Lecture #3

Fundamentals of Mass Transfer in Electrochemical Reactions

This lecture introduces the fundamental principles of mass transfer in electrochemical systems and explains how these processes influence the rate and efficiency of electrode reactions. The discussion includes mathematical formulations, physical interpretations, and examples of how diffusion, migration, and convection affect measurable current densities in practical electrochemical setups.

The simplest electrode reactions are those in which the rates of all associated chemical reactions are very rapid compared to those of the mass-transfer processes. Under these conditions, the chemical reactions can usually be treated in a particularly simple way. If, for example, an electrode process involves only fast heterogeneous charge-transfer kinetics and mobile, reversible homogeneous reactions, we will find below that (a) the homogeneous reactions can be regarded as being at equilibrium and (b) the surface concentrations of species involved in the faradaic process are related to the electrode potential by an equation of the Nernst form. The net rate of the electrode reaction, v_{rxn}, is then governed totally by the rate at which the electroactive species is brought to the surface by mass transfer, v_{mtv}. Hence, from equation 1:

$$v_{rxn} = v_{mt} = \frac{i}{nFA}$$

Such electrode reactions are often called *reversible* or *Nernstian*, because the principal species obey thermodynamic relationships at the electrode surface. Since mass transfer plays a big role in electrochemical dynamics, we review here its three modes and begin a consideration of mathematical methods for treating them. Mass transfer, that is, the movement of material from one location in solution to another, arises either from differences in electrical or chemical potential at the two locations or from movement of a volume element of solution. The modes of mass transfer are:

Migration. Movement of a charged body under the influence of an electric field (a gradient of electrical potential).A change in the applied potential to a solid electrode in a solution containing ions affects charge migration as illustrated in Figure 1 for increasing negative charge at the electrode surface.

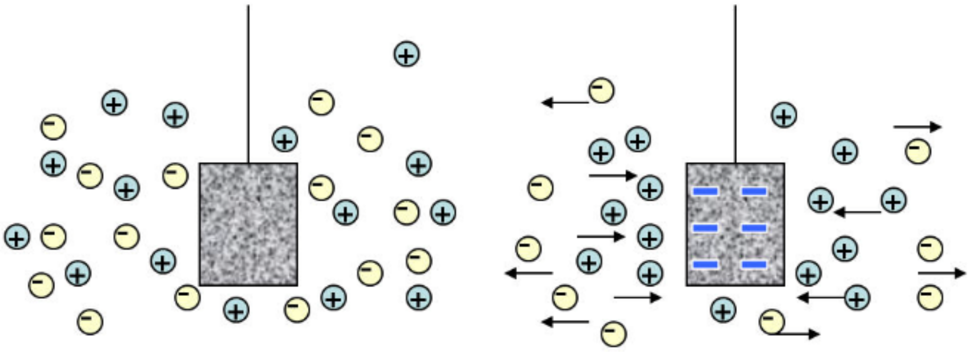

Figure 1. Migration of particles.

Diffusion. Movement of a species under the influence of a gradient of chemical potential (i.e., a concentration gradient).

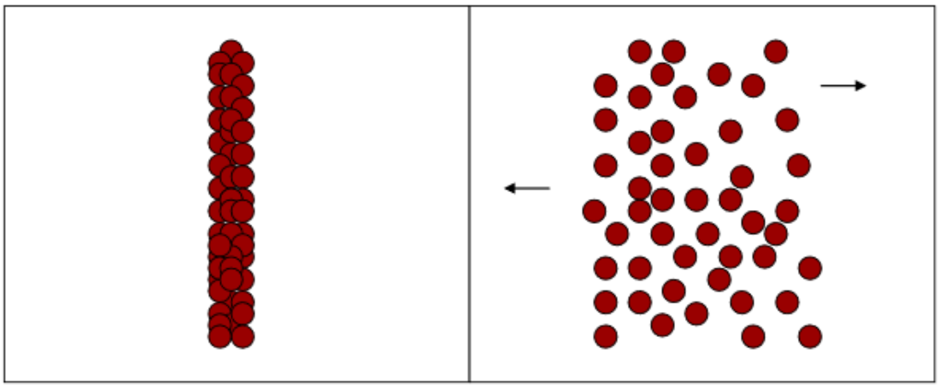

Figure 2. Diffusion.

This movement of a chemical species under the influence of a concentration gradient is described by Fick's first law. A particle i will diffuse through a cross-sectional area as a function of the concentration gradient across the selected area. Flux, as particles per unit time across the given segment, is expressed as Ji according to

$$J = -D \frac{dC}{dx}$$

where J is the diffusion flux (mol m^{-2} s^{-1}), D is the diffusion coefficient (m^2 s^{-1}), and $\frac{dC}{dx}$ is the concentration gradient. At the electrode surface, reactant molecules are consumed, creating a lower concentration compared to the bulk solution. Example in Electrochemistry: During CO_2 electroreduction on a copper electrode, dissolved CO_2 diffuses from the bulk electrolyte to the surface where it is reduced to CO, CH_4, or C_2H_4. The slower the diffusion, the smaller the limiting current.

Fick's Second Law:

$$\frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial x^2}$$

This describes how concentration changes with time during diffusion. Diffusion dominates when the supporting electrolyte concentration is high enough to suppress migration.

Convection – stirring or hydrodynamic transport. Generally, fluid flow occurs because of natural convection (convection caused by density gradients) and forced convection, and may be characterized by stagnant regions, laminar flow, and turbulent flow. Convection as it applies to electrochemistry is forced movement of solution species by mechanical (stirring) or other means. The rate at which a solution is stirred can generally be controlled, with the convective contribution (in one dimension) to total flux of a species described in terms of its hydrodynamic velocity, vx. The effect of stirring a solution is shown in Figure 3.

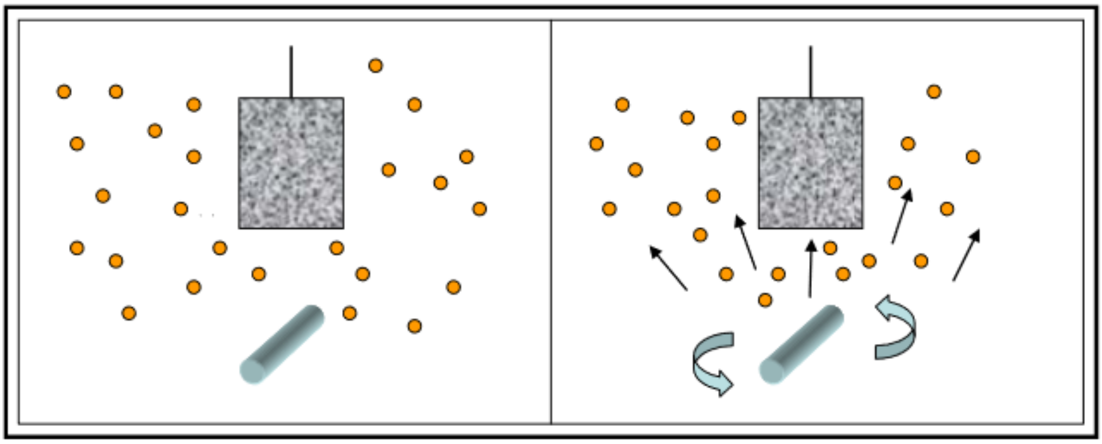

Figure 3. Migration

Migration arises when charged particles move due to the electric field (E) between electrodes.
The flux of ions due to migration is:

$$J_{mig} = -zFuCE$$

where z is the ionic charge, F is the Faraday constant, u is ionic mobility, and C is the concentration. In most electrochemical experiments, a supporting electrolyte is added to minimize migration and maintain charge neutrality.

Convection refers to the bulk movement of the solution. It can be:

Natural convection – due to density gradients caused by concentration or temperature changes.

Forced convection – caused by external stirring, rotation (e.g., rotating disk electrode, RDE), or gas bubbling.

Increasing convection reduces the thickness of the diffusion layer and therefore enhances mass transfer. In an RDE, the diffusion layer thickness (δ) is inversely proportional to the square root of the rotation rate ($\omega^{-1/2}$).

The total mass transport of material, or *flux*, to an electrode is described for one dimension by the Nernst-Planck equation:

$$J = J_{diff} + J_{mig} + J_{conv}$$

$$J(x,t) = -D\frac{\partial C(x,t)}{\partial x} - \frac{zFD}{RT}C(x,t)\frac{\partial \varphi(x,t)}{\partial x} + C(x,t)\,V_x(x,t)$$

where J is the flux (mol cm^{-2} s^{-1}), D is the diffusion coefficient of the solution species (cm^2 s^{-1}), C is the concentration of the species (mol cm^{-3}), φ is the electrostatic potential, and v_x is the hydrodynamic velocity. The Nernst-Planck equation combines the individual contributions from diffusion (concentration gradient), migration (electric field), and convection (hydrodynamic velocity). This equation shows that the flux of material towards the electrode surface is proportional to either of three slopes of concentration, electrostatic potential, or hydrodynamic velocity, all as a function of distance from the electrode surface. Electrochemical experiments can be designed to eliminate the contributions of electrostatic potential and hydrodynamic velocity to the overall flux of electroactive species, limiting mass transport to the contribution from diffusion. The currents resulting from these experiments can then be classified as diffusion controlled. Contributions from migration can be effectively eliminated by adding an inert electrolyte to the solution at a 10 – 100 fold excess with respect to the redox couple of interest. The electric field between the two electrodes involved in the measurement is dissipated over all of the ions in solution and not just the electroactive material. Under these conditions, the contribution of migration to the observed current is < 1%. Contributions from convection can be reduced or eliminated by working in quiet (unstirred) solutions. With careful control of external vibration and temperature, diffusion controlled measurements for up to 20 seconds or so can be made without significant convective effects.

References

1. Bard, Allen J., and Larry R. Faulkner. "Fundamentals and applications." Electrochemical Methods 2.482 (2001): 580-632