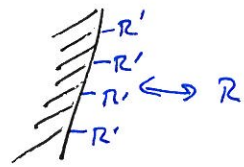
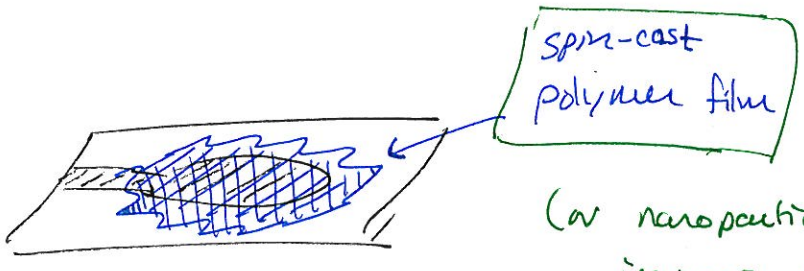
Voltammetry of absorbed species (B+F chap. 14)

Examples:

electrode surface



in situ absorption



(or nanoparticle or inorganic oxide → any electroactive film)

Q. What is different about the response of this electrode compared to a dissolved redox species?

A. No mass transfer effects due to diffusion to the electrode surface!

(in simple case, in more complex case can have both adsorbed and soluble species)

Q. What do we expect the CV curves to look like?

14.3.2 CV → Nernstian Reaction, Only Absorbed O and R electroactive – Nernstian Reaction

Γ_O = surface coverage of O

Γ_R = surface coverage of R

$$\Gamma_O + \Gamma_R = \Gamma_O^* \quad *$$

total coverage, that does not change with time.

We want to calculate the current:

$$i = -nFA \frac{\partial \Gamma_O(t)}{\partial t} = nFA \frac{\partial \Gamma_R(t)}{\partial t}$$

(opposite in sign only, since

and

$$\frac{\Gamma_O(t)}{\Gamma_R(t)} = \frac{C_O(0,t)}{C_R(0,t)} = \exp\left[\left(\frac{nF}{RT}\right)(E - E^\circ)\right]$$

if $E > E^\circ$ species should be only in the oxidized form.

We want $\frac{\partial \Gamma_O(t)}{\partial t}$, what is time dependence of the potential?

$E = E_i - vt$ where v is the scan rate

can either plug in directly or use the chain rule to simplify:

$$\frac{\partial I_o}{\partial t} = \frac{\partial I_o}{\partial E} \cdot \frac{\partial E}{\partial t} = -\left(\frac{\partial I_o}{\partial E}\right) \checkmark$$

$$I_o(t) = I_R(t) \exp\left[\frac{nF}{RT}(E - E^\circ)\right]$$

$$I_R(t) = I_o^* - I_o(t)$$

$$I_o(t) = I_o^* \exp\left[\frac{nF}{RT}(E - E^\circ)\right] - I_o(t) \exp\left[\frac{nF}{RT}(E - E^\circ)\right]$$

$$I_o(t) = \frac{I_o^* \exp\left[\frac{nF}{RT}(E - E^\circ)\right]}{1 + \exp\left[\frac{nF}{RT}(E - E^\circ)\right]}$$

(apply quotient rule

$$\left(\frac{f(x)}{g(x)}\right)' = \frac{g(x)f'(x) - f(x)g'(x)}{(g(x))^2}$$

work out on next page.

$$\frac{\partial \Gamma_0(t)}{\partial t} = \left(\underbrace{\overset{f'(x)}{\frac{nF}{RT}\Gamma_0^* \exp\left[\frac{nF}{RT}(E-E^0)\right]} \cdot \overset{g(x)}{\left(\exp\left[\frac{nF}{RT}(E-E^0)\right]+1\right)}} \right.$$

cancels

$$\left. - \overset{f(x)}{\Gamma_0^* \exp\left[\frac{nF}{RT}(E-E^0)\right]} \overset{g'(x)}{\frac{nF}{RT}\exp\left[\frac{nF}{RT}(E-E^0)\right]} \right)$$

$$\cdot \left(g(x)\right)^2$$

$$= \frac{\frac{nF}{RT}\Gamma_0^* \exp\left[\frac{nF}{RT}(E-E^0)\right]}{\left(g(x)\right)^2}$$

$$\frac{\partial \Gamma_0}{\partial t} = \frac{\frac{nF}{RT}\Gamma_0^* \exp\left[\frac{nF}{RT}(E-E^0)\right]}{\left(1+\exp\left[\frac{nF}{RT}(E-E^0)\right]\right)^2}$$

Note similarity to equation derived for a very thin film. (we haven't done this yet...)

from previous definition of $\underline{i}$

$$\boxed{i = \frac{n^2F^2 v A}{RT} \frac{\Gamma_0^* \exp\left[\frac{nF}{RT}(E-E^0)\right]}{\left(1+\exp\left[\frac{nF}{RT}(E-E^0)\right]\right)^2}}$$

The peak current is thus given by

$$i_p = \frac{n^2F^2}{4RT} v A C_0^*$$

(found via calculus, or realizing that i_p occurs at $E = E^\circ$ for reversible reaction)

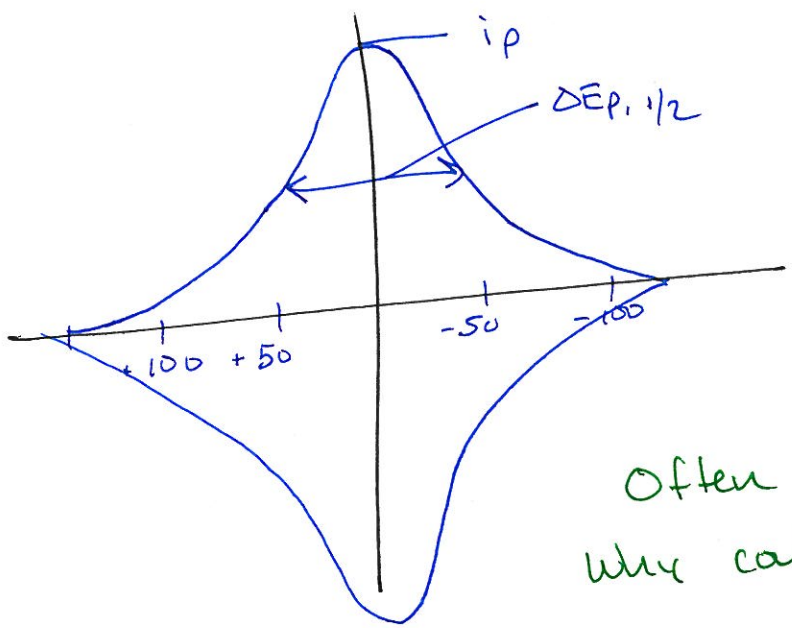
Notice now that $i \propto v$

<u>not</u> $v^{1/2}$!

this is signature of surface reaction that is <u>not</u> influenced by diffusion.

the peak width is

$$\Delta E_{p,1/2} = 3.53 \frac{RT}{nF} = \frac{90.6}{n} mV$$



perfectly reversible, surface absorbed reaction...

Often $E_{p,a} \neq E_{p,c}$, why could this be??

Kinetics!

now the current is given by

C/mol

area units cm^2

$$i = F A k_f \Gamma_O(t) \qquad (n=1$$

current, units C/s

rate constant for $O + e^- \rightarrow R$, units 1/s

concentration of O on the surface (mol) ($/cm^{-2}$)

for a voltage sweep need to account for dependence of rate constant on the applied voltage!

(transition state theory, remember $\Delta G^{\ddagger}$)

$$k_f = k^0 \exp[-\alpha f (E(t) - E^0)]$$

and $E(t) = E_i - vt$

so that $k_f = k_{fi} e^{at}$

time dependence contained in this term

$$k_{fi} = k^0 \exp[-\alpha f (E_i - E^0)]$$

an $a = \alpha f v$ $\left(f = \frac{F}{RT}\right)$

So the total current is just given by

$$i = FA\, k_f\, T_0(t) = -FA \frac{\partial T_0(t)}{\partial t}$$

so

$$k_{fi}\, e^{at}\, T_0(t) = \frac{-\partial T_0(t)}{dt}$$

Separate and integrate

$$\int_0^t -e^{at} k_{fi}\, dt = \int_{T_0^*}^{T_0(t)} \frac{1}{T_0(t)}\, d T_0(t)$$

$$\left.\frac{-k_{fi} e^{at}}{a}\right|_0^t = \ln T_0(t) \Big|_{T_0^*}^{T_0(t)} = \ln \frac{T_0(t)}{T_0^*}$$

where does this term come from?

$$\frac{-\boxed{k_{fi} e^{at}}}{a} + \cancel{\frac{k_{fi}}{a}} = \qquad = k_f$$

$k_{fi} \to \emptyset$ as sweep starts very negative

$$\frac{-k_f}{a} = \ln\left(\frac{T_0(t)}{T_0^*}\right) \Rightarrow \boxed{T_0(t) = T_0^* e^{-k_f/a}}$$

maximum value

$$e^{-k_f/a} = T_0(t)/T_0^*$$

$$i = FA\, k_f\, \Gamma_0(t) = FA\, k_f\, \Gamma_0^*\, e^{-k_f/a}$$

$$a = \alpha f v$$

$$f = \frac{F}{RT}$$

$$= FA\, k_f\, \Gamma_0^* \exp\left(\frac{-RT}{\alpha F}\,\frac{k_f}{v}\right)$$

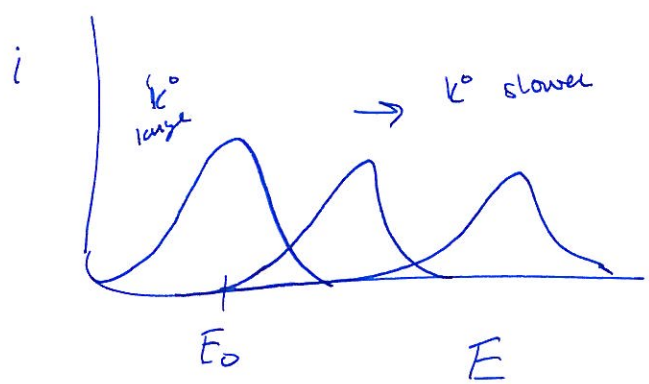
concentration of species to reduce decreases w/ time.

rate increases w/ time / applied E

where k_f has a time-dependence

$$\underline{k_f = k_{fi}\, e^{at}}$$

So what do the curves look like?



→ so slow kinetics shifts peaks again to larger overpotentials and distorts peak shape (with the exponential term)