The Materials Science of Rechargeable Batteries

HW #4

1. Derive a relationship for the critical thermodynamic radius of nucleation of an electrodeposited lithium nucleus, that also includes the effect of compressive stress, $P$.

\[ r_c = \frac{2\gamma\Omega}{zF\eta + P} \]

a. \[ r_c = \frac{2\gamma\Omega}{zF\eta + \gamma} \]

b. \[ r_c = \frac{2\gamma\Omega}{zF\eta + \frac{P^2}{2E}} \]

c. \[ r_c = \frac{2\gamma\Omega}{zF\eta + P^2/2E\Omega} \]

d. \[ r_c = \frac{2\gamma\Omega}{zF\eta + (\Delta G_f + P)\Omega} \]

e. \[ r_c = \frac{2\gamma\Omega}{zF\eta + \frac{2\Delta G_f\Omega}{P^2/2E}} \]

2. Will the critical radius increase, decrease, or remain the same with compressive stress?

a. Will remain the same

b. Will increase in size

c. Will decrease in size

3. Will the critical free energy increase or decrease with compressive stress?

a. Will remain the same

b. Will increase in size

c. Will decrease in size
4. For the case where the driving force for plating is very small as compared to the thermal energy, what is the dendrite radius as a function of time, \( r(t) \), if you include the effect of stress, for the following cases:

4.1. For a flat surface and non-zero overpotential.

\[ r(t) = r_o + \frac{\Omega j_o}{RT} (zF\eta) t + P\Omega \]

a.

\[ r(t) = r_o + \frac{\Omega j_o}{RT} (zF\eta + P\Omega) t \]

b.

\[ r(t) = r_o + \frac{\Omega j_o}{RT} (zF\eta - P\Omega) t \]

c.

\[ r(t) = r_o + \frac{\Omega j_o + P}{RT} (zF\eta) t \]

d.

4.2. For a flat surface and non-zero overpotential, will the electrodeposit grow faster, slower, or at the same rate?

a. Will grow at a slower rate

b. Will grow at the same rate

c. Will grow at a faster rate

4.3. For a flat surface and zero overpotential.

\[ r(t) = -\frac{2\gamma}{P} \left( 1 + W \left[ -\frac{P}{2\gamma} \exp \left[ -1 - \frac{P}{2\gamma} \left( r_o + \frac{j_o P\Omega t}{RT} \right) \right] \left( \frac{2\gamma}{P} + r_o \right) \right] \right) \]

a.

\[ r(t) = r_o + \frac{\Omega j_o}{RT} (zF\eta + P\Omega) t \]

b.

\[ r(t) = \pm \sqrt{r_o^2 + \frac{4j_o \Omega^2 \gamma t}{RT}} \]

c.

\[ r(t) = -\frac{2\gamma \Omega}{zF\eta} \left( 1 + W \left[ -\frac{zF\eta}{2\gamma \Omega} \exp \left[ -1 - \frac{zF\eta}{2\gamma \Omega} \left( r_o + \frac{j_o \Omega zF\eta t}{RT} \right) \right] \left( \frac{2\gamma \Omega}{zF\eta} + r_o \right) \right] \right) \]

d.
4.4. For a curved surface and zero overpotential, will the electrodeposit grow faster, slower, or at the same rate?

   a. Will grow at a slower rate
   
   b. Will grow at the same rate
   
   c. Will grow at a faster rate