

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 .

a.
$$r_c = \frac{2\gamma\Omega}{zF\eta + P}$$

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

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.

a.
$$r(t) = r_o + \frac{\Omega j_o}{RT} (zF\eta)t + P\Omega$$

b.
$$r(t) = r_o + \frac{\Omega j_o}{RT} (zF\eta + P\Omega)t$$

c.
$$r(t) = r_o + \frac{\Omega j_o}{RT} (zF\eta - P\Omega)t$$

d.
$$r(t) = r_o + \frac{\Omega j_o + P}{RT} (zF\eta)t$$

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.

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

b.
$$r(t) = r_o + \frac{\Omega j_o}{RT} (zF\eta + P\Omega)t$$

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

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

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