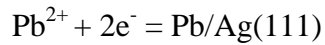


**ECE 6397**  
**Electrochemical Nanofabrication Technology**

**HOMEWORK # 5.**

Considering that UPD process of Pb on Ag (111) can be expressed using *Langmuir* adsorption isotherm presented below:



$$\frac{\theta}{1-\theta} = \exp\left[\frac{nF}{RT}(\Delta E^{\theta=0.5} - \Delta E_{ap})\right].$$

Here  $n$ , and  $\Delta E$  terms stand for number of electrons in the UPD reactions and underpotential. If potential is swept from  $\Delta E_1$  where  $\theta$  is  $\sim 1$  to  $\Delta E_2$  where  $\theta$  is  $\sim 0$ , and the registered current can be expressed as the contribution of the Faradic current related to stripping of the UPD layer, and non Faradic current related to the charging of the  $C_{DL}$ , viz

$$j = j_{UPD} + j_{DL} = nF \cdot \Gamma_{Pb-ML} \cdot \frac{d\theta}{dt} + C_{DL} \cdot \frac{dE}{dt}$$

- a) Assume that  $C_{DL} = const = C_H \neq f(E)$  and describe this assumption validity with in the realm of the double layer models discussed in the class.
- b) Describe what the meaning of the  $\Gamma_{Pb-UPD}$  is and what the unit of this term is?
- c) Find conditions at which conditions,

$$j_{UPD} = j_{DL}$$

and discuss the potential regions, coverage of UPD layer and sweep rate at which this is possible to occur.

Hint: Express your result as a general formula in terms of parameters  $\Gamma_{Pb-UPD}$ ,  $nF$ ,  $R$ , and  $C_{DL}$ , underpotential  $\Delta E^{\theta=0.5}$  assuming that  $\Delta E^{\theta=0.5} = (\Delta E_2 - \Delta E_1)/2$ .