HW # 3
MENG 7891

For direct methane oxidation in an SOFC at the anode the net reaction is —

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

At the anode, $CH_4 + 2H_2O \rightarrow CO_2 + 8H^+ + 8e^-$

cathode, $O_2 + 4e^- \longrightarrow 2O^{2-}$

Thus 1 mole of CH_4 reacts with 2 moles of $O_2 \rightarrow 8$ electrons transferred.

Given, operating temperature, $T = 700^\circ C = 973\ K$

Gas pressure, $P = 1\ atm = 101325\ Pa$

Gas constant, $R = 8.314\ J/mole \cdot K$

Faraday's constant, $F = 96485\ C/mol$.

Charge transfer coefficient, $\alpha = 0.5$

Effective diffusivity of O_2, $D_e^{eff} = 3.66 \times 10^{-7}\ m^2/s$

Ohmic potential, $\eta_{ohmic} = j \cdot R_{ohmic} = 10^4 \times 0.1\ \Omega \cdot cm^2$

$= 10^4 \times 1 \times 10^{-5}\ \Omega \cdot m^2$

$= 0.1\ V$

Total molar concentration from ideal gas law —

$$C_{total} = \frac{P}{RT} = \frac{101325}{8.314 \times 973} = 12.53\ mol/m^3$$

From volume fractions,

O_2 (18%), $C_{O_2} = 0.18 \times 12.53 = 2.26\ mol/m^3$

CH_4 (60%), $C_{CH_4} = 0.60 \times 12.53 = 7.52\ mol/m^3$

Exchange current density, at cahode,

$$I_0^c = 3.8 \times 10^6 \exp\left(-\frac{8170}{T}\right) \times C_{O_2}$$

$$= 3.8 \times 10^6 \exp\left(-\frac{8170}{273}\right) \times 2.26$$

$$= 3117.86 \ A/m^2$$

At anode, $I_0^a = 1.3 \times 10^6 \exp\left(-\frac{8427}{T}\right) \times C_{CH_4}$

$$= 1.3 \times 10^6 \exp\left(-\frac{8427}{273}\right) \times 7.52$$

$$= 38768.34 \ A/m^2$$

concentration over potential,

$$\eta_{conc} = -\frac{RT}{nF} \ln\left(\frac{C_s}{C_b}\right)$$

C_b = bulk concentration

C_s = surface concentration

$$C_s = C_b - \frac{j \cdot \delta}{nFD}$$

At $j = 1.0 \ A/cm^2 = 10^4 \ A/m^2$, diffusion layer thickness at cathode/electrolyte interface, $\delta = 10 \ \mu m = 10 \times 10^{-6} \ m$

Cathode: $C_{s,O_2} = 2.26 - \frac{10^4 \times 10 \times 10^{-6}}{8 \times 96485 \times 3.66 \times 10^{-7}} = 2.20$

$$\eta_{c,conc} = -\frac{8.314 \times 973}{8 \times 96485} \ln\left(\frac{2.20}{2.26}\right) = 0.00179 V$$

Anode: $C_{s,CH_4} = 7.52 - \frac{10^4 \times 200 \times 10^{-6}}{8 \times 96485 \times 9.66 \times 10^{-7}} = 7.30$

$[D_a^{eff} = 9.66 \times 10^{-7}]$

$$\eta_{a,conc} = -0.00463 \ V$$

Activation overpotential, $\eta_{act} = \frac{RT}{\alpha n F} \sinh^{-1}\left(\frac{j}{2i_o}\right)$

At $j = 10^4 \, A/m^2$,

Cathode: $\eta_{c,act} = \frac{8.314 \times 973}{0.5 \times 8 \times 96485} \sinh^{-1}\left(\frac{10^4}{2 \times 3117.86}\right)$

$= 0.03518 \, V$

Anode: $\eta_{a,act} = \frac{8.314 \times 973}{0.5 \times 8 \times 96485} \sinh^{-1}\left(\frac{10^4}{2 \times 38768.34}\right)$

$= 0.00610 \, V$

Total overpotential $= \eta_{c,act} + \eta_{ohmic} + \eta_{c,conc} + \eta_{a,conc} + \eta_{a,ac}$

$\eta_{total} = 0.03518 + 0.1 + 0.00179 + 0.00463 + 0.00610$

$\boxed{\eta_{total} = 0.1477 \, V}$

Assume open-circuit voltage, $E_o = 1.1 \, V$

$V_{operating} = E_o - \eta_{total}$

$= (1.1 - 0.1477) V$

$\boxed{V_{ope} = 0.9523 \, V}$

Concentration over potential at $j = 2.5\ A/cm^2$

$= 2.5 \times 10^4\ A/m^2$

Cathode: $c_{s,O_2} = 2.26 - \frac{2.5\times10^4 \times 10 \times 10^{-6}}{8 \times 96485 \times 3.66\times10^{-7}}$

$= 2.18\ mol/m^3$

$\eta_{c,conc} = -\frac{RT}{nF}\ln\left(\frac{2.18}{2.26}\right) = 0.00523\ V$

Anode: $c_{s,CH_4} = 7.52 - \frac{2.5\times10^4 \times 200\times10^{-6}}{8\times96485\times9.66\times10^{-7}}$

$= 6.97\ mol/m^3$

$\eta_{a,conc} = -\frac{RT}{nF}\ln\left(\frac{6.97}{7.52}\right) = 0.02337\ V$

Activation overpotentials, at $j = 2.5\ A/cm^2$

Cathode: $\eta_{c,act} = \frac{RT}{\alpha nF}\sinh^{-1}\left(\frac{j}{2i_{0,c}}\right)$

$= \frac{8.314\times273}{0.5\times8\times96485}\sinh^{-1}\left(\frac{2.5\times10^4}{2\times3117.86}\right)$

$= 0.05377\ V$

Anode: $\eta_{a,act} = \frac{RT}{\alpha nF}\sinh^{-1}\left(\frac{2.5\times10^4}{2\times38768.34}\right)$

$= 0.01432\ V$

Ohmic overpotential $= j.R_{ohmic} = 2.5\times10^4 \times 1\times10^{-5}$

$= 0.25\ V$

Total Overpotential, $\eta_{total} = 0.00523 + 0.02337 + 0.05377 + 0.01432 + 0.25$

$$\eta_{total} = 0.3467\ V$$

Operating voltage, $V_{operating} = E_o - \eta_{total}$

$= (1.1 - 0.3467)\ V$

$$V_{operating} = 0.7533\ V$$

→ The operating voltage drops from 0.95 V to 0.75 V as current density increases.

→ Ohmic loss is the dominant loss at higher current density.