Rotating Disc Electrode

Chemicals and Instruments

N_2-purged aqueous solution of 0.15 M $K_4Fe(CN)_6$ and 0.015 M $K_3Fe(CN)_6$ in 0.5 M KOH
N_2-purged aqueous solution of 0.15 M $K_4Fe(CN)_6$ and 0.0075 M $K_3Fe(CN)_6$ in 0.5 M KOH
Cell with rotating platinum disk electrode and controller
Pt wire counter electrode
Ag/AgCl/KCl(sat'd) reference electrode
Potentiostat

Mass-Transport Limited Reactions (B&F Chapter 9)

Task

Determine the diffusion coefficient for the $\mathrm{Fe(CN)_6^{3-}}$ ion and the exchange-current density for the $\mathrm{Fe(CN)_6^{3-/4-}}$ system.

Fundamentals

In many electrochemical reactions, the rate of reaction is not limited by the charge-transfer step, but by slower steps, for example, transport of reactants to the electrode. If a mathematical treatment is available that enables the calculation of the mass-transport effects, then those effects can be eliminated from the experimental data, allowing the study of the charge-transfer step. There are a few systems where such a mathematical treatment is available; one of these systems is the rotating disc electrode (RDE).

For the RDE, the Koutecky-Levitch equation describes the relationship between the current and the angular velocity of the electrode:

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{0.62nFAD_O^{2/3}\omega^{1/2}\nu^{-1/6}C_O^*}$$

Where i_K represents the current in the absence of any mass-transfer effects, D_O is the diffusion coefficient of the oxidized species, ω is the angular velocity of the electrode, F is Faraday's constant, A is the area of the electrode, ω is the angular velocity of the RDE (rad/s), ν is the kinematic viscosity of the electrolyte, and $C_O^*$is the concentration of the oxidized species in the bulk. Thus, a plot of $\omega^{-1/2}$ versus i^{-1} is linear, and by doing a linear regression, the values of the two coefficients can be obtained.

Procedure

Purge the electrolytes with nitrogen. Collect a cyclic voltammogram (CV) for the system at a scan rate of 100 mV/s in the potential range of -100 mV to 700 mV. You should see a reversible wave (i.e., anodic and cathodic peaks of the same size).

Next, record several CVs for the system at a scan rate of 20 mV/s as a function of rotation rate. Suggested rates of rotation are 200 – 2500 rpm.

Work-Up and Questions

1) Determine the limiting current as a function of rotation rate and construct a graph of $\omega^{-1/2}$ versus i^{-1}.
2) Use linear regression to determine the values for i_k and D_O, assuming $\nu = 1.0074\times10^{-6}$ m^2s^{-1} for these solutions.