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APPENDIX

A1: Exchange current density

A limiting current density can be calculated for each reactant species which provides the net current from the forward and reverse currents.

Forward current:

$$j_1 = j_0 e^{\alpha nF\eta/(RT)}$$

Reverse current:

$$j_2 = j_0 e^{-(1-\alpha)nF\eta/(RT)}$$

Net current $j = j_1 - j_2$:

$$\therefore j = j_0(e^{\alpha nF\eta/(RT)} - e^{-(1-\alpha)nF\eta/(RT)})$$

The net current is considered on a concentration gradient at the double layer.

$$j = j_0(\frac{C_R^*}{C_R^{0*}} e^{\alpha nF\eta/(RT)} - \frac{C_P^*}{C_P^{0*}} e^{-(1-\alpha)nF\eta/(RT)}) \qquad (1)$$

Give:

$j = i$ = Current

$j_0 = i_0$ = Exchange current

$C_R^* = C_O$ and $C_P^* = C_R$ = The actual surface concentration of the rate-limiting species in the reaction

$C_R^{0*} = C_O^*$ and $C_P^{0*} = C_R^*$ = The reference concentration value

α = Transfer coefficient

$\eta = E - E_{eq}$ = Over potential

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

Then Eq. (1) becomes:

$$i = i_0(\frac{C_O}{C_O^*} e^{\alpha f\eta} - \frac{C_R}{C_R^*} e^{-(1-\alpha)f\eta}) \qquad (2)$$

From the rate of mass transfer (proportional to concentration gradient at electrode surface):

$$r_{mt} = k_g[C_O - C_O^*]$$

Where k_g = Mass transfer coefficient

When the mass transfer controls an electrode reaction:

$$r_{mt} = \frac{i}{nFA}$$

Therefore:

$$\frac{i}{nFA} = k_g[C_O - C_O^*]$$

At the limiting current, the largest rate of mass transfer of R occurs when $C_O = 0$ and anode limiting current = $i_{l,a}$

$$\frac{i_{l,a}}{nFA} = k_g[0 - C_O^*]$$

$$\therefore\ C_O^* = -\frac{i_{l,a}}{nFAk_g} \qquad (3)$$

And from:

$$\frac{i}{nFAk_g} = C_O - C_O^*$$

$$\frac{i}{nFAk_g} + C_O^* = C_O$$

$$\frac{i}{nFAk_g} + (-\frac{i_{l,a}}{nFAk_g}) = C_O$$

$$\therefore\ C_O = \frac{i - i_{l,a}}{nFAk_g} \qquad (4)$$

Determine the value of $\frac{C_O}{C_O^*}$; thus, from this can be obtained the following relation:

$$\frac{C_O}{C_O^*} = 1 - \frac{i}{i_{l,a}}$$

At high over-potential, the cathodic current becomes insignificant. From Equation (2), the term of $\frac{C_R}{C_R^*} e^{-(1-\alpha)f\eta}$ can be negligible, then:

$$i = i_0(\frac{C_O}{C_O^*} e^{\alpha f\eta})$$

$$i = i_0((1 - \frac{i}{i_{l,a}})e^{\alpha f\eta})$$

Then the over-potential is calculated:

$$\eta = \frac{1}{\alpha f} ln\frac{1}{i_0} + \frac{1}{\alpha f} ln\frac{i i_{l,a}}{i_{l,a} - i} \qquad (5)$$

This Equation (5) can be simplified to Tafel plot as linear equation ($Y = c + mX$)

Give:

$$c = \frac{1}{\alpha f} ln\frac{1}{i_0}$$

$$m = \frac{1}{\alpha f}$$

There the exchange current density (i_0) can be calculated when $X = 0$ or $Y = c$

$$\eta_{x=0} = \frac{1}{\alpha f} ln\frac{1}{i_0} = m ln\frac{1}{i_0}$$

$$\therefore\ i_0 = \frac{1}{e^{(\eta_{x=0}/m)}}$$

A2: Reversible cell voltage

(1) Reversible cell voltage at an arbitrary temperature T (at constant pressure):

$$E_T = E^0 + \frac{\Delta \hat{s}}{nF}(T - T_0) \quad (1)$$

(2) Reversible cell voltage varies with temperature, pressure and activity:

$$E_T = E^0 + \frac{\Delta \hat{s}}{nF}(T - T_0) - \frac{RT}{nF} ln \frac{\prod a_{products}^{v_i}}{\prod a_{reactants}^{v_i}} \quad (2)$$

In terms of activities, this can be considered from the reaction of methanol in fuel cell: $CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O$ and then simplified to aA + bB → cC + dD

$$\frac{RT}{nF} ln \frac{\prod a_{products}^{v_i}}{\prod a_{reactants}^{v_i}} = \frac{RT}{nF} ln \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

Where $a = \frac{P}{P_0}$:

$$= \frac{RT}{nF} \ln \frac{\left(\frac{P_{CO_2}}{P_0}\right)\left(\frac{P_{H_2O}}{P_0}\right)^2}{\left(\frac{P_{CH_3OH}}{P_0}\right)\left(\frac{P_{O_2}}{P_0}\right)^{3/2}}$$

$$= \frac{RT}{nF}\left(\ln \frac{(P_{CO_2})(P_{H_2O})^2}{(P_{CH_3OH})(P_{O_2})^{3/2}} + ln \frac{1}{(P_0)^{1/2}}\right)$$

Where:

$$P_{CH_3OH} = \alpha P$$

$$P_{O_2} = \beta P$$

$$P_{CO_2} = \varepsilon P$$

$$P_{H_2O} = \delta P$$

$$= \frac{RT}{nF}\left(\ln \frac{(\varepsilon P)(\delta P)^2}{(\alpha P)(\beta P)^{3/2}} + ln \frac{1}{(P_0)^{1/2}}\right)$$

$$= \frac{RT}{nF}\left(\ln \frac{(\varepsilon)(\delta)^2}{(\alpha)(\beta)^{3/2}} + ln \frac{(P)^{1/2}}{(P_0)^{1/2}}\right) \quad (3)$$

The fraction of partial pressure as $\alpha, \beta, \varepsilon and\ \delta$ can be calculated from the reactance and product of a direct methanol fuel cell.

At the anode:

$CH_3OH + H_2O \rightarrow CO_2 + 6H_2$

From Raoult's law:

$$yP = xP^{sat}$$

Then:

$$y_{MeOH}P = x_{MeOH}P^{sat} \qquad (4)$$

$$y_{H_2O}P = x_{H_2O}P^{sat} \qquad (5)$$

$$x_{MeOH} + x_{H_2O} = 1 \qquad (6)$$

$$y_{MeOH} + y_{H_2O} = 1 \qquad (7)$$

Consider x_{H_2O} at cell temperature of 70°C with the following equation:

$$h_{fg} = h_f + xh_g \qquad (8)$$

From the stream table

$h_{f@70°C}$ =293.0 kJ kg^{-1}

$h_{g@70°C}$ =2626.0 kJ kg^{-1}

$h_{fg@70°C}$ =2334.0 kJ kg^{-1}

To obtain these values in Eq. (8):

$$2334.0 = 293.0 + x(2626.0)$$

$$\therefore x = 0.77 = x_{H_2O}$$

From Eq. (5), give $P_{H_2O}^{sat\ @70°C}$ = 31.16 kPa and P =100 kPa = P_{system}

Then:

$$y_{H_2O} = 0.23$$

$$= y_{H_2O@\ anode} = y_{H_2O@\ cathode}$$

So, the partial pressure of H_2O given by y_{H_2O} is then:

$$P_{H_2O} = 0.23P$$

$$\therefore \delta = 0.23$$

Obtaining y_{H_2O} from Eq. (7), then:

$$y_{MeOH} = 1 - 0.23 = 0.77$$

So, the partial pressure of MeOH given by y_{MeOH} is then:

$$P_{MeOH} = 0.77P$$

$$\therefore \alpha = 0.77$$

For the partial pressure of CO_2, this can be evaluated under a gas phase condition (CO_2 + $6H_2$):

$$P_{CO_2} = \frac{1}{1+6}P$$

$$= 0.14P$$

$$\therefore \varepsilon = 0.14$$

<u>At the cathode</u>:

$$3/2O_2 + 6H_2 \rightarrow 3H_2O$$

Partial pressure of O_2:

$$P_{O_2} = \frac{\frac{3}{2}}{\frac{3}{2}+6}P$$

$$= 0.2P$$

For air, the partial pressure of O_2 becomes:

$$P_{O_2} = (0.21)0.2P$$

$$= 0.042P$$

$$\therefore \beta = 0.042$$

Therefore, the term of activities is evaluated for each partial pressure of reactance and product, and Eq. (3) becomes:

For MeOH-Air operated at 70°C:

$$\frac{RT}{nF} ln \frac{\prod a_{products}^{v_i}}{\prod a_{reactants}^{v_i}} = \frac{RT}{nF}\left(\ln \frac{(0.14)(0.23)^2}{(0.77)(0.042)^{3/2}} + ln \frac{(P)^{1/2}}{(P_0)^{1/2}}\right)$$

For the reversible cell voltage varies with temperature, pressure and activity, Eq. (2) becomes:

$$E_T = E^0 + \frac{\Delta \hat{s}}{nF}(T - T_0) - \frac{RT}{nF}\left(\ln \frac{(0.14)(0.23)^2}{(0.77)(0.042)^{3/2}} + ln \frac{(P)^{1/2}}{(P_0)^{1/2}}\right)$$

A3: Fuel consumption

This calculation is used to check for sufficient concentration of re-circulated fuel of 1M methanol within 24 h. First, amount of charge is evaluated from the integration area under the curve of I-t plot.

The charge can be determined from:

$$I = \frac{Q}{t}$$

$$\therefore Q = It \qquad (1)$$

And then, the mole of fuel can be evaluated from:

$$mole\ of\ fuel = \frac{amount\ of\ charge}{nF} \qquad (2)$$

For an example:

The methanol-air system used the re-circulated fuel of 1 M MeOH for 24 h. At the period time of 0 – 24 h, amount of charge was calculated from the area under the I-t curve. The mode of LR-100 and SCO provided the electricity charge of 31,551.33 and 18,766.53 coulombs, respectively. The mole of fuel requirement was evaluated by Eq. (2) and give n = 4 (partial oxidation of methanol).

Then

$$mole\ of\ fuel_{LR-100} = \frac{31{,}551.33}{4(96485)}$$
$$= 0.0817\ mole\ per\ 24\ h$$

and

$$mole\ of\ fuel_{SCO} = \frac{18{,}766.53}{4(96485)}$$
$$= 0.0486\ mole\ per\ 24\ h$$

Therefore, 1 molar of methanol re-circulation was enough for this experiment of methanol-air system within 24 h.