5.5 (a). OXYGEN EVOLUTION

Oxygen is usually evolved on the oxidized metal surface at potentials more positive than its SRP. (SRP =1.23V) , depending on the pH of the medium.

i. $4\ OH^- \longrightarrow 2\ H_2O + O_2 + 4e$ (Alkaline solution-Fe group metals)

ii. $2\ H_2O \longrightarrow 4\ H^+ + O_2 + 4e$ (Acid solution-Pt group metals)

The evolution of O_2 is a complex mechanism and occurs with side reactions.

Some possible mechanisms

Mechanism-I

$$2\ OH^- \longrightarrow 2\ OH + 2\ e^-$$

$$2\ OH + 2\ OH^- \longrightarrow 2\ O^- + 2\ H_2O$$

$$2\ O^- \longrightarrow 2\ O + 2\ e^-$$

$$2\ O \longrightarrow O_2$$

Mechanism-II

$$2\ OH^- \longrightarrow 2\ OH + 2\ e$$

$$2\ OH + 2\ OH^- \longrightarrow 2\ O^- + 2\ H_2O$$

$$2\ O^- + 2\ MO_x \longrightarrow 2\ MO_{x+1} + 2\ e$$

$$2\ MO_{x+1} \longrightarrow O_2 + 2\ MO_x$$

Mechanism-III

$$4\ OH+M \longrightarrow 4\ MOH + 4e^-$$

$$4\ MOH \longrightarrow 2\ MO + 2\ M + 2\ H_2O$$

$$2\ MO \longrightarrow 2\ M + 2\ O_2$$

Mechainsm-IV

$$2\ OH^- \longrightarrow 2\ OH + 2\ e^-$$

$$2\ OH + 2\ OH^- \longrightarrow 2\ H_2O^-_2$$

$$2\ H_2O_2^- \longrightarrow O_2^{2-} + 2\ H_2O$$

$$O^{2-}_2 \longrightarrow O_2 + 2\ e$$

One has to constructs the experimental anodic Tafel plot and compare it with the theoretical values.

Consider mechanism: IV

$$2\,OH^- \xrightarrow{k_1} 2\,OH + 2e^-$$

$$\mathbf{2\,OH + 2\,OH^- \xrightarrow{k_2} 2\,H_2O^-_2}$$

$$2\;H_2O_2^- \longrightarrow O_2^{2-} + 2H_2O$$

$$O^{2-}_2 \longrightarrow O_2 + 2e$$

Consider **, step-2** (non electrochemical) **RDS**

Rate = $\nu_2 = k_2\,[OH^-]^2\;[OH]^2$

This should be eliminated for [OH] and incorporated with current

Therefore,

$$[OH^-] = \frac{\nu_2^{1/2}}{k_2^{1/2}\,[OH]} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..1$$

NOTE: The non-electrochemical rds will also have its effect on the over all currect (rate) of the process.

Considering the preceding electrochemical step (**Step-1**).

$$2OH^- \xrightarrow{k_1} 2OH + 2e^-$$

$$\vec{i} = 2F\,k_1[OH^-]\,e^{(1-\beta)\,\Delta\Phi F/RT} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots2$$

Substituting for $[OH^-]$ in equation-2 as given by the rds step above in equation-1

$$\vec{i} = 2F\,k_1\,\frac{\nu_2^{1/2}}{k_2^{1/2}\,[OH]}\;e^{-\beta\,\Delta\Phi F/RT} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..3$$

$$= (2F)^{1/2}\,k_1\,\frac{\nu_2^{1/2}\,(2F)^{1/2}}{k_2^{1/2}\,[OH]}\;e^{(1-\beta)\,\Delta\Phi F/RT}$$; 2F can be written as $(2F)^{1/2}\,(2F)^{1/2}$

We know that $i = nF\upsilon$

Hence, $\nu_2^{1/2}\,(2F)^{1/2} = i^{1/2}$ for the 2nd step which is same as that for the first etep

5.5(a).Oxygen Evolution

Therefore, equation-3 becomes

$$\vec{i} = (2F)^{1/2} k_1 \frac{\vec{i}^{1/2}}{k_2^{1/2} [OH]} e^{(1-\beta)\Delta\Phi F/RT}$$

$$\vec{i}^{1/2} = (2F)^{1/2} k_1 \frac{1}{k_2^{1/2} [OH]} e^{(1-\beta)\Delta\Phi F/RT}$$

Squaring both sides we get,

$$\vec{i} = (2F)k_1^2 \frac{1}{k_2[OH]^2} e^{2(1-\beta)\Delta\Phi F/RT}$$

$$= \frac{2Fk_1^2 e^{2(1-\beta)\Delta\Phi F/RT}}{k_2[OH]^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots 4$$

$$= i_o e^{2(1-\beta)\eta F/RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 5$$

$$\log \vec{i} = \log i_o + \frac{2(1-\beta)\eta F}{2.303\ RT}$$

$$\frac{2.303\ RT}{2(1-\beta)F} \log \vec{i} = \frac{2.303\ RT}{2(1-\beta)F} \log i_o + \eta$$

$$\text{Slope } \frac{(\partial\eta)}{(\partial \log i)} = 2.303RT / \{2(1-\beta)F\} = b_o$$

NOTE: The species [OH] is an intermediate & must be eliminated to get the order with respect stable species.

HW: *Alternatively step-2 of mechanism-IV could be considered as fast equilibrium*

$$F.2.k_1 e^{(1-\beta)\Delta\Phi F/RT} [OH^-] = F.2.k_{-1} e^{-\beta\Delta\Phi F/RT} [OH]$$

$[OH] = K_2 e^{\Delta\Phi F/RT}[OH^-]$

$$= \frac{2Fk_1^2 e^{2(1-\beta)\Delta\Phi F/RT}}{k_2 K_2^2 e^{2\Delta\Phi F/RT}[OH^-]^2}$$

$$= \frac{2Fk_1^2 e^{-2\beta\Delta\Phi F/RT}}{k_2 K_2^2 [OH^-]^2}$$

$$\mathbf{i = i_o e^{-2\beta\eta F/RT}}$$

Consider Mechanism III, step – 2 as rds

$$4\,OH^- + 4\,M \xrightarrow{k_1} 4\,MOH + 4\,e^-$$

$$\mathbf{4\,MOH \xrightarrow{k_2} 2\,MO + 2\,M + 2\,H_2O}$$

$$2\,MO \longrightarrow 2\,M + O_2$$

$\nu_2 = k_2 (MOH)^4$ …………………………………………..6

and $i = 4 F\nu_2$

$[MOH] = \theta_{MOH} = (\nu_2 / k_2)^{1/4}$ ………………………………..7

For step-1 (fast equilibrium); cathodic rate = anodic rate

$$4\,F\,k_{-1}\theta_{MOH}\, e^{-\beta\Delta\Phi F/RT} = 4\,F\,k_1\,(1-\theta_{MOH})\,[OH^-]\,e^{(1-\beta)\Delta\Phi F/RT}$$

Hence, for $\theta_{MOH} << 1$, we get

$\theta_{MOH} = MOH = K_1[OH^-]e^{\Delta\Phi F/RT}$ ……..……………………..8

Hence,

$$\theta_{MOH} = K_1 (\nu_2 / k_2)^{1/4} e^{\Delta\Phi F/RT}$$

Substituting $\theta_{MOH,}$ anodic current is given as,

$$i = 4F k_{-1} k_1 [(i/4F) / k_2]^{1/4} e^{(1-\beta)\Delta\Phi F/RT}$$

$$i^{3/4} = \frac{(4F)^{3/4} k_{-1} k_1 e^{(1-\beta)\Delta\Phi F/RT}}{(k_2)^{1/4}}$$

$$i = \frac{(4F k_{-1} k_1)^{4/3} e^{4/3 (1-\beta)\Delta\Phi F/RT}}{(k_2)^{1/4}}$$

$$\log i = \log i_o + \frac{4(1-\beta)\eta F}{3(2.303 RT)}$$

NOTE: The type of mechanism & rds depends on the nature of the electrode used.