1. Review on Marcus Theory

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

\[ \text{R-ne}^- \rightarrow \text{O} \]

![Reaction coordinate](image)

**Figure 1** Reaction coordinate of reaction \( \text{R-ne}^- \rightarrow \text{O} \)

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)

\[
\begin{align*}
    k_{\text{red}} &= k_0 e^{\frac{(\tilde{\eta} + \lambda)^2}{4\lambda}} = k_0 e^{\frac{(e\eta + \lambda)^2}{4\lambda k_B T}} \\
    k_{\text{ox}} &= k_0 e^{\frac{(\tilde{\eta} - \lambda)^2}{4\lambda}} = k_0 e^{\frac{(e\eta - \lambda)^2}{4\lambda k_B T}}
\end{align*}
\]

\( \lambda \) is the reorganization energy, which is the difference in \( \mu^{\text{ex}} \) when reactants and products are both reactants’ coordinate position or products’ coordinate position and the reactants and products have the same ground state energy.
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:

$$n_{e}^{FD} = \frac{1}{1 + e^{\frac{\varepsilon - \mu_e}{k_BT}}}$$

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). $\mu_e$ is usually called Fermi-level, which is the chemical potential of electrons. $\varepsilon$ is the electron energy at that state.
At $T = 0K$, all electrons occupy all states with energy levels just below $\mu_e$. For higher temperature, the filling fraction as a function of state’s energy is showed below:

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 $\mu_e$. In an electrode reaction, the energy distribution of electrons are mainly shifted up and down equally with $\mu_e$ 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.

Figure 3 Fermi-Dirac distribution
\[ n_e (\varepsilon - \mu_e) = \frac{g(\varepsilon - \mu_e)}{1 + e^{\frac{\varepsilon - \mu_e}{k_B T}}} \]

Where \( g(\varepsilon - \mu_e) \) is the DOS at electron energy \( \varepsilon \), i.e. \( \varepsilon - \mu_e \) deviation from \( \mu_e \).

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 DOS there.

3. Marcus-Hush-Chidsey Theory

For reaction

\[ O + e^- \rightarrow R \]

\[ e\eta = \mu_R - (\mu_O + \mu_e) \]

Previously we use \( e\Phi_e \) to denote \( \mu_e \). Now we know it’s not correct. And \( \eta \) now is not a constant. Denote:

\[ x = \frac{\varepsilon - \mu_e}{k_B T} \]

Which represents the deviation of electron energy with respect to \( \mu_e \) 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.
\[
k_{red}^{MHC} = \int_{-\infty}^{+\infty} k_{red}^{Marcus}(\tilde{\eta} - x)n_e(x)dx = \int_{-\infty}^{+\infty} k_0 e^{-\frac{(\tilde{\eta} - x + \lambda)^2}{4\lambda}} n_e(x)dx
\]

\[
\tilde{\eta} = \frac{\eta e}{k_B T'} \quad \tilde{\lambda} = \frac{\lambda}{k_B T}
\]

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 \(g(\epsilon) = 1\) across the dominant part of this integral (if you plot function \(y = k_0 e^{-\frac{(\tilde{\eta} - x + \lambda)^2}{4\lambda}}\) 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:

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

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

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.

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

As overpotential increases, the trend in oxidized state make cold electrons dominate electron transfer.

This gives a further simplification since $1+e^x$ is roughly 1 only.

Figure 6 A illustration of “hot” and “cold” electrons
\[ \lim_{\eta \to \infty} k_{red} = k_0 \int_{-\infty}^{+\infty} \frac{e^{-\frac{(\eta-x+\lambda)^2}{4\lambda}}}{1+e^x} \, dx \]
\[ \approx k_0 \int_{-\infty}^{+\infty} e^{-\frac{(\eta-x+\lambda)^2}{4\lambda}} \, dx \]

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

Let \( u = \frac{x-\eta-\lambda}{2\sqrt{\lambda}} \)
\[ \lim_{\eta \to \infty} k_{red} = k_0 2\sqrt{\lambda} \int_{-\infty}^{+\infty} e^{-u^2} \, du = 2k_0\sqrt{\pi} \sqrt{\lambda} \]

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

References


