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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:

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

Reverse current:

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

Net current $j = j_1 - j_2$:

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

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

$$j = j_0 \left(\frac{C_R^*}{C_R^{0*}} e^{\alpha n F \eta / (RT)} - \frac{C_P^*}{C_P^{0*}} e^{-(1-\alpha) n F \eta / (RT)} \right) \quad (1)$$

Give:

$$j = i = \text{Current}$$

$$j_0 = i_0 = \text{Exchange current}$$

$C_R^* = C_O$ 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:

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

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 = $i_{l,a}$

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

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

And from:

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

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

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

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

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:

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

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

Then the over-potential is calculated:

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

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:

$\text{CH}_3\text{OH} + 3/2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ and then simplified to $aA + bB \rightarrow cC + dD$

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

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

$$\begin{aligned} &= \frac{RT}{nF} \ln \frac{\left(\frac{P_{\text{CO}_2}}{P_0}\right) \left(\frac{P_{\text{H}_2\text{O}}}{P_0}\right)^2}{\left(\frac{P_{\text{CH}_3\text{OH}}}{P_0}\right) \left(\frac{P_{\text{O}_2}}{P_0}\right)^{3/2}} \\ &= \frac{RT}{nF} \left(\ln \frac{(P_{\text{CO}_2})(P_{\text{H}_2\text{O}})^2}{(P_{\text{CH}_3\text{OH}})(P_{\text{O}_2})^{3/2}} + \ln \frac{1}{(P_0)^{1/2}} \right) \end{aligned}$$

Where:

$$P_{\text{CH}_3\text{OH}} = \alpha P$$

$$P_{\text{O}_2} = \beta P$$

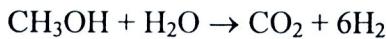
$$P_{\text{CO}_2} = \varepsilon P$$

$$P_{\text{H}_2\text{O}} = \delta P$$

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

The fraction of partial pressure as α , β , ε and δ can be calculated from the reactance and product of a direct methanol fuel cell.

At the anode:



From Raoult's law:

$$yP = xP^{sat}$$

Then:

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

$$y_{\text{H}_2\text{O}}P = x_{\text{H}_2\text{O}}P^{sat} \quad (5)$$

$$x_{\text{MeOH}} + x_{\text{H}_2\text{O}} = 1 \quad (6)$$

$$y_{\text{MeOH}} + y_{\text{H}_2\text{O}} = 1 \quad (7)$$

Consider $x_{\text{H}_2\text{O}}$ at cell temperature of 70°C with the following equation:

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

From the stream table

$$h_f@70^\circ\text{C} = 293.0 \text{ kJ kg}^{-1}$$

$$h_g@70^\circ\text{C} = 2626.0 \text{ kJ kg}^{-1}$$

$$h_{fg}@70^\circ\text{C} = 2334.0 \text{ kJ kg}^{-1}$$

To obtain these values in Eq. (8):

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

$$\therefore x = 0.77 = x_{\text{H}_2\text{O}}$$

From Eq. (5), give $P_{\text{H}_2\text{O}}^{sat}@70^\circ\text{C} = 31.16 \text{ kPa}$ and $P = 100 \text{ kPa} = P_{\text{system}}$

Then:

$$y_{\text{H}_2\text{O}} = 0.23$$

$$= y_{\text{H}_2\text{O}@ \text{anode}} = y_{\text{H}_2\text{O}@ \text{cathode}}$$

So, the partial pressure of H₂O 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:

$$P_{MeOH} = 0.77P$$

$$\therefore \alpha = 0.77$$

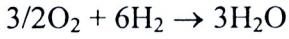
For the partial pressure of CO₂, this can be evaluated under a gas phase condition (CO₂ + 6H₂):

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

$$= 0.14P$$

$$\therefore \varepsilon = 0.14$$

At the cathode:



Partial pressure of O₂:

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

$$= 0.2P$$

For air, the partial pressure of O₂ 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 reactant 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:

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

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



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

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

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

$$\text{mole of fuel}_{LR-100} = \frac{31,551.33}{4(96485)}$$

$$= 0.0817 \text{ mole per 24 h}$$

and

$$\text{mole of fuel}_{SCO} = \frac{18,766.53}{4(96485)}$$

$$= 0.0486 \text{ mole per 24 h}$$

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

