Problem 5.4 (25 points) To find the limiting current density, we need to calculate the diffusion constant and the bulk concentration of oxygen. First, the diffusion constant is

$$D^{eff}_{O_2 N_2} = \epsilon^{1.5}\frac{a}{p}\left(\frac{T}{\sqrt{T_{c,O_2}T_{c,N_2}}}\right)^b (p_{c,O_2}p_{c,N_2})^{1/3}(T_{c,O_2}T_{c,N_2})^{5/12}\left(\frac{1}{M_{N_2}}+\frac{1}{M_{O_2}}\right)^{0.5} \tag{110}$$

The relevant properties are $a = 2.745\times10^{-4}, b = 1.823, T_{c,O_2} = 154.4\,K, T_{c,N_2} = 126.2\,K, p_{c,O_2} = 49.7\,atm, p_{c,N_2} = 33.5\,atm, M_{O_2} = 32, M_{N_2} = 28$. Plugging in,

$$D^{eff}_{O_2 N_2} = 0.4^{1.5}\frac{2.745\times10^{-4}}{1\,atm}\left(\frac{298\,K}{\sqrt{(154.4\,K)(126.2\,K)}}\right)^{1.823}$$

$$* ((49.7\,atm)(33.5\,atm))^{1/3}((154.4\,K)(126.2\,K))^{5/12}\left(\frac{1}{28}+\frac{1}{32}\right)^{0.5}$$

So $D^{eff} = 0.0520\,cm^2/s$. Finding the bulk concentration of oxygen is easier. Neglecting the consumption of oxygen as air travels down the flow path, we can say that the concentration of oxygen in air is 21%. From the ideal gas law, we find the concentration in bulk is $c^o_R = 0.21 * \frac{N}{V} = 0.21 * \frac{P}{RT} = 0.21 * \frac{1\,atm}{(0.08205\,L\cdot atm/mol\cdot K)(298\,K)} = 8.59\cdot10^{-3}\,mol/L = 8.59\cdot10^{-6}\,mol/cm^3$.

Note that $n = 4$ because the species we are considering is oxygen, which transfers 4 electrons per mole. Finally, the limiting current density is

$$j_L = (4*96485\,C/mol)(0.0520\,cm^2/s)\frac{8.59\cdot10^{-6}\,mol/cm^3}{500\cdot10^{-4}\,cm} \tag{111}$$

$$\boxed{j_L = 3.44\,A/cm^2}$$

Problem 5.10 Mass concentration effects become important at high current density, so we will use the Tafel approximation to the Butler Volmer equation

$$j = j^0_0\frac{c^*_R}{c^{0*}_R}e^{\alpha m F\eta/RT} \tag{135}$$

If we assume that voltage, and therefore overpotential is constant along the flow channel, the only part that varies in x is the concentration of oxygen. Via a control volume analysis, you can find that the ODE governing concentration along the flow channel is

$$\frac{dc(x)}{dx} = -\frac{j^0_0 e^{\alpha m F\eta/RT}}{c^{0*}_R}c(x) \tag{136}$$

That is, the amount of oxygen flowing into the catalyst layer from the flow channel is proportional to the concentration in the flow channel. The solution is a decaying exponential

$$c(x) = Ae^{-ax} \tag{137}$$

where

$$a = \frac{j^0_0 e^{\alpha m F\eta/RT}}{c^{0*}_R} \tag{138}$$

Applying the boundary condition at the inlet gives the constant A

$$c(0) = c_{in} = A \tag{139}$$

Plugging this into equation 5.62, we get

$$\rho_{O_2}|_{x=X,y=C} = \rho_{\bar{O}_2}|_{x=0,y=channel} - \frac{M_{O_2}}{4F}\left(\frac{j(X)}{h_m}+\frac{H_E j(X)}{D^{eff}_{O_2}}+\frac{a}{u_{in}H_C}\int_0^X c^*_{O_2}(x)dx\right) \tag{140}$$

$$= \rho_{\bar{O}_2}|_{x=0,y=channel} - \frac{M_{O_2}}{4F}\left(\frac{j(X)}{h_m}+\frac{H_E j(X)}{D^{eff}_{O_2}}+\frac{a}{u_{in}H_C}\int_0^X c_{in}e^{-ax}dx\right) \tag{141}$$

$$= \rho_{\bar{O}_2}|_{x=0,y=channel} - \frac{M_{O_2}}{4F}\left(\frac{j(X)}{h_m}+\frac{H_E j(X)}{D^{eff}_{O_2}}+\frac{ac_{in}}{u_{in}H_C}(-\frac{e^{-ax}}{a}|_0^X)\right) \tag{142}$$

$$= \rho_{\bar{O}_2}|_{x=0,y=channel} - \frac{M_{O_2}}{4F}\left(\frac{j(X)}{h_m}+\frac{H_E j(X)}{D^{eff}_{O_2}}+\frac{c_{in}}{u_{in}H_C}(1-e^{-aX})\right) \tag{143}$$

$$= \rho_{\bar{O}_2}|_{x=0,y=channel}[1-\frac{M_{O_2}}{4Fu_{in}H_C}(1-e^{-aX})] - \frac{M_{O_2}}{4F}\left(\frac{j(X)}{h_m}+\frac{H_E j(X)}{D^{eff}_{O_2}}\right) \tag{144}$$

This says that the oxygen falloff in the channel is exponential rather than linear. The falloff is faster for larger overpotential or higher exchange current (faster kinetics meaning faster use of reactant).