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Model to Demonstrate Effects of Mass Transfer and Applied Current in an Electrolytic Cell

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Abstract

This study investigates the relationship between applied current and resulting cell potential in an electrolytic system, considering the transport of electroactive species. By applying Michael Faraday's laws of electrolysis and the Nernst-Planck equation, the behavior of electroactive species in diffusion-controlled systems with and without stirring is modeled. The plots demonstrate how stirring enhances ion transport and establishes a stable Nernst diffusion layer, affecting the kinetics of electrochemical reactions. Understanding these dynamics is crucial for optimizing electrolysis processes.

Keywords: current, diffusion, potential, ion transport, concentration

1 Introduction

An electrochemical process is a chemical reaction that involves the movement of electrical current. This current can either cause the reaction or be a result of it. These processes are fundamentally linked to oxidation-reduction (redox) reactions, where one atom or molecule loses an electron to another. As Michael Faraday famously stated, "chemical action or the decomposing power is exactly proportional to the quantity of electricity which passes" [1]. In simpler terms, we could say the amount of a substance undergoing reduction or oxidation in an electrochemical reaction is directly proportional to the amount of electricity flowing through the system.

1.1 Thermodynamics of Electrochemical Cells

The cell potential, also known as the voltage of a cell, represents the driving force behind an electrochemical reaction. It is a measure of the difference in electrical potential between two electrodes in an electrochemical cell. The cell potential is a key parameter that indicates the direction and spontaneity of an electrochemical reaction. It determines whether a reaction will proceed.

The increasing interest in potentiometry in 1890s stressed the need for standard values of electrode

potentials. Ostwald introduced the calomel electrode, calibrating it against what is called the dropping mercury electrode [2]. Walter Nernst chose to calibrate electrode potential against the normal hydrogen electrode, assigning to it a potential of zero. These pioneering efforts established these electrodes as references for determining electrode potentials, shaping the foundation of electrochemical research.

Later, Nernst was successful in relating the principle of thermodynamics to electrochemical systems. He developed a mathematical expression that relates electrode potential of an electrochemical cell to the temperature and concentration of reactants and products involved in a redox reaction.

$$E = E^{0'} + \frac{RT}{nF} \ln \frac{C_O}{C_R} \quad (1)$$

where E is the cell potential, $E^{0'}$ is the formal potential, R is the gas constant, T is the temperature of the system, n is the number of electrons transferred, F is the Faraday constant, C_O and C_R are the concentration of the oxidizing and reducing species, respectively.

1.2 Electroactive Species Transport

Movement of electroactive species toward an electrode is key in electrochemical systems. Three main modes have been identified of how ions are

transported in electrochemical systems for chemical reactions.

The Nernst Planck equation extends Fick's law (diffusion) to situation where electrostatic forces (migration) and advection (convection) cause the movement of ions to the electrode surface [3].

$$J_i(x) = -D_i \frac{\partial C_i}{\partial x} + \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x) \quad (2)$$

Diffusion Migration Convection

where D_i is the diffusion coefficient, C_i is the species concentration, x is distance, z is the signed charge on species, ϕ is the electric potential and $v(x)$ is velocity in the x-direction.

1.2.1 Diffusion

When a reaction occurs at an electrode surface, it affects the surrounding solution. This creates a concentration gradient, where the concentration of electroactive species and molecules involved in the reaction is higher farther away from the electrode and lower near its surface. This difference in concentration drives the diffusion of electroactive species towards the electrode surface.

However, in some cases, the reaction consumes these species at the electrode surface faster than they can be replenished by diffusion. This depletion zone creates a situation where electroactive species move from the bulk solution to the electrode surface at a slower rate than the consumption of electroactive species at the surface. When this happens, the rate of the entire electrochemical reaction becomes limited by the diffusion process, and the system is considered diffusion controlled.

1.2.2 Migration

The movement of these species is not solely driven by concentration differences. In the presence of an electric field within the solution, charged ions (electroactive species) can also migrate. This migration occurs because the ions are attracted or repelled by the electrode, depending on their charge, to maintain electrical neutrality in the solution. This phenomenon, as

referred to by Allen Bard et.al is caused by electrical gradients [4].

1.2.3 Convection

Thermal and density gradients can also cause ion transport in solutions. Additionally, external forces, such as stirring, can be applied to promote the movement of electroactive species.

2 Theory

Based on Michael Faraday's first law of electrolysis,

$$Q = nFN \quad (3)$$

$$\frac{dQ}{dt} = nF \left(\frac{dN}{dt} \right) \quad (4)$$

$$I = nF \left(\frac{dN}{dt} \right) \quad (5)$$

where Q is the charge, N is the amount of substance (moles), and I is the current.

If diffusion is only occurring, the rate of reaction can be related to the flux (J),

$$J_0 = D_0 \frac{dC_0}{dx} = \frac{i}{nFA} \quad (6)$$

where J_0 is the flux of the oxidizing species.

2.1 Assumptions

It is assumed in this work that the limiting parameter for the electrochemical cell is mass transfer. With a supporting electrolyte concentration larger than that of the electroactive species, it can be inferred that there is no significant transfer of electroactive species to the electrode due to migration. Transfer due to migration was ignored in the model [4]. Solubility effects were not considered for this model.

Two cases are used to develop the model. In Case 1, where the electrolyte solution is quiescent (no stirring), the transport of the electroactive species is assumed to occur solely through diffusion, driven by the

concentration gradient. In the second case, diffusion occurs alongside stirring of the solution.

Current is applied and the resulting potential is calculated. It is assumed that the diffusion coefficient of both oxidizing and reducing species is 10^{-6} cm²/s. The surface area of the anode is 40 cm² and the cathode is 30cm². A Sn/Sn²⁺ redox couple is used for this model [4]. The resistance of the electrolyte, lithium chloride, potassium chloride and calcium chloride eutectic mixture is assumed to be 2 ohms for this model. The temperature of the model cell is 673 K.

The current is proportional to the rate of reaction. Since the electrochemical system is mass transfer limited. The rate of the reaction can be related to the flux.

$$J = D_i(C_{i,bulk} - C_{i,surface})/\delta \quad (7)$$

where $C_{i,bulk}$ and $C_{i,surface}$ are the concentration of electroactive species in the bulk and at the electrode's surface, respectively, and δ is diffusion layer thickness (see Figure 1).

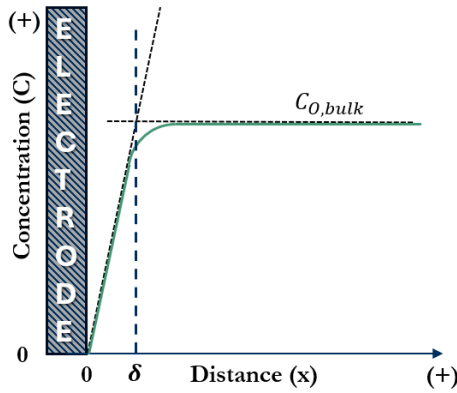


Figure 1 Concentration profile near the electrode surface depicting the diffusion layer thickness.

The surface concentration at the cathode is,

$$C_{O,surface} = C_{O,bulk} - \frac{\delta J_O}{D_O} \quad (8)$$

The potential of the cell can be calculated using the Nernst equation.

$$E = E^{0'} - \frac{RT}{nF} \ln \frac{1}{C_O} \quad (9)$$

where the activity of a pure solid (reduced species) has a value of 1. The potential for the reduction of Sn²⁺ is taken to be -0.14V relative to the normal hydrogen electrode (NHE) [4].

To facilitate the movement of ions from the bulk solution to the electrode surface for the reaction, the solution is gently stirred. This stirring action helps establish a stable diffusion layer [4].

3 Results and Discussion

At the cathode, the electroactive species, Sn²⁺, is gradually depleted as it is reduced to form Sn metal. Due to the depletion of Sn ions at the cathode, a concentration gradient is created, which causes the electroactive species to move from the bulk solution to the cathode surface through diffusion.

At the anode surface, Sn²⁺ ions are liberated through oxidation, leading to an accumulation of ions. These Sn²⁺ ions then move into the bulk solution due to the concentration gradient.

Figure 2 and 3 show plots of time dependent applied current plotted against the concentration at the electrode surface. In the case of diffusion only, the δ increases with time, there is an increase in the concentration of electroactive species at the anode and a decrease in concentration of the electroactive species at the cathode.

In case 2 of this model, convective ion transport by stirring is included to aid Sn²⁺ transport and establish a thin and stable diffusion layer. Despite stirring, a concentration gradient is still present.

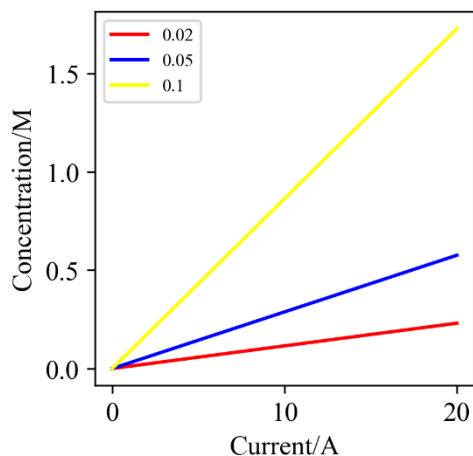


Figure 2 A plot of applied current vs the concentration at the anode for different diffusion layer thickness (in mm).

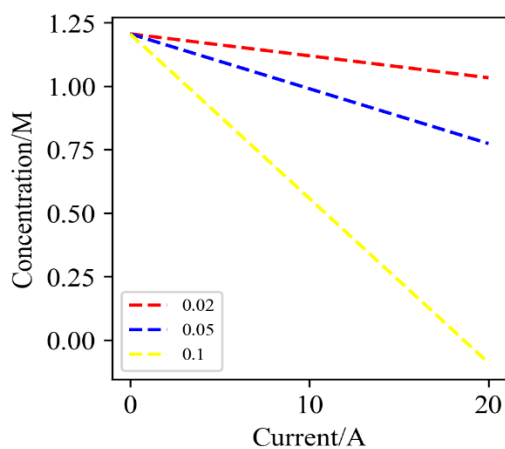


Figure 3 A plot of applied current vs the concentration at the cathode at varied diffusion layer thickness (in mm).

The thickness of the diffusion layer depicts how the applied current affects the resulting cell potential, as shown in Figures 4 and 5. This representation may not intuitively convey the rate of reaction. As the applied current increases, the cell potential also increases to accommodate the additional energy necessary to propel the oxidation of Sn into Sn^{2+} ions. The energy that drives the oxidation-reduction reaction is the potential difference between the electrodes, that is electrons will be removed from Sn metal to form Sn^{2+} ions at the anode which has a higher potential. The Sn^{2+} ions are then reduced at the cathode which has a lower potential.

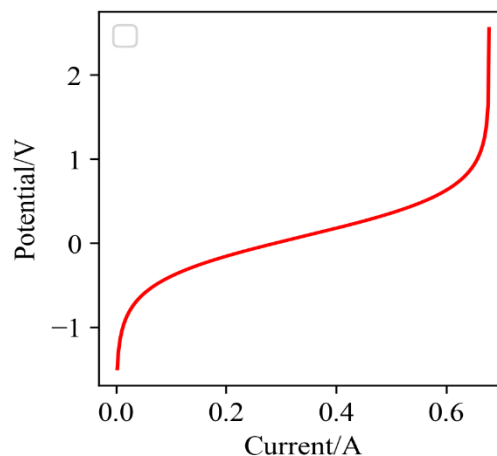


Figure 4 A plot of applied current vs the resulting cell potential for a diffusion and convective transport system with a diffusion layer thickness of 0.012 mm.

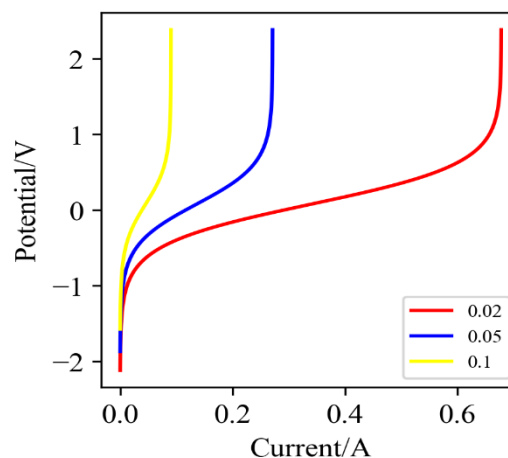


Figure 5 A plot of time dependent applied current vs the resulting cell potential for different diffusion layer thickness (in mm). The mode of electroactive species transport is assumed to be diffusion only.

The plots for applied current in relation to the potential at the anode and cathode are shown in Figure 6 and 7, respectively. As the applied current is increased, the concentration of the oxidizing species at the cathode decreases due to reduction. The reaction at the cathode becomes mass-transfer controlled when the available Sn^{2+} ions at the surface is low and, ultimately, limits the cell current. This causes a rapid increase in potential to negative values which follows the Nernst equation.

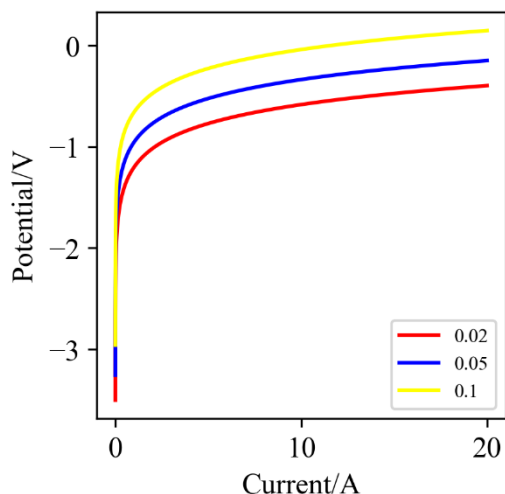


Figure 6: A plot of applied current vs anode potential at varied diffusion layer thickness (in mm).

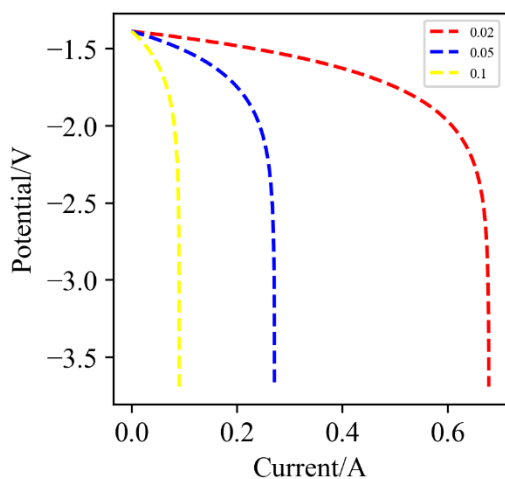


Figure 7 A plot of applied current vs potential at cathode at varied diffusion layer thickness (in mm).

At the anode, the increase in potential at higher current is evident of the continued increase in the concentration of Sn^{2+} ions due to oxidation of Sn metal.

4 Conclusion

It was demonstrated that stirring, which facilitates convective mass transfer, significantly enhances the transport of Sn^{2+} ions toward the cathode for reduction. Stirring also aids in the movement of Sn^{2+} as they are liberated at the anode to the bulk region. However, a concentration gradient even when the solution

is stirred suggests that convective ion transport is effective away from the electrode surfaces and not near electrode surface. This reinforces the concept of a consistent diffusion layer thickness when solution is stirred, and that convective ion transport is experienced in the bulk region of an electrochemical system as observed in literature.

This study also demonstrates the critical role of electroactive species transport in electrochemical systems. When the supply of Sn^{2+} ions (electroactive species) at the cathode became low at surface, the reduction reaction stalled despite the continuous application of current to drive the reaction.

5 Acknowledgements

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6 References

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