

Problem Set 5 – Transport

1. **Diffusion in Linear Sweep Voltammetry.** The transient response of a cell is limited by the diffusion of a reactant,

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

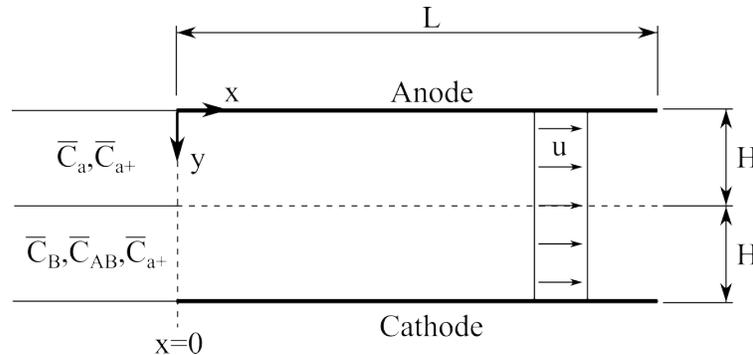
in a semi-infinite domain $x > 0$. Relative to open circuit conditions where $c(x) = c_0$, the change in cell voltage is small enough to linearize the Nernst equation,

$$V - V_0 = \frac{kT}{ne} \frac{\Delta c}{c_0}$$

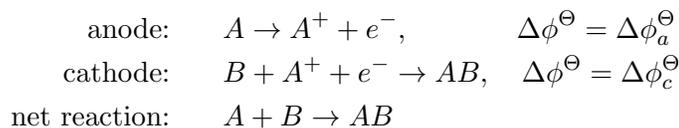
during a linear voltage sweep, $V(t) = V_0 + St$, where S is the sweep rate. The current is given by

$$I(t) = -neAD \frac{\partial c}{\partial x}(x = 0, t)$$

- (a) Show that $u(x, t) = \frac{\partial c}{\partial t}$ satisfies the diffusion equation, and solve by inspection.
 (b) Derive $c(x, t)$.
 (c) Derive and plot the current-voltage relation, $I(V, S)$.
2. **Membraneless fuel cell.** Two streams of liquid electrolyte containing initially separated reactants flow through a porous separator with uniform velocity u between parallel plate electrodes of length L separated by $2H$. The inlets each cover half of the channel width, H . Fuel A enters in the stream near the anode, and oxidant B and product AB enter in the other stream near the cathode.



The electrochemical reactions are:



where standard electrode potentials $\Delta\phi^\ominus$ are given for the Faradaic reactions (with all reactants at 1 M concentration). Assume that the incoming streams contain enough A^+ ions

that their concentration remains roughly constant throughout the cell. Let \bar{c}_A , \bar{c}_B , and \bar{c}_{AB} be the concentrations at the inlets, and D_A , D_B , and D_{AB} the diffusivities. Assume $\bar{c}_A \ll \bar{c}_B$ and fast reactions, so that the limiting current I_{lim} is controlled only by the transport of fuel A to the anode. The cell is operated in steady state.

- (a) Determine the fuel utilization of species A, $\gamma(I, u)$, (fraction of incoming fuel consumed by reactions) at a given current I (per width into the page).
- (b) Make a scaling argument to estimate the minimum fluid velocity u_{min} required to avoid fuel crossover (i.e. A reaching the cathode or B reaching the anode before exiting the cell, thereby reducing the voltage).
- (c) Assuming $u \gg u_{min}$ and dilute solutions, determine the open circuit voltage, V_0 .
- (d) For $u \gg u_{min}$, neglect axial diffusion and derive $I_{lim}(u)$ by setting $c_A = 0$ on the anode.
- (e) As a first approximation for $I < I_{lim}$, assume a uniform concentration c_A of fuel A over the anode surface, given by

$$\frac{c_A}{\bar{c}_A} = 1 - \frac{I}{I_{lim}}$$

and calculate the power $P(I, u)$ of the fuel cell.

- (f) For the typical case, $\tilde{V}_0 = eV_0/k_B T \gg 1$, estimate the maximum power $P_{max}(u)$ of the fuel cell at a given flow rate, and show that $P_{max}\gamma \approx \text{constant}$.

3. Electrocatalytic impedance. The interfacial impedance of electrocatalytic reactions involves not only charge transfer, but also surface adsorption and surface diffusion of reactants to the triple phase boundary (TPB,) where the electrolyte, electrode, and reactant phases meet. In a solid oxide fuel cell (Figure below), oxygen gas adsorbs and dissociates on the LSM electrode surface and diffuses to the YSZ electrolyte TPB where charge transfer occurs. At high frequency, charge transfer impedance dominates, and the oxygen surface coverage remains unperturbed, as in Homework #3. Here we consider lower frequencies, where charge transfer is fast, and the surface adsorption/diffusion process is rate limiting.

- (a) Set up the problem.
 - i. Assume a Langmuir adsorption model.¹ Let \tilde{c} be the dimensionless surface coverage, scaled to the maximum surface concentration c_s (sites/area). Let p be the partial pressure (in atm) of oxygen gas. Let K_a be the equilibrium constant of the adsorption reaction, $\text{O}_2(\text{gas}) \rightarrow 2 \text{O}(\text{surface})$, and k_d be the backward (desorption) rate constant. What is the net adsorption rate R_a (number/time) per surface site? What is the equilibrium coverage \tilde{c}_{eq} where $R_a = 0$?
 - ii. Let $\Delta\tilde{c}(x, t) = \tilde{c}(x, t) - \tilde{c}_{eq}$ be the surface coverage perturbation in response to an applied voltage $\Delta V(t)$. Consider one-dimensional diffusion in a coordinate x away from the TPB (at $x = 0$). Linearize for $|\Delta\tilde{c}| \ll \tilde{c}_{eq}$, and derive the linear response equation

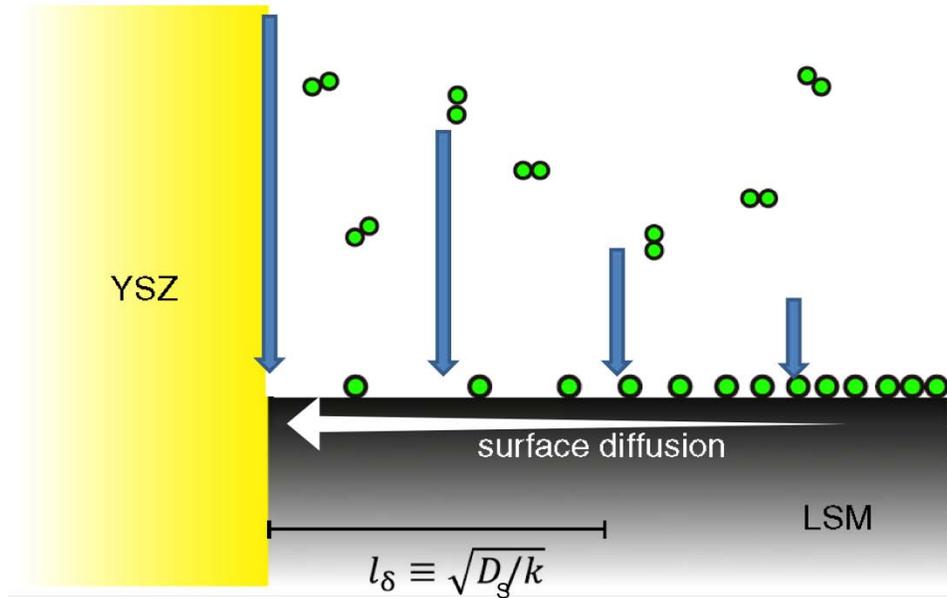
$$\frac{\partial \Delta\tilde{c}}{\partial t} = D_s \frac{\partial^2 \Delta\tilde{c}}{\partial x^2} - k \Delta\tilde{c}$$

where D_s is the surface diffusivity of adsorbed oxygen. What is k ?

- iii. Let A be the electrode area and l_{TPB} the TPB density (length/area). Relate $\Delta V(t)$ and $\Delta I(t)$ (change in total current) to $\Delta\tilde{c}(0, t)$ and $\frac{\partial \Delta\tilde{c}}{\partial x}(0, t)$. Consider AC forcing at frequency ω , and relate the impedance $Z(\omega)$ to the complex amplitude $\Delta\tilde{c}^*(x)$.

¹A lattice gas or ideal solution of particles and vacancies on the surface with two excluded sites in the transition state.

- (b) Consider a semi-infinite catalytic surface.
- Derive $Z = Z_\infty(\omega)$.²
 - Sketch the Nyquist plot. [Hint: square root of a semi-circle.]
 - Show and explain why the high frequency limit $\omega \gg k$ is a Warburg element.
 - Show and explain why the low frequency limit $\omega \ll k$ is a resistance for quasi-steady diffusion across a boundary-layer thickness (Fig. 1).
- (c) Now consider a finite catalytic surface of width $2L$ with symmetry about $x = L$, i.e. $\frac{\partial \Delta \tilde{c}}{\partial x}(L, t) = 0$. Let $\tilde{k} = kL^2/D_s$ be the Thiele modulus.
- Derive $Z(\omega)$.
 - For $\tilde{k} \gg 1$, show and explain why $Z(\omega) \sim Z_\infty(\omega)$.
 - For $\tilde{k} \ll 1$, show and explain why $Z(\omega)$ reduces to a bounded Warburg element for $\omega \gg k$.
 - For $\tilde{k} \ll 1$, show and explain why $Z(\omega) \propto Z_\infty(\omega)$ for $\omega \ll k$ with a much larger low-frequency resistance (i.e. poor catalytic activity).



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Figure 1: Heterogeneous electrocatalysis of oxygen reduction in a solid oxide fuel cell. (Courtesy of Yeqing Fu)

²This form was introduced by Gerischer 1951 and carries his name.

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