M.Sc (Chemistry)

ELECTRODE KINETICS – ELECTRODICS-I

LECTURE NOTES

02-DISCUSSION OF BUTLER -VOLMER EQUATION for Different values of β

(i) $\beta = 0.5$: Equal tendency for **anodic and cathodic** process. i vs η is a symmetrical curve.

$$i = i_o[e^{(1-\beta)\eta F/RT} - e^{-\beta\eta F/RT}]$$

The above equation for $\beta = 0.5$ becomes

$$i = i_o [e^{\eta F/2RT} - e^{-\eta F/2RT}] = 2\, i_o \,\mathrm{Sinh}(\eta F/2RT) \quad = i_o(\eta F/RT) \text{ , For } \eta << 1$$

ALITER:

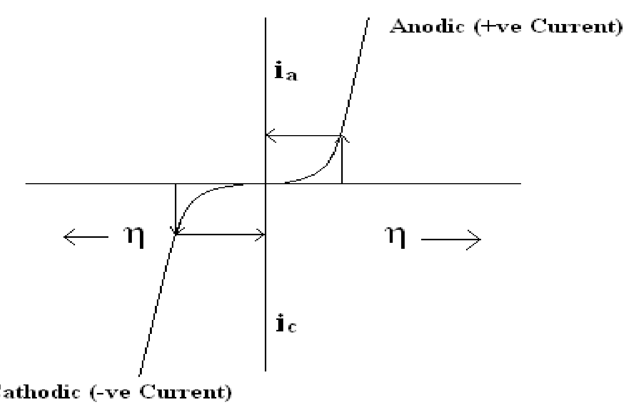
$$i = i_o [e^{(1-\beta)\eta F/RT} - e^{-\beta\eta F/RT}] = i_o [e^{x} - e^{-y}] = i_o \left[1 + \frac{x}{1!} + \frac{x^2}{2!} + \ldots\ldots - \left(1 - \frac{y}{1!} + \frac{y^2}{2!} - \ldots\ldots\right)\right]$$

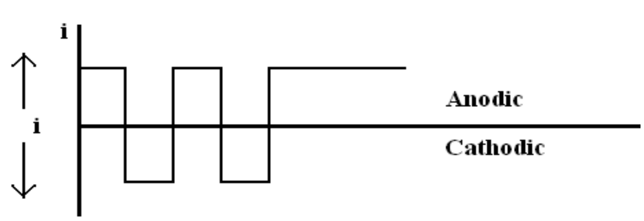
Terms with higher powers of x & y can be neglected

$$i = i_o [x + y] = i_o(\eta F/RT)$$

(i) **Plot of i vs η for β = 0.5**

Consider a definite over potential, η be varied rapidly and periodically as +η or - η. The corresponding period current across the electrode +i or -i will be as given below:





Variation of current for a definite periodic variation of applied potential, η

(The electrode does not act as rectifier)

NOTE:A definite over potential, η variation periodically as +η or - η varies current periodical across the electrode as +i or -i equally like a **cos** function.

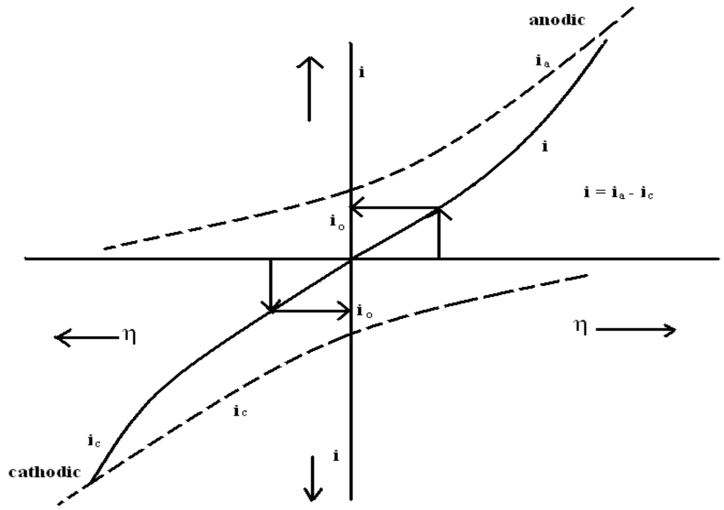
1.

Butler-Volmer plot of **i vs. η (β = 0.5)**

$i = i_o [e^{(1-\beta)\eta F/RT} - e^{-\beta\eta F/RT}]$

$i_a = i_c$

$i_+ = i_-$ for all η



The electrode responses equal current (anodic and cathodic) for a given same over potential when β= **0.5.**

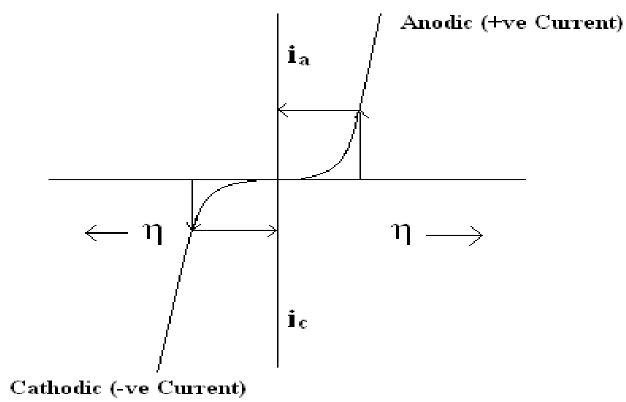
Equal net current (i_+ and i_-) flows on both sides of equal over potential.

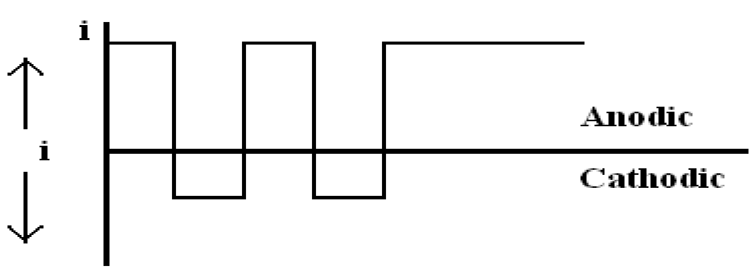
(ii) β < 0.5: Electrode shows greater tendency for anodic process & acts as **ANODIC RECTIFIER**

$i = i_o [e^{(1-\beta)\eta F/RT} - e^{-\beta\eta F/RT}]$

The above equation for β < 0.5 or (1- β) > 0.5 becomes $e^{(1-\beta)\eta F/RT} > e^{-\beta\eta F/RT}$ for a given magnitude of η .

That is $i_a > i_c$





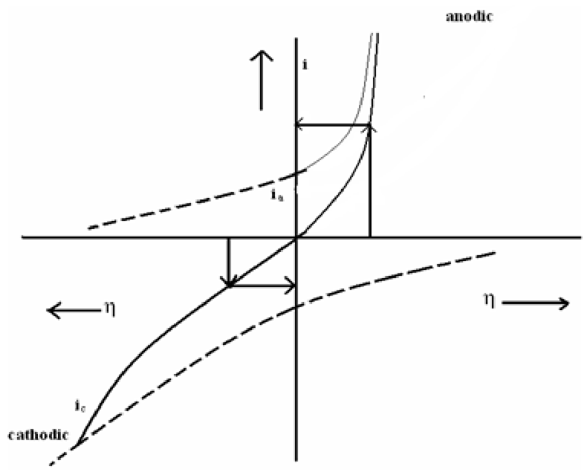
Variation of current for a definite periodic variation of applied potential, η
*(The electrode acts as **anodic rectifier)***

NOTE: Positive over potential across the electrode allows mostly positive current across it provided its $\beta < 0.5$

2.

BUTLER-VOLMER plot of **i vs.** η **(β< 0.5)**; $i_a > i_c$

$i = i_o\,[e^{(1-\beta)\eta F/RT} - e^{-\beta\eta F/RT}]$
$i_a > i_c$ for $\beta < 0.5$
$i_+ > i_-$ for a given η



The electrode responses un equal current (anodic> cathodic) for a given same over potential when $\beta <$ **0.5.** Unequal net current ($i_+ > i_-$) flows on both sides of equal over potential

Note: when $\eta = 0$

i) $i_a = i_c = i_o$

ii) Deviation ($i_a \neq i_c$) occurs only when $\eta > 0$ or < 0

(iii) β > 0.5: Electrode shows greater tendency for cathodic process & acts as **CATHODIC RECTIFIER**.

$$i = i_o\,[e^{(1-\beta)\eta F/RT} - e^{-\beta\eta F/RT}]$$

The above equation for β > 0.5 becomes $e^{(1-\beta)\eta F/RT} < e^{-\beta\eta F/RT}$ for a given magnitude of η. That is $i_a < i_c$

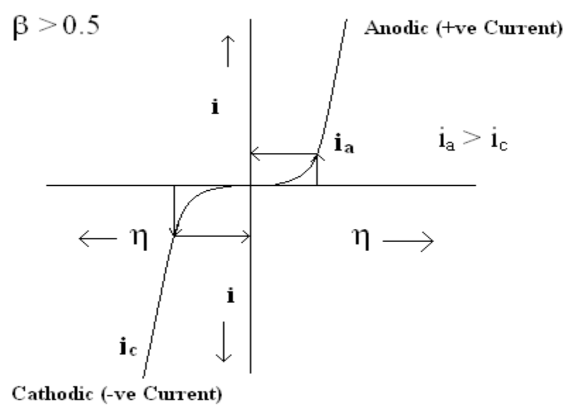
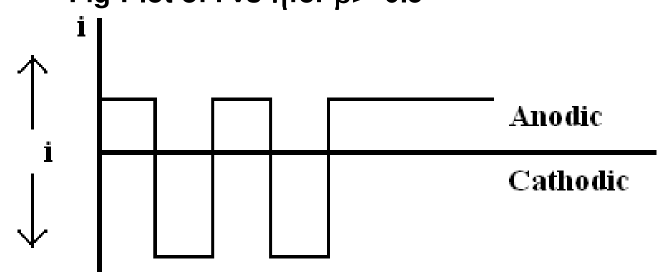


Fig-Plot of i vs η for β> 0.5



Variation of current for a definite periodic variation of applied potential. η (*The electrode acts as cathodic rectifier*)

NOTE: Negative over potential across the electrode allows mostly negative current across it provided its β > 0.5 Hence, the electrode can pass only anodic current or cathodic current depending on the value of β (not equal to 0.5) periodically when connected it to an AC in put. That is it can act as a rectifier if β is n equal to 0.5. The efficiency of the rectification depends on how much the electrode has it's β away fro 0.5.

Butler-Volmer plot of **i vs.** η **(β > 0.5)**; $i_a > i_c$

$i = i_o\,[e^{(1-\beta)\eta F/RT} - e^{-\beta\eta F/RT}]$

$i_a < i_c$ for $\beta > 0.5$

$i_+ < i_-$ & for a given η

The electrode responses unequal current (anodic< cathodic) for a given same over potential when β > **0.5.** Unequal net current ($i_+ < i_-$) flows on both sides of equal over potential.

Note: when $\eta = 0$

i) $i_a = i_c = i_o$

ii) Deviation ($i_a \neq i_c$) occurs only when $\eta \gg 0$ or $\ll 0$