10.426/10.626 Electrochemical Energy Systems
Spring 2014 MIT, M. Z. Bazant

Problem Set 2 – Equivalent Circuits and Equilibrium Thermodynamics

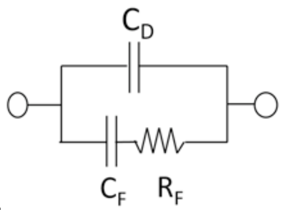

Fig. 1a

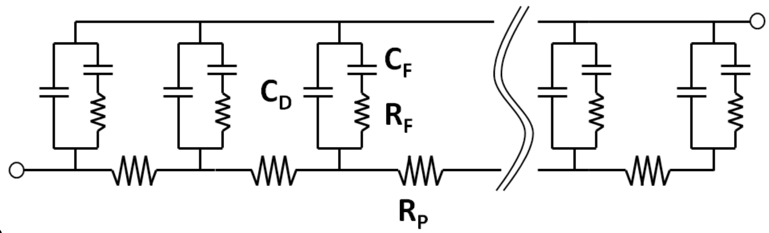

Fig. 1b

1. **Pseudocapacitor impedance.**

   (a) Derive the impedance $Z_i(\omega)$ of an electrode/electrolyte interface ($\Omega\times$ area), where the double-layer capacitance C_D is in parallel with the Faradaic reaction circuit, given by the charge-transfer resistance R_F in series with pseudocapacitance C_F (Fig. 1a).

   (b) Assume that pseudocapacitance dominates, $C_F \gg C_D$, and derive simple approximations of the impedance $Z_i(\omega)$ for low and high frequency, in which one of the three circuit elements can be neglected. Use these results to draw a Nyquist plot of $-\mathrm{Im}Z_i$ vs. $\mathrm{Re}Z_i$, and label approximate points where $\omega = (R_F C_D)^{-1}$ and $\omega = (R_F C_F)^{-1}$.

   (c) Now consider a *porous* pseudocapacitor electrode with constant electron potential, whose impedance can be modeled as an RC transmission line (Fig. 1b) with interfacial impedance Z_i, pore area per volume a_p, electrode area A, and macroscopic pore conductivity σ_p. Each repeated unit of the transmission line represents a cross-sectional slice of width dx with total pore resistance $R_p = dx/(A\sigma_p)$ and total interfacial impedance $Z_i/(Aa_p dx)$. Derive the total electrode impedance $Z(\omega)$ for sufficiently high frequency that the transmission line is effectively infinite (recursive circuit, $dx \to 0$), and sketch the Nyquist plot, assuming again $C_F \gg C_D$.

2. **Redox reactions in a multicomponent regular solution.** Consider a homogeneous mixture of N different species M_i with numbers $n_1, n_2, ...n_N$ on a lattice of N_s sites. The empty sites of number $n_0 = N_s - \sum_{i=1}^{N} n_i$ represent liquid solvent molecules or crystal vacancies.

   (a) Derive the entropy density per site, $s(x_1, x_2, ..., x_N) = S(n_1, n_2, ..., n_N)/N_s$, in the thermodynamic limit $n_i, N_s \to \infty$ at fixed volume fractions $x_i = n_i/N_s$.

   (b) Consider the enthalpy density for a regular solution,

   $$h = \sum_{i=1}^{N} x_i (A_i + \sum_{j=1}^{N} B_{ij} x_j)$$

   where $B_{ii} = 0$ and $B_{ij} = B_{ji}$, and assign each particle of species i a charge $z_i e$. Derive the electrochemical potential difference $\mu_i(x_1, .., x_N) = \partial g/\partial x_i$ for adding species i.

   (c) Derive the Nernst voltage $\Delta\phi$ of the general half-cell redox reaction, $\sum_{i=1}^{N} s_i M_i^{z_i} \to ne^-$.

3. **Fruit batteries.** Prof. Bazant has agreed to demonstrate a "fruit battery" at his daughter's science fair, but he needs your help to explain it to the kids. The anode is a galvanized nail (zinc), and the cathode is a shiny penny (copper), which are stuck into a grapefruit (pH=3) or lemon (pH=2), whose acidic juices serve as the electrolyte. The fruit is rolled to breakup the tissue and produce well connected juice pathways between the electrodes. The anode reaction is zinc electro-dissolution

$$\mathrm{Zn} \to \mathrm{Zn}^{2+} + 2e^- \quad \Delta\phi^\Theta = -0.76V$$

Some websites and textbooks say the cathode reaction is copper electrodeposition

$$\mathrm{Cu}^{2+} + 2e^- \to \mathrm{Cu} \quad \Delta\phi^\Theta = 0.34V$$

and others, hydrogen evolution

$$2\mathrm{H}^+ + 2e^- \to \mathrm{H}_2 \quad \Delta\phi^\Theta = 0V$$

The observed open circuit voltage (OCV) is typically in the range 0.8-1.0 V.

(a) Which cathode reaction is more likely to occur, and why?

(b) Derive the theoretical OCV vs. pH (of the fruit juice), p_{H_2} (hydrogen partial pressure in atm), and $c_{Zn^{2+}}$ (zinc ion concentration in M, assuming a dilute solution). What quasi-steady conditions are consistent with the observed voltage $V_0 = 0.9$ V?

(c) Which fruit (grapefruit or lemon) can produce more power? Consider both OCV and internal resistance.

(d) What will happen to the voltage if the lemon battery is soaked in a beaker of 0.1 M copper sulfate solution ($\mathrm{CuSO_4}$)?