24-643 || 27-700

Energy Storage Materials & Systems

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1: Battle of the Solids (6 points)

As we discussed in Module 5, solid electrolytes are an attractive class of materials that can enable lithium metal anodes. The setup of the problem is shown in Fig 1. A thin-film solid electrolyte is in contact with a lithium-metal foil as shown. The thickness of the solid electrolyte is l_{SE}. In this problem, we will analyze the electrostatic potential inside the solid electrolyte.

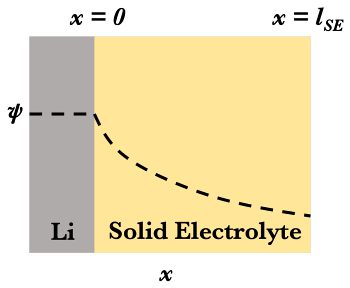

Figure 1: Schematic of the cross-section of the Li-metal anode and solid electrolyte.

(a) Using the lattice-plane model, write down the general form of the solution for the electrostatic potential inside the solid electrolyte. Discuss the assumptions made in the model. (1 point)

(b) Apply the following boundary conditions to this equation:

$$\psi(x = 0) = \psi_0 = 0.1 \text{ V}$$

Different from the boundary condition applied in Module 5.2, we will assume that the the first layer is storing charge in the form of capacitance

$$\frac{d\psi}{dx}(x = 0) = -0.1\psi_0$$

(in units of V/μm). (2 points)

(c) Plot the solution for solid electrolytes with two different thickness, $l_{SE} = 10$, 50μm? Discuss the differences you see in the plot. ($l_D = 100$ nm, $l_{SP} = 1$ nm) (1.5 points)

(d) An engineer at Solidscape company decides to engineer the solid electrolyte considered in the previous parts to increase its conductivity, and finds that the material now has a lower dielectric constant. The dielectric constant of the new material is 4 times lower than the original material. Plot the solution for the two solid electrolytes (original and new) with their different dielectric constants at a thickness of $l_{SE} = 10\mu$m. Discuss the differences. (1.5 points)

(e) Bonus: The solid electrolyte is in-contact with a liquid electrolyte on the cathode. Which of the three cases from the previous two parts will lead to the lowest reactivity with the liquid electrolyte. (1 point)

2: Concentrated transport (8 points)

Concentrated electrolytes are solutions where the amount of salt in the system is comparable to the amount of solvent and exhibit different behavior from dilute electrolytes. In this problem, we will analyze the transport inside concentrated electrolytes.

(a) Dividing the electrolyte volume into voxels and making the simplifying assumption that each voxel can be occupied by only one species (cation, anion or solvent). Derive the expression for mixing entropy of the cation, assuming x is the fraction of cation in the system. (1 point)

(b) We add c mole of salt, $LiPF_6$ into a 1 kg solution of water, i.e. (55.55 moles of water). Derive an expression that relates x to c. (1 point)

(c) Using the derived expression for the mixing entropy from part a, derive the chemical potential, μ as a function of x. Then, using this expression, derive an expression for μ as a function of c. (1 point)

(d) Using the standard definition of the activity coefficient, i.e. $\mu = k_B T ln(\gamma c)$, derive an expression for the activity coefficient as a function of c. Plot the activity coefficient as a function of c. (2 points)

(e) Derive an expression for the diffusivity, D_{chem}, in this concentrated solution, of the following form:

$$D_{\text{chem}} = D(1 + B)$$

Plot the concentrated solution term, B, as a function of c. (3 points)

3: Tortuosity (10 points)

Tortuosity is important to understand the behavior of porous media. In this problem, we will analyze the tortuosity in two-dimensional porous structures. The microstructure files are given in mat file as matrices with 0, 1 with 0 being the solid phase and 1 being the pore phase.
The ions are being transported from left to right.

Below is an example code to load the files and visualize the images in MATLAB:

```
load tort_file.mat
for i=1:length(a)
    tort_img = tort_img_stored(:,:,i);
    subplot(1,length(a),i),imshow(tort_img)
    grid on
    title(i)
end
```

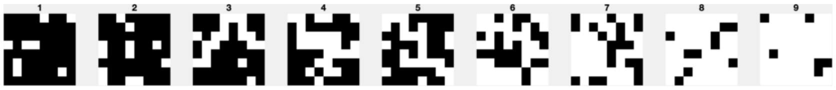

Figure 2: Microstructures

Or equivalently in python:

```
import matplotlib.pyplot as plt
from scipy.io import loadmat
mats = loadmat("tort_file.mat")["tort_img_stored"]
for i in range(9):
    plt.matshow(mats[:,:,i])
```

(a) Re-create the plot shown in the Figure above. (0.5 point)

(b) Give a definition of tortuosity in terms of the relevant path length. Mark in one of the figures the two relevant lengths needed to calculate tortuosity, τ. (1 point)

(c) Determine the relevant path lengths needed to calculate tortuosity for each of the nine microstructures given. Then calculate the tortuosity for each of the microstructures. (4.5 points)

(d) Calculate the porosity for each of the microstructures. (1 point)

(e) Plot the tortuosity as a function of porosity. Plot the Bruggeman's law and Percolation theory (use $\phi_c = 0.2$). (1 point)

(f) Discuss the applicability of these two theories for the tortuosity. In particular, discuss in which regions, each of the theory is applicable. (2 points)

4: Pressure-driven transport (6 points)

Most-next generation batteries apply external pressure to improve cycle life. This leads to changes in the transport of electrolyte. In this problem, we will analyze the transport of a liquid electrolyte solution when a pressure is applied as shown in Figure 3.

Treat the motion of ions inside a solvent, with volume V and pressure p, as that of an ideal gas of molecules moving within a container of the same volume V and pressure p.

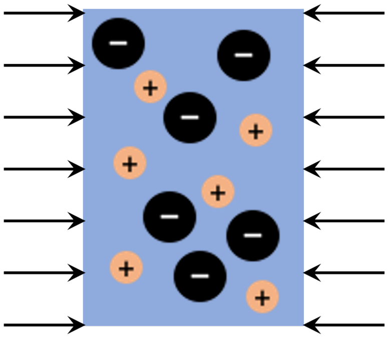

Figure 3: Schematic of the cross-section of the electrolyte under stack pressure.

(a) Using the connection to the ideal gas, write down the expression for chemical potential of the system as a function of the pressure, p. (1 point)

(b) Discuss at least two assumptions made in this connection between ions in solution and ideal gas. Justify those assumptions (2 points)

(c) Which regime of electrolyte solutions is this assumption reasonably valid? (0.5 point)

(d) Using the derived expression for chemical potential, derive a pressure-driven transport law, using the chain rule of differentiation, to derive an expression of the form, $J = -D_{pres}\frac{\partial c}{\partial x}$. Write down the expression for D_{pres}. (1.5 points)

(e) Discuss modifications to the ideal gas formulation that would be made to account for concentrated solutions. (1 points)

(f) Bonus: Using the appropriate modified equation of state that can account for concentrated solutions, derive an expression for the pressure-concentration derivative, $\frac{\partial p}{\partial c}$. (Hint: Think about what changes happen to the concentration when pressure is applied. Concentration is the moles of salt in unit volume of the solution). (2 points)