\varepsilon - \mu_e)}{1 + e^{\frac{\varepsilon - \mu_e}{k_B T}}}$$

Where $g(\varepsilon - \mu_e)$ is the DOS at electron energy ε , i.e. $(\varepsilon - \mu_e)$ deviation from μ_e . Different materials have different structures of DOS (also called band structure).

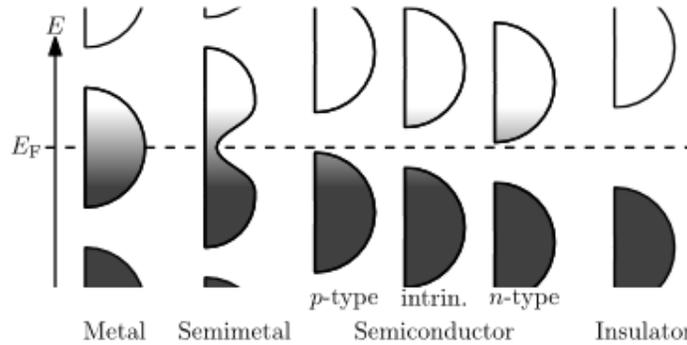
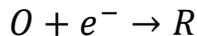


Figure 4 Band structure of different kinds of materials^[1]

For example, metal has high DOS at the Fermi-level but semimetal has a minimum DO there.

3. Marcus-Hush-Chidsey Theory

For reaction



$$e\eta = \mu_R - (\mu_O + \mu_e)$$

Previously we use $e\Phi_e$ to denote μ_e . Now we know it's not correct. And η now is not a constant. Denote:

$$x = \frac{\varepsilon - \mu_e}{k_B T}$$

Which represents the deviation of electron energy with respect to μ_e scaled by thermal voltage. x spans from a very negative value to a very positive value because of the distribution of energy. Chidsey modifies the Marcus theory with a generalized relationship taking into consideration of the quantum effects. The equation is called "Marcus-Hush-Chidsey" (MHC) Theory

$$k_{red}^{MHC} = \int_{-\infty}^{+\infty} k_{red}^{Marcus}(\tilde{\eta} - x) n_e(x) dx = \int_{-\infty}^{+\infty} k_0 e^{-\frac{(\tilde{\eta}-x+\tilde{\lambda})^2}{4\tilde{\lambda}}} n_e(x) dx$$

$$\tilde{\eta} = \frac{\eta e}{k_B T}, \quad \tilde{\lambda} = \frac{\lambda}{k_B T}$$

Note: $k_{red}^{Marcus}(\tilde{\eta} - x)$ is not a notation for multiplication. It means plugging in $\tilde{\eta} - x$ instead of $\tilde{\eta}$ into the Marcus theory expression.

This is basically a weighted average taking into account the energy distribution of electron. And the $\tilde{\eta}$ in Marcus theory now is replaced by a non-constant variable ($\tilde{\eta} - x$) and get averaged across all x .

Assume $g(\varepsilon) = 1$ across the dominant part of this integral (if you plot function $y = k_0 e^{-\frac{(\tilde{\eta}-x+\tilde{\lambda})^2}{4\tilde{\lambda}}}$ you will find it has a dominant region where function value is relatively large and contributes more to the integral) and the electrode is a Fermi-Dirac metal, this integral becomes:

$$k_{red}^{MHC} = \int_{-\infty}^{+\infty} \frac{k_0 e^{-\frac{(\tilde{\eta}-x+\tilde{\lambda})^2}{4\tilde{\lambda}}}}{1 + e^x} dx$$

$$k_{ox}^{MHC} = \int_{-\infty}^{+\infty} \frac{k_0 e^{-\frac{(\tilde{\eta}+x+\tilde{\lambda})^2}{4\tilde{\lambda}}}}{1 + e^x} dx$$

Again we have the De Donder relationship.

$$k_{red}^{MHC} = e^{-\tilde{\eta}} k_{ox}^{MHC}$$

Which is always a good check for the validity of a new model.

Using Marcus-Hush-Chidsey Theory, a typical Tafel plot is shown below.

Tafel plot removed due to copyright restrictions. See: Figure 4 in Bai, P., and M. Z. Bazant. "Charge Transfer Kinetics at the Solid-solid Interface in Porous Electrodes." *Nature Communications* 5, no. 3585 (2014).

Figure 5 relationship between overpotential and reaction rate for LiFeO_4 electrode in Li-ion battery^[2]

For very large overpotential limit, most of the electrons participating in electron transfer are “cold electrons” which has very small x .

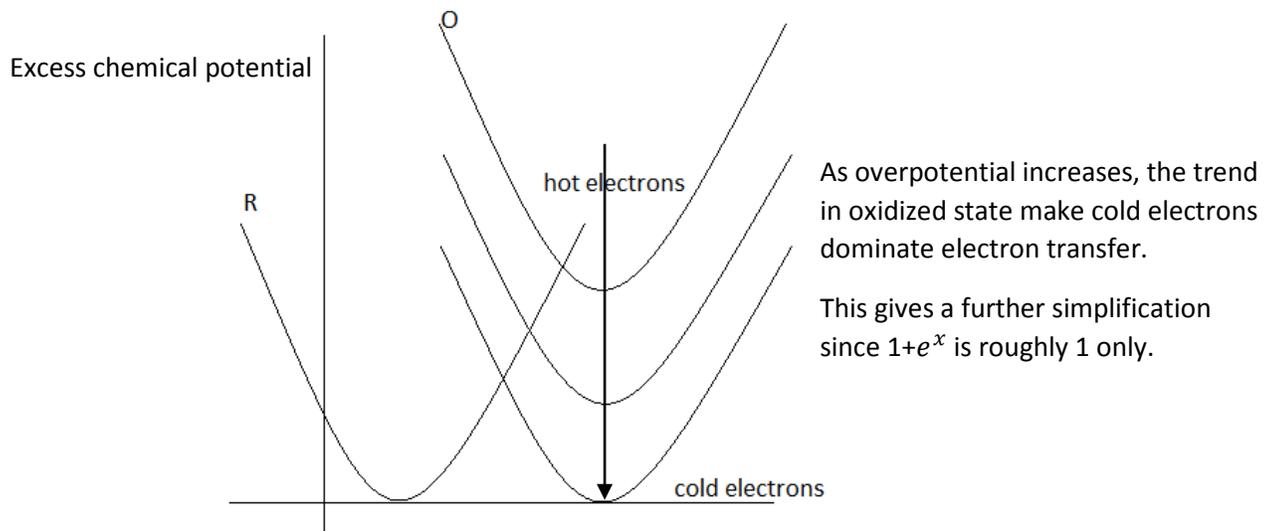


Figure 6 A illustration of “hot” and “cold” electrons

$$\lim_{\eta \rightarrow \infty} k_{red} = k_0 \int_{-\infty}^{+\infty} \frac{k_0 e^{-\frac{(\tilde{\eta}-x+\tilde{\lambda})^2}{4\tilde{\lambda}}}}{1+e^x} dx$$

$$\approx k_0 \int_{-\infty}^{+\infty} e^{-\frac{(\tilde{\eta}-x+\tilde{\lambda})^2}{4\tilde{\lambda}}} dx$$

(Because cold electrons dominate the integral so $e^x \ll 1$)

Let $u = \frac{x-\tilde{\eta}-\tilde{\lambda}}{2\sqrt{\tilde{\lambda}}}$

$$\lim_{\eta \rightarrow \infty} k_{red} = k_0 2\sqrt{\tilde{\lambda}} \int_{-\infty}^{+\infty} e^{-u^2} du = 2k_0 \sqrt{\pi \tilde{\lambda}}$$

The constant means plot will finally reach horizontal which is shown in figure 5

References

- [1] Wikipedia http://en.wikipedia.org/wiki/File:Band_filling_diagram.svg
- [2] Bai, P. & Bazant M.Z. Charge transfer kinetics at the solid-solid interface in porous electrodes. *Nat. Commun.* 5:3585 doi:10.1034/ncomms4585(2014)
- [3] Bard, Allen J *Electrochemical methods: fundamentals and applications 2nd ed*, page 125

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