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Undergraduate Project Report

Modelling and Simulation of Electrochemical Systems

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Background

Simulation in electrochemistry is a tool used to predict, evaluate or optimise the performance of the proposed system under study. It runs over a specific input to generate a model, and the model then generates the output. A comparison between the generated output to the actual performance gives the analysis for simulations. Simulations help designers and engineers understand how a part could fail, the loads it can withstand and avoid frequent usage of physical prototypes to analyse designs for new and existing parts. Electrochemical simulations frequently involve phenomena related to transport and reactions close to the electrode.

Numerical techniques are commonly involved because we cannot solve the mathematical model in a closed-form in many cases. The method of finite-difference based on differential equations is one of the most commonly applied approaches for numerical simulation.

Furthermore, the need to produce organic products with net carbon neutrality paved the path to use electrochemical reactions to substitute traditional natural fuel requirements. Optimised theoretical and practical solutions let us implement these technologies, which give us a net negative carbon emission.

We discuss some of these models in the following report.

Contents

Introduction

As the world continues to transition toward carbon emissions-free energy technologies, there remains a need to reduce the carbon emissions of the chemical production industry. Electrochemical conversion of carbon dioxide (CO_2) into chemical feedstocks offers a way to turn waste emissions into valuable products, closing the carbon loop. When coupled to renewable sources of electricity, these products can be made with a net negative carbon emissions footprint, helping to sequester CO_2 into usable goods. Many catalytic reactions for various organic products implement zero or even negative carbon emissions. A comparison between the production cost and carbon emissions across different catalytic processes can be seen in Table 1[1].

Product	Technology	Production Cost ($/tonne)	Carbon Emission (tonne CO_2 emitted/tonne produced)
Ethylene	Electrocatalytic	1100	-0.01
	Biocatalytic	1200-2600	2.5
	Fossil fuel–derived	600-1300	6
Carbon Monoxide	Electrocatalytic	200	-0.85
	Biocatalytic	-	-
	Fossil fuel–derived	150	0.05
Ethanol	Electrocatalytic	515	-1.00
	Biocatalytic	670	2.1
	Fossil fuel–derived	-	-
Formic Acid	Electrocatalytic	108	-1.63

|	Biocatalytic	-	-
	Fossil fuel–derived	570	0.01

In this project, we focus on one such method of CO_2 reduction, i.e., copper membrane electrode assembly (Cu-MEA) for CO_2 removal. Since we are new to the subject, we carve our path through some basic models and simulations in Electrochemistry. We programmed a discrete state-space model in 1D for numerical simulation of coupled differential equations involving mass transport and charge-transfer kinetics. We then go about the Nernst and Butler–Volmer equation and then solve two fundamental but principal problems using MATLAB simulations. These are copper electrowinning and fuel cell simulations. We aim to predict the voltammetry curves of the systems. We later delve much deeper to find some complex research on these simulations.

Discrete State Space Model

Here we use the **finite difference method** to discretise coupled differential equations that govern mass transport and chemical reactions.[2]

Discrete Model

We consider a 1-dimensional model featuring a sequence of volume elements extending away from the interface. Then take the electrode surface in the centre of each box (the volume element). We take each box j to characterise the solution at a distance (j-1)Δx from the interface. Here Δx is the length of each box. The concentration of species A in box j is C$_A$(j). The time for simulation is broken into time steps Δt. Therefore time t for simulation is k·Δt, where k is the number of iterations. Figure 1 explains the model.
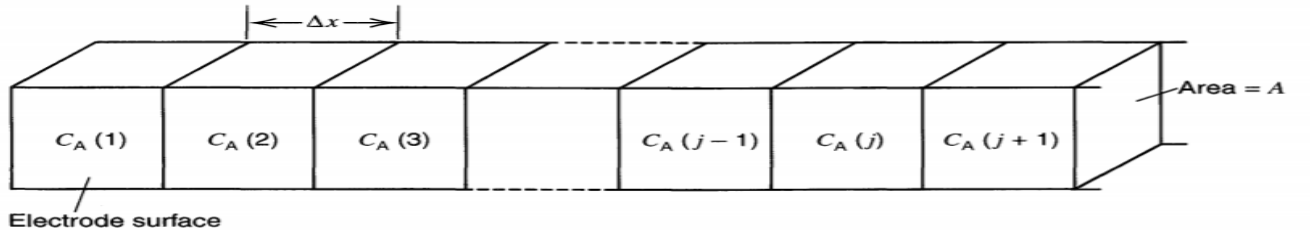
Governing equations and discretisation

Fick's Laws of Diffusion can be discretized to obtain the following equation,

$$C(k + 1, j) = C(k, j) + \frac{D\Delta t}{\Delta x^2}[C(k, j + 1) - 2C(k, j) + C(k, j - 1)]$$

Thus, we obtain a new concentration C(j,k+1) using concentration from the previous iteration k. Here D is the diffusion coefficient.

We assume that the value of the diffusion coefficient for both the oxidised species and the reduced species is the same for simplicity.

Boundary Conditions:

We implement two different boundary conditions:

- *CASE I*: Initially the solution is uniform; hence every box has a concentration $C_O(1,j) = C$ and R is initially absent $C_R(1,j) = 0$. The step magnitude is large enough that the surface concentration of O is zero at all times, i.e., $C_O(k,1) = 0$ $\forall$ k.

  We calculate the current density by the flux of the electroactive species between boxes 1 and 2 :

  $$i(k) = \frac{FDC_O(k-1,2)}{\Delta x}$$

  D   → Diffusion Coefficient

  Δx   → size of the box

- *CASE II*: In this model, the charge-transfer kinetics follow the **Butler-Volmer equation**. The surface concentrations of O and R ultimately control the measured current.

  $$i(k) = FAk^0[C_O(k-1,1)\,exp(-\tfrac{\alpha nF}{RT}(E - E^0)) - C_R(k-1,1)exp(-\tfrac{(1-\alpha)nF}{RT}(E - E^0))]$$

  α → transfer coefficient

  $E-E^0$ → overpotential

  F → Faraday's Constant

  n → electrons transferred

  O → species oxidised

  R → species reduced

  k^0 → standard electrochemical rate constant

  T → temperature

The thickness of Diffusion Layer

In doing these calculations, one needs to know the number of boxes for the simulation. Any experiment that has proceeded for time t will alter the solution from its bulk character for a distance no larger than about $6(Dt)^{1/2}$. Thus,

$$j_{max} = 6(Dt)^{1/2}/\Delta x + 1$$

MATLAB Codes: Case I

```matlab
%clear, clc, close all
%% INDEPENDENT VARIABLES %%
C      = 1.0;            % [=] mol/L, initial concentration of O
D      = 1E-5;          % [=] cm^2/s, O & R diffusion coefficient
n      = 1.0;           % [=] number of electrons transferred


%% SIMULATION VARIABLES %%
L      = 500;           % [=] number of iterations per t_k
DM     = 0.45;          % [=] model diffusion coefficient


%% DERIVED CONSTANTS %%
tk  = 800 ;             % [=] s, simulation time
Dt  = tk/L;             % [=] s, delta time
Dx  = sqrt(D*Dt/DM);    % [=] cm, delta x
j   = ceil(4.2*L^0.5)+5;  % number of boxes . If L~200, j=65


%% PRE-INITIALIZATION %%
C = C / 1000;           % Convert C from mol/L to mol/cm3
k = 0:L;                % time index vector
t = Dt * k;             % time vector


O = ones(L+1,j);        % [=] mol/cm^3, concentration of O
R = zeros(L+1,j);       % [=] mol/cm^3, concentration of R
Z = zeros(1,L+1);       % [=] mol/cm^2-s, dimensionless current density


%% START SIMULATION %%
```

```matlab
% i1 = time index. i2 = distance index
for i1 = 1:L
    % Update bulk concentrations of O and R
    for i2 = 2:j-1
        O(i1+1,i2) = O(i1,i2) + DM*(O(i1,i2+1)+O(i1,i2-1)-2*O(i1,i2));
        R(i1+1,i2) = R(i1,i2) + DM*(R(i1,i2+1)+R(i1,i2-1)-2*R(i1,i2));
    end

    O(i1+1,1) = O(i1,1) + DM*(O(i1,2)-O(i1,1));
    R(i1+1,1) = R(i1,1) + DM*(R(i1,2)-R(i1,1));
    Z(i1+1)   = sqrt(L/DM)*O(i1+1,1) ;
    R(i1+1,1) = R(i1+1,1) + O(i1+1,1) ;
    O(i1+1,1) = 0 ;

end

% Calculate current density, Z, from flux of O
i = n*F*sqrt(D)*C*Z ;
plot(i,"LineWidth", 2 , "color" , 'g');
grid on;
xlabel('time (in s)'), ylabel('Current Density (mA/cm^2)')
```
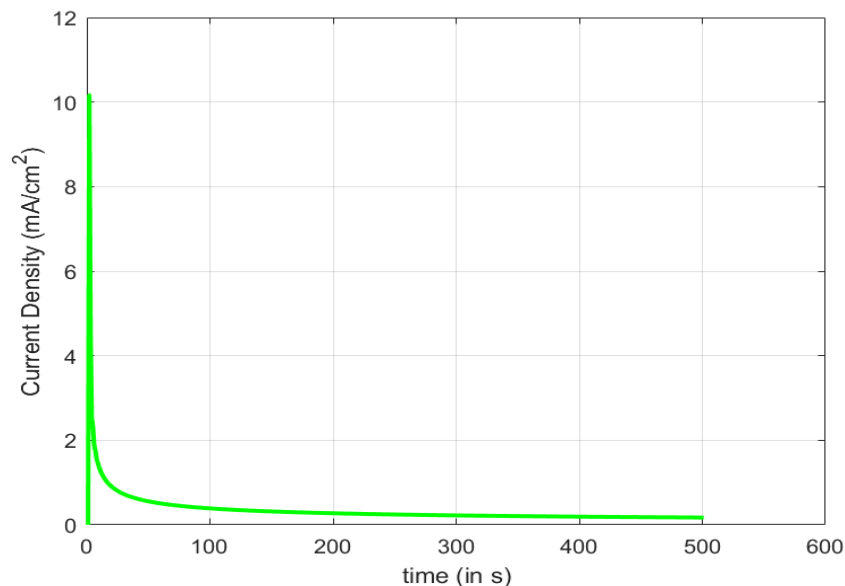
OBTAINED CURRENT DENSITY & SIMULATION TIME PLOT (figure 2)

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MATLAB Codes: CASE II (B-V Boundary Condition)

```matlab
%clear, clc, close all
%% INDEPENDENT VARIABLES %%
C      = 1.0;                % [=] mol/L, initial concentration of O.
D      = 1E-5;              % [=] cm^2/s, O & R diffusion coefficient.
n      = 1.0;               % [=] number of electrons transferred.
alpha  = 0.5;               % [=] dimensionless charge-transfer coefficient.
k0     = 1E-2;              % [=] cm/s, electrochemical rate constant.
kc     = 1E-3;             % [=] 1/s, chemical rate constant.
T      = 298.15;            % [=] K, temperature.
%% PHYSICAL CONSTANTS %%
F      = 96485;             % [=] C/mol, Faraday's constant
R      = 8.3145;            % [=] J/mol-K, ideal gas constant
f      = F/(R*T);         % [=] 1/V, normalized Faraday's constant at room temp
%% SIMULATION VARIABLES %%
L      = 500;               % [=] number of iterations per t_k
DM     = 0.45;              % [=] model diffusion coefficient
%% DERIVED CONSTANTS %%
tk  = 800                   % [=] s, simulation for 800sec
Dt  = tk/L;                 % [=] s, delta time
Dx  = sqrt(D*Dt/DM);        % [=] cm, delta x
j   = ceil(4.2*L^0.5)+5;    % number of boxes  If L~200, j=65
%% PRE-INITIALIZATION %%
C = C / 1000;               % Convert C from mol/L to mol/cm3
k = 0:L;                    % time index vector
t = Dt * k;                 % time vector
eta = 0.2 ;
Enorm = eta*f;              % normalized overpotential
kf = k0*exp(alpha *n*Enorm);     % [=] cm/s, fwd rate constant
kb = k0*exp(-(1-alpha)*n*Enorm); % [=] cm/s, rev rate constant
O = C*ones(L+1,j);          % [=] mol/cm^3, concentration of O
R = zeros(L+1,j);           % [=] mol/cm^3, concentration of R
JO = zeros(1,L+1);          % [=] mol/cm^2-s, flux of O at the surface
%% START SIMULATION %%
% i1 = time index. i2 = distance index
for i1 = 1:L
```

```matlab
    % Update bulk concentrations of O and R
    for i2 = 2:j-1
        O(i1+1,i2) = O(i1,i2) + DM*(O(i1,i2+1)+O(i1,i2-1)-2*O(i1,i2));
        R(i1+1,i2) = R(i1,i2) + DM*(R(i1,i2+1)+R(i1,i2-1)-2*R(i1,i2));
    end
    % Update flux
    JO(i1+1)   = ( kf*O(i1+1,2) - kb*R(i1+1,2) ) / (1 + Dx/D*(kf + kb) );
    % Update surface concentrations
    O(i1+1,1) = O(i1+1,2) - JO(i1+1)*(Dx/D);
    R(i1+1,1) = R(i1+1,2) + JO(i1+1)*(Dx/D);
end


% Calculate current density, Z, from flux of O
Z = -n.*F.*JO * 1000; % [=] A/cm^2 -> mA/cm^2, current density
plot(Z,"LineWidth",2 , "color" , 'r');
grid on ;
xlabel('time'), ylabel('Current Density (mA/cm^2)')
```

## OBTAINED CURRENT DENSITY & SIMULATION TIME PLOT (figure 3)
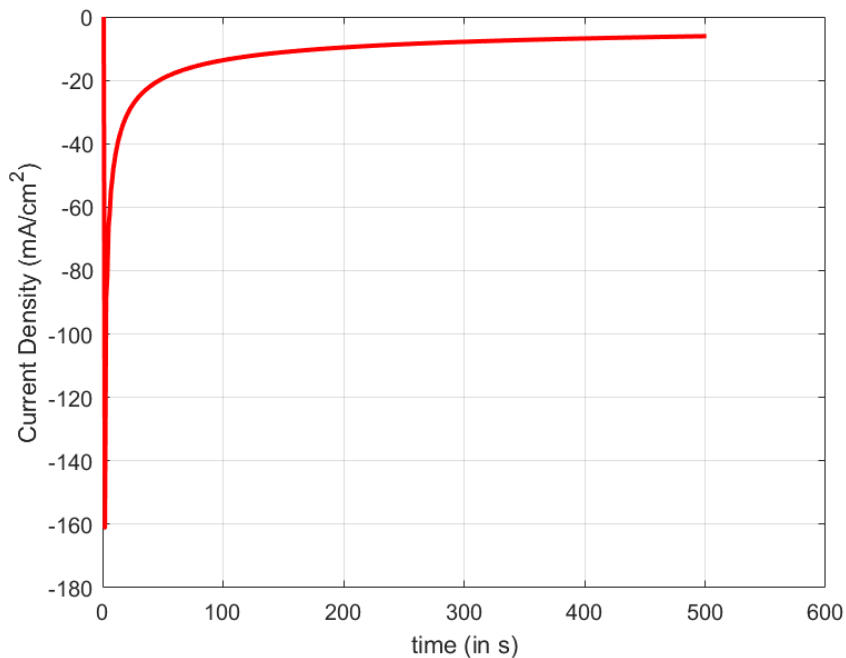
Copper Electrowinning

Electrowinning is the electrodeposition of metals from their ores that have been put in solution via a process referred to as leaching.

Theory & Governing Equations[3]

The overall reaction in copper processing from leach solutions of copper salts for the electrowinning of copper from acid sulphate matrix: $Cu^{2+}(aq) + H_2O \rightarrow Cu(s) + 2H^+(aq) + 1/2O_2(g)$
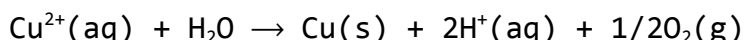
Anodic Reaction: $H_2O(aq) \rightarrow 2H^+(aq) + 1/2O_2(g) + 2e^-$, $E_0 = 1.229V$

Cathodic Reaction: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$, $E_0 = -0.337V$

Mechanism of Electron Transfer

For elementary reactions at an electrode, the following two mechanisms are primarily responsible for electron transfer:

1. **Mass Transfer Controlled:** Diffusion of copper cations from the bulk phase to where the reaction occurs at the surface.

$$Cu^{2+}(bulk) \rightarrow Cu^{2+}(surface)$$
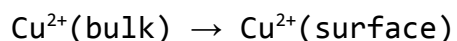
2. **Reaction Kinetics Controlled:** Heterogeneous transfer of electrons from the solid electrode to the copper cation at the surface of the electrode.

$$Cu^{2+}(surface) + 2e^- \rightarrow Cu(surface)$$
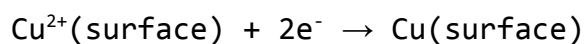
We control the overall step by the slowest step, either mass transfer or reaction kinetics.

The maximum current that can be applied to maintain a reaction is known as the **Diffusion Limited Current**. Assuming an adequate supply of reactants to the electrode surface, the Butler-Volmer equation describes the surface that constrains the current.

If the applied potential is adequate to maximise the Heterogeneous Electron Transfer reactions, the reaction rate is then limited by the supply of reactants to the electrode surface and is said to be mass transfer limiting (or controlled).

Heterogeneous Electron Transfer

The heterogeneous electron transfer reaction can be described using the Butler-Volmer Equation:[4]

$$i = i_0[\frac{C_O(s)}{C_O(b)} exp(-\frac{\alpha nF}{RT}(E - E^0)) - \frac{C_R(s)}{C_R(b)} exp(-\frac{(1-\alpha)nF}{RT}(E - E^0))]$$

i_0 → exchange current density

C(s) → surface concentration

C(b) → Bulk concentration

$E-E^0$ → overpotential

This relationship shows that the surface constrains the current to bulk concentration ratios of oxidant and reductant species. The reaction rates do not grow as potential is increased. Thus, it is limited by the transport of species to the electrode.

Mass Transfer

During Cu Electrowinning, the movement of species from the bulk solution to the electrode surface occurs via diffusion and convection.

$$i = nFk_d[C_O(b) - C_O(s)]$$

Obtaining Diffusion Limited Current

DLC is given by the equation,

$$i_L = nFk_dC_O(b)$$

The DLC should always be greater than the Faradaic current for a plant to ensure that suitable inadequate flow conditions do not limit production adherent copper cathode is produced and that the hydrodynamics of the system are sufficient to ensure inadequate flow conditions do not limit production.

The value of k_d is calculated using Sherwood Approximation for parallel plate electrodes of finite width and fully developed laminar flow. For Sh = 7.54, $k_d = 7.54*\frac{D}{2 \cdot h}$, D = $2*10^{-9}$ m/s, h = 5mm, $k_d = 1.5 \cdot 10^{-6}$ m/s, $C_0(b)$ = 0.6M $\Rightarrow i_L$ = 174 A/m²

The surface concentration can be eliminated using the limiting current by using the relation,

$$\frac{C(s)}{C(b)} = \frac{i_L - i}{i_L}$$

Using this in the B-V equation the following equation can be obtained for the cathodic overpotential :

$$\eta_c = \frac{RT}{n\alpha F}\left(ln(i_0) - ln(i) - ln(\frac{i_L}{i_L - i})\right) \underline{\hspace{3cm}} (i)$$

MATLAB Code for Voltammogram Plots

```
n = 2 ;              %no of electrons transferred
F = 96485 ;          %Faraday's Constant
                     %iL = n*F*Dm*Cmb/dm  ,  km = Dm/dm
km = 1.54e-6 ;       %using sherwood approximation
                     %km = 7.54*D/2*h where D = 2e-9m/s and h = 5mm
Cmb = 600 ;          %bulk copper concentration in mol/m3 (0.6M)
                     %iL = n*F*km*Cmb ;
                     %i = i0*(Cs/Cb)*exp(-n*F*eta_c/R*T)
i0 = 245 ;           %i0 == exchange current is taken to be 245A/m2
```

```matlab
                    %eta_c = (R*T/n*beta*F)*(ln(i0) - ln(i) - ln(iL/(iL-i)))
R = 8.314 ;              % gas constant
T = 298 ;               %at 25 C
beta=0.5 ;
%eta_c = (R*T/(n*beta*F))*(log(i0) - log(i) - log(iL/(iL-i)) ) ;
eta = linspace(-0.4 ,0.3 ,100);
t = length(eta);
i = zeros(1,t);
for iL = 150:50:350
    for itr = 1:t
            i(itr) = (iL*i0)/((iL*exp((eta(itr)*beta*n*F)/(R*T)))+i0);
    end
    plot(eta , i , 'linewidth' ,1.5 ) ;
    hold on;
end
xlabel('Overpotential') ;
ylabel('Current density (in m/A^2)' ) ;
title('Voltammograms for different DLC') ;
legend('150' ,'200' , '250' , '300' , '350');
grid on ;
```

Result

- **Cell Current**

  In operating reactors, a current lower than the DLC is used to achieve a good adherent product. The cell current is taken to be 80% of DLC. Therefore i = 0.8*174 = 139.2 A/m^2.
  The exchange current density i_0 = 245 A/m^2.

- **Cell Potential**

  The total voltage across the cell can be divided into three components:
  - Reversible Decomposition Potentials (V_{min})
  - Activation and Concentration Overpotentials (η_a, η_c)

- Potential drop due to Ohmic resistance of the electrolyte and the electrical contacts (V_{ohm}).
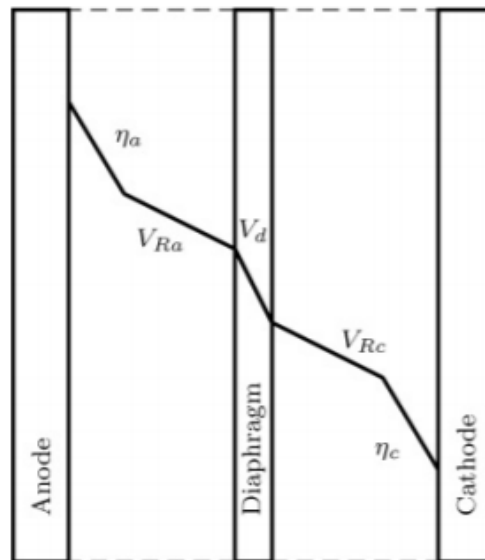
$$V = V_{min} + |\eta_a| + |\eta_c| + V_{ohm}$$

The <u>reversible Potential</u> $V_{min} = V_a - (-V_c) = -1.229 + 0.337 = -0.892$

The <u>potential drop due to ohmic resistance</u> from the solution and the contacts is given by:

$$V_{ohm} = i \cdot \frac{h}{k}$$

Where h is the interelectrode distance is taken to be 5mm, and k is the specific conductivity $k = F\sum n_i^2 \mu_i^2 C_i$, ($\mu$ is the ionic mobility). Substituting h = 5mm, k = 1.647 S/m, $i = 0.8i_L$ we get $V_{ohm} = 0.423$ V.

The <u>cathodic overpotential</u> η_c can be calculated using equation (i) given above. The value of η_c comes out to be 0.335 V.

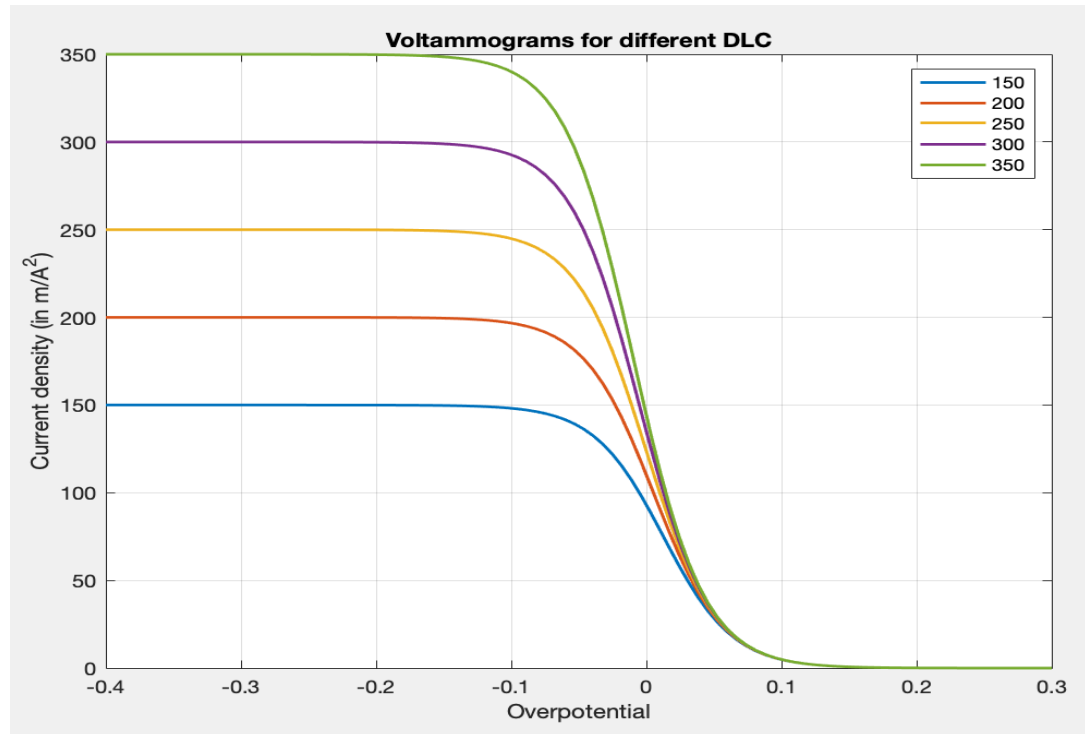The <u>anodic overpotential</u> η_a can be calculated using the Tafel Equation,

$$\eta_a = a + b*\log(i),\ \text{where a=0.303, b=0.12}$$

Therefore, η_a = 0.56 V.

Therefore, **the cell potential V = 0.892 + 0.56 + 0.335 + 0.423 = 2.21V**

- **Graph**

  The result of the above code, i.e., the current density and overpotential (voltammogram) graph, is in figure 5.

Further Research

The local reaction rate (in terms of current density i) can be related to the required voltage for a given copper concentration. This can be used to develop a Meso-Scale Model for the electrolyser. The model can be set up as,[5]

$$Whv_x \frac{dC_A}{dx} = -\frac{i}{nF}W$$

W   → cell width

X   → coordinate along the cell length

i/nF   → local rate of reaction

Here i is not known at each position and usually as the voltage applied across the system. Hence i should be iteratively calculated at each location.

Fuel Cells

A fuel cell is an electrochemical cell that converts the chemical energy of a fuel (often hydrogen) and an oxidising agent (often oxygen) into electricity through a pair of redox reactions. Hydrogen gas produced from renewable energy, stored and then reconverted back into electricity in a PEM fuel cell is an increasingly important option for storing electricity.
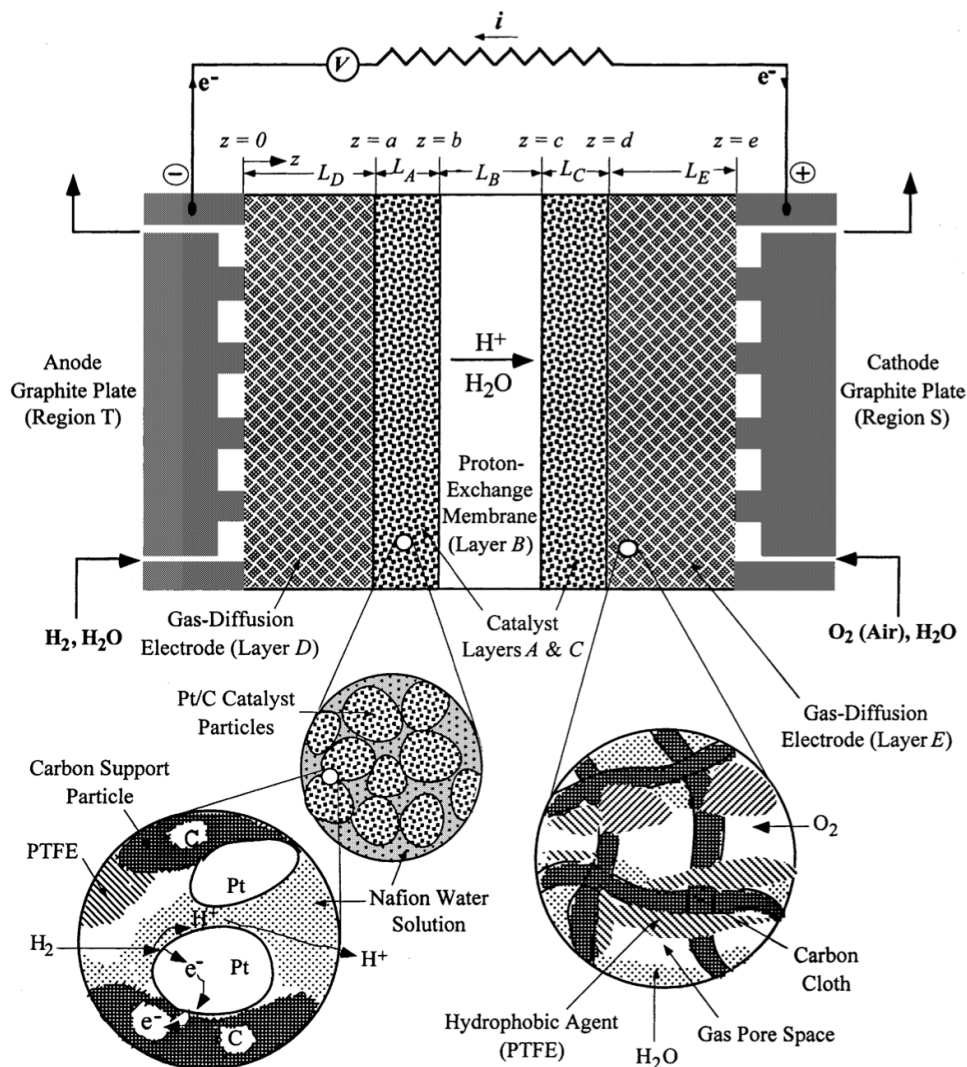
Theory & Governing Equations

Figure 6 shows the schematic diagram of a hydrogen fuel cell.

Anodic Reaction: $H_2(g) \rightarrow 2H^+(aq) + 2e^-$

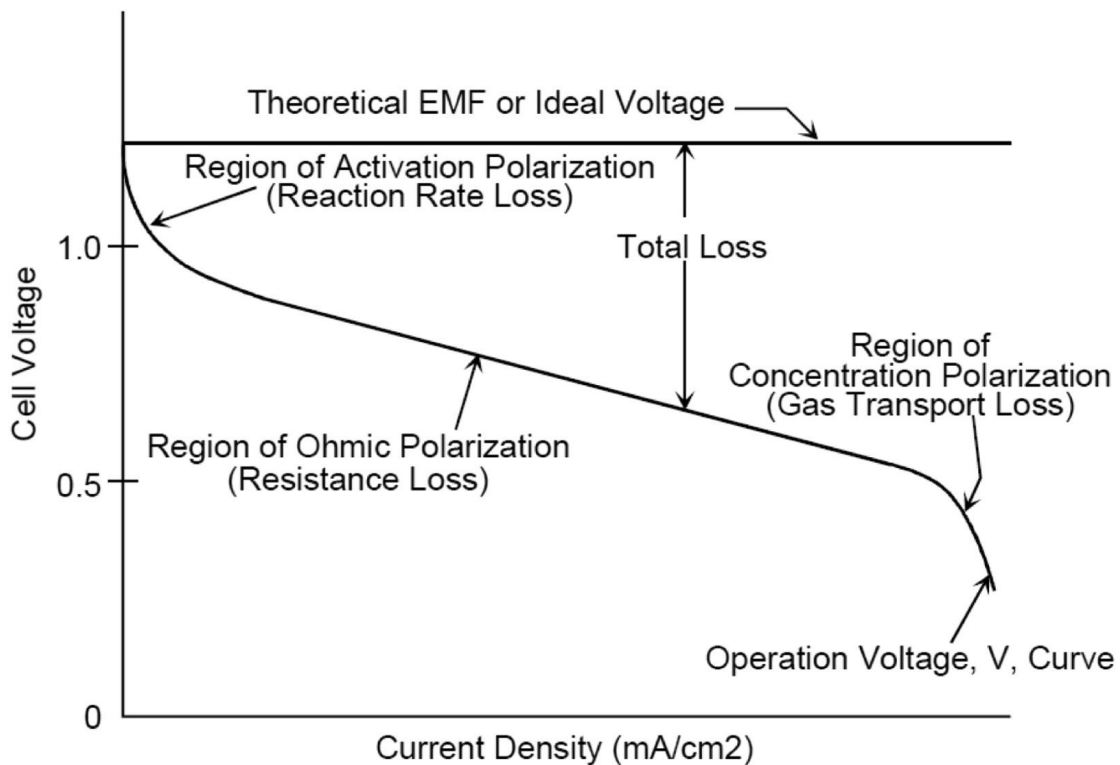**Cathodic Reaction:** $1/2O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O$

Overall Reaction: $H_2(g) + 1/2O_2(g) \rightarrow H_2O$

There are three distinct regions of a proton exchange membrane (PEM) fuel cell polarization curve:

- **Activation polarisation**
- **Ohmic losses**
- **Concentration polarization (mass transport losses)**

The polarization curve for a PEM fuel cell is in Figure 7[6].

Activation polarisation

Activation losses are the voltage required to overcome the activation energy of the electrochemical reaction on the catalytic surface. This type of polarisation dominates losses at low current density and measures the catalyst effectiveness at a specific temperature. The catalyst reduces the height of the activation barrier, but a loss in voltage remains due to the slow oxygen reaction. Activation overpotential expressions derive from the Butler-Volmer equation.

Ohmic polarisation

Conductive materials have an intrinsic resistance to charge flow, which results in a loss in cell voltage. The cell components contributing to the electrical resistance are the electrolyte, the catalyst layer, the gas diffusion layer, bipolar plates, interface contacts, and terminal connections.

Concentration polarisation

A fuel cell must continuously be supplied with fuel and oxidant to produce electricity, and products must continuously be removed for maximum fuel cell efficiency. The reactant and product concentrations within the catalyst layer determine the fuel cell performance. Concentration loss can be minimised by optimising the mass transport in the fuel cell electrodes and flow structures.

MATLAB Codes

```matlab
T = 333;            %   temperature of the fuel cell 60^C
R = 8.314;          %   gas constant R = 8.314 J/molK
pH2O = 2.931;       %   partial pressure of H20
pH2 = 1.265;        %   partial pressure of H2
pO2 = 2.527;        %   partial pressure of O2
```

```matlab
F = 96485;              %   Faraday's Constant
i0 = 10^(-6.912) ;      %   current density A/cm2
al = 0.5;               %   transfer coefficient
b = (R*T)/(2*al*F);     %   constant1
c = (R*T)/(2*F);        %   constant2
iL = 1.4;               %   diffusion limited current A/cm2
Resistance = 0.19;      %   resistance value Î©cm2
Er = 1.229 ;
i = linspace(0.0001 , 1.4 , 10000) ;
E = zeros(1, length(i));
for itr=1: length(i)
E(itr) =   Er+(- b*log(i(itr)/i0) - c*log(iL/(iL-i(itr)) ) - i(itr)*Resistance);
end
plot(i , E , 'linewidth' , 2);
grid on;
xlabel('Current Density (A/cm^2)');
ylabel('Voltage (in V)');
title('Proton Exchange Membrane Fuel Cell Polarisation Curve');
```

Results & Discussions

The result of the above code, i.e., polarisation curve of the proton exchange membrane(PEM) fuel cell, is shown in figure 8.

Further Research

The potential generated at any operating current is found using the following relation,

$$V = E_{eq} - \eta_a - |\eta_c| - V_M$$

E_{eq} is the thermodynamic potential; η_a is the anodic potential, which includes the concentration overpotential; η_c is a similar term for the cathode, and V_M is the voltage drop in the membrane. Further,

$$E_{eq} = 1.23 - 0.9 \times 10^{-3}(T - 298) + \frac{RT}{4F}\ln(p_{H2}^2 p_{O2})$$

we can use the Butler-Volmer equation in the hyperbolic form to find η_a and η_c, [4]

$$\eta_a = \frac{RT}{\alpha F}\text{sinh}^{-1}(\frac{1}{2}(\frac{i/ia0}{1-i/iaL}))$$

Where α_a is the effective transfer coefficient of the anode reaction (usually taken as 1/2), i_{a0} is the exchange current at the anode, and i_{aL} is the diffusion limiting current.
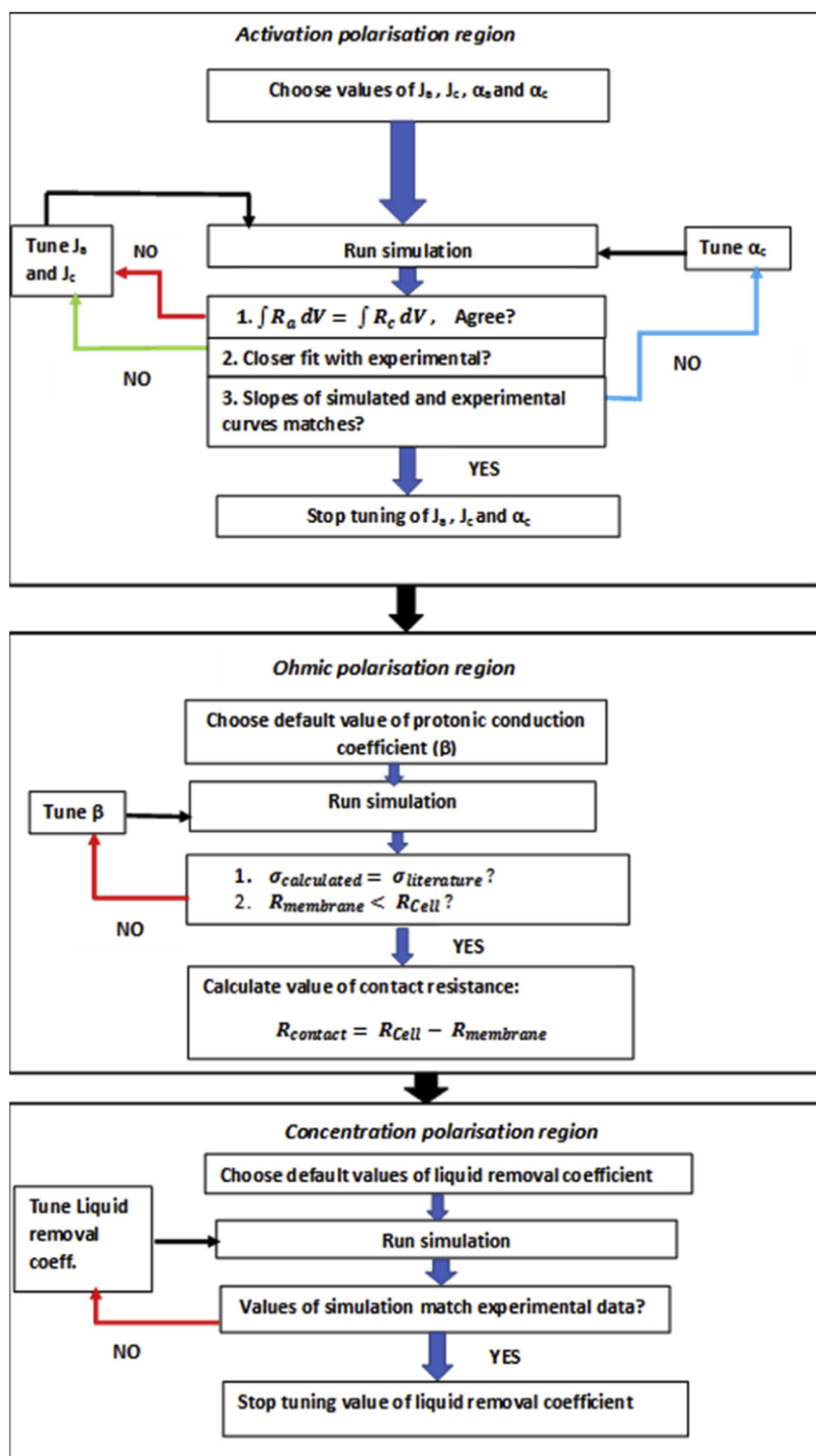
$$\eta_c = \frac{RT}{n\beta F}\text{sinh}^{-1}(\frac{1}{2}(\frac{i/ic0}{1-i/icL}))$$

A similar inference applies to this equation.
Details of the derivation are presented by Thampan et al. (2001)[7].

Proton Exchange Membrane Fuel Cell Polarisation Curve
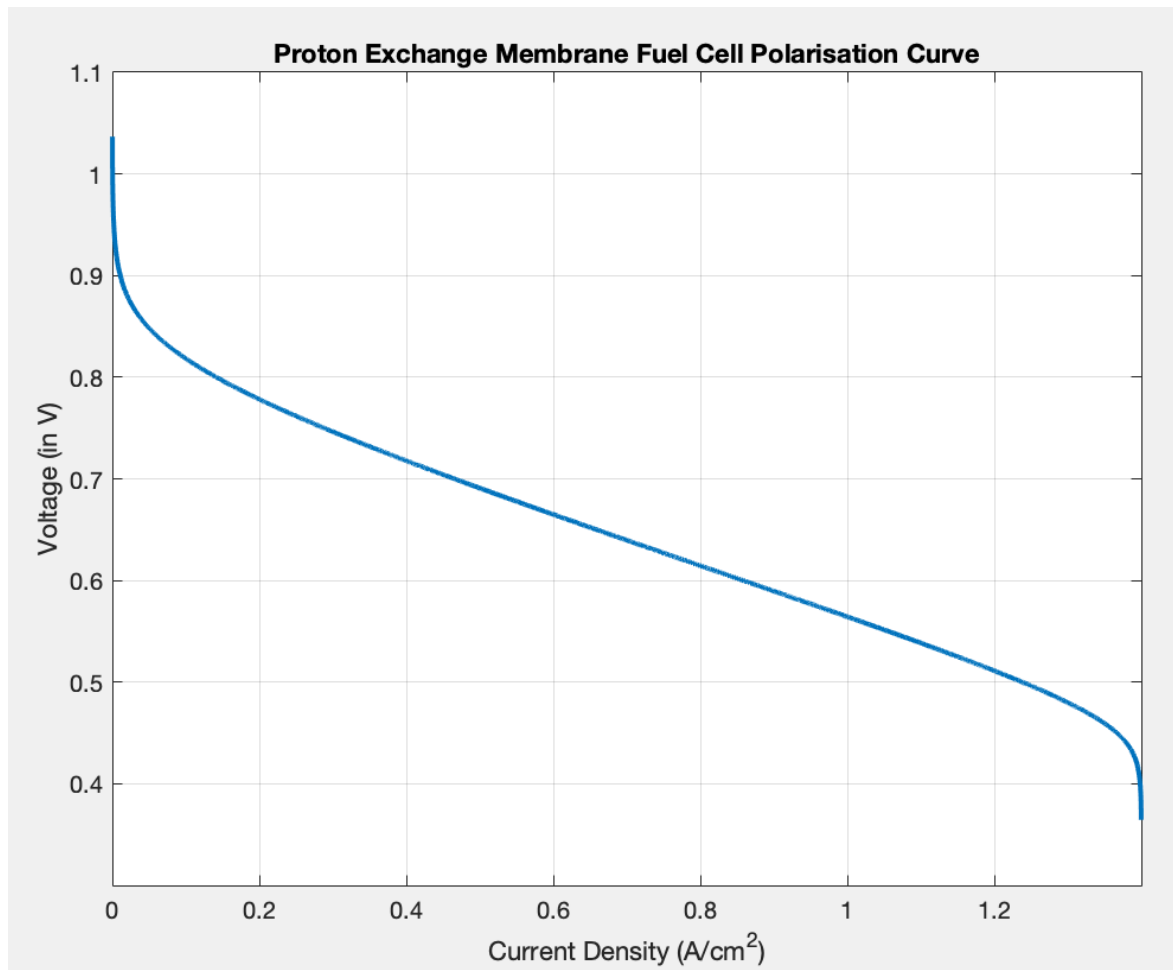
A similar approach using ANSYS simulation was proposed by Arif et al. (2020)[8]. The research presents a simulation model that considers activation polarisation, ohmic polarisation, and concentration polarisation. A major highlight from the research is that the maximum percentage difference between the simulation and experimental data is 5%. A detailed diagram explaining the stepwise simulation of the PEM fuel cell is in figure 9.

Activation polarisation region

Choose values of J_a, J_c, α_a and α_c

Run simulation

Tune J_a and J_c

Tune α_c

1. $\int R_a\, dV = \int R_c\, dV$, Agree?
2. Closer fit with experimental?
3. Slopes of simulated and experimental curves matches?

NO

NO

NO

YES

Stop tuning of J_a, J_c and α_c

Ohmic polarisation region

Choose default value of protonic conduction coefficient (β)

Tune β

Run simulation

1. $\sigma_{calculated} = \sigma_{literature}$?
2. $R_{membrane} < R_{Cell}$?

NO

YES

Calculate value of contact resistance:

$$R_{contact} = R_{Cell} - R_{membrane}$$

Concentration polarisation region

Choose default values of liquid removal coefficient

Tune Liquid removal coeff.

Run simulation

Values of simulation match experimental data?

NO

YES

Stop tuning value of liquid removal coefficient
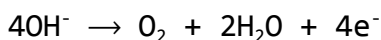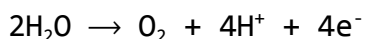
Cu-MEA for CO_2 reduction

Techno-economic analysis shows that we need to operate CO_2R at current densities above 100 mA cm^{-2} for industrial viability, and gas-diffusion electrodes (GDEs) play an essential role in achieving such high rates. The operation of Cu-based GDEs under alkaline conditions has also been shown to attain higher faradaic efficiencies for C$_{2+}$ products, which are desirable because of their high energy densities and market value. An upgraded system, i.e., membrane electrode assembly (MEAs), has proven to be effective in minimising cell ohmic losses and circumventing issues associated with having the GDE in direct contact with the aqueous electrolyte, such as electrode flooding and salt precipitation.
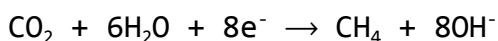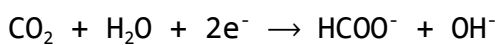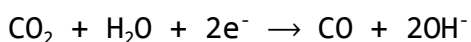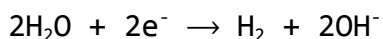
- ## Theory & Governing Equations
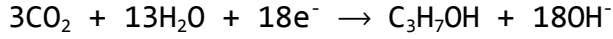
  A schematic diagram of the Cu-MEA system is in figure 10.[9]
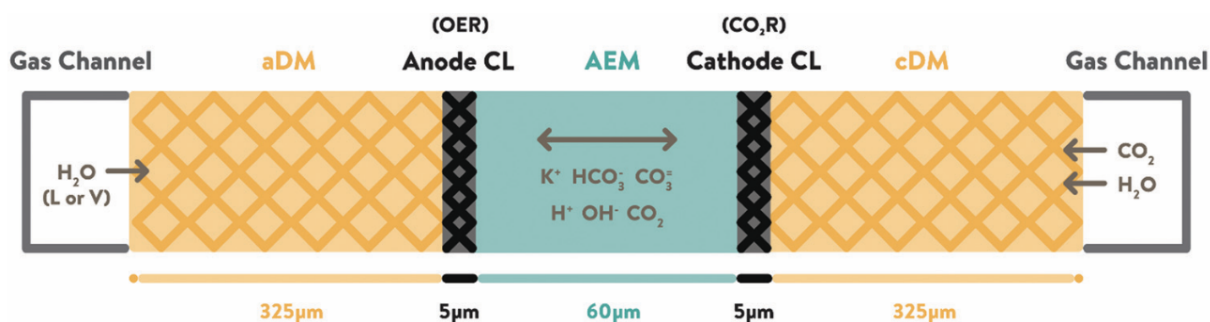
  Governing oxygen evolution reaction:

  $$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

  $$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$$

  Governing hydrogen evolution reaction:

  $$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

  $$CO_2 + H_2O + 2e^- \rightarrow CO + 2OH^-$$

  $$CO_2 + H_2O + 2e^- \rightarrow HCOO^- + OH^-$$

  $$CO_2 + 6H_2O + 8e^- \rightarrow CH_4 + 8OH^-$$

$$2CO_2 + 8H_2O + 12e^- \rightarrow C_2H_4 + 12OH^-$$

$$2CO_2 + 9H_2O + 12e^- \rightarrow C_2H_5OH + 12OH^-$$

$$3CO_2 + 13H_2O + 18e^- \rightarrow C_3H_7OH + 18OH^-$$
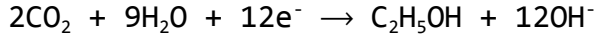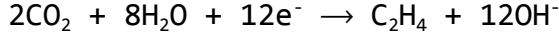
The charge transfer kinetics are described by Tafel's equation as,

$$i_k = i_{o,k} \prod_j \left(\frac{cj}{cj,ref}\right)^{yj,k} \cdot \exp\left(-\frac{\alpha c,k \cdot F}{RT}\eta_k\right)$$

Gas and liquid phase material balance are calculated by mole balance, mass conservation and Darcy's law. Since the Nernst-Planck equation assumes dilute-solution theory and the system described is not necessarily diluted under all conditions, a need to assign material balance is needed for the system independently.

The temperature profile in the system is obtained by solving the energy conservation equation,

$$\nabla(-k_{T,m} \cdot \nabla T) = \Omega_{CT} + \Omega_B + \Omega_{PT} + \Omega_J$$

$k_{T,m} \rightarrow$ thermal conductivity of medium m

$\Omega_{CT} \rightarrow$ heat generation terms for charge transfer reactions

$\Omega_B \rightarrow$ heat generation terms for bulk buffer reactions

$\Omega_{PT} \rightarrow$ heat generation terms for phase transfer

$\Omega_J \rightarrow$ heat generation terms for Joule heating

Lastly, for the calculation of the applied voltage breakdown, we use the following equation,

- Standard cell potential,

$$U^o_{cell} = U^o_{anode} - U^o_{cathode}$$

- Kinetic Overpotential

$$\eta_{kinetic} = \sum_k \frac{RT}{i_T \alpha_{a/c} F} \int_{CL} i_{v,k} \ln\left(\frac{i_k}{i_{o,k} \prod_j a_{0,j}^{\gamma_j}}\right)$$

- Mass Transport Overpotential

$$\eta_{mass\ transport} = \sum_k \frac{2.303 RT}{i_T F} \int_{CL} i_{v,T} (pH_0 - pH) + \frac{1}{i_T} \int_{CL} i_{v,k} \eta_k - \eta_{k,\ kinetic}$$

- Ohmic Overpotential

$$\eta_{ohmic} = \frac{1}{i_T} \int_{CL+MEM} \frac{i^2}{K^{eff}}$$

We can make a comprehensive COMSOL model using these governing these equations, and we can solve it using certain boundary conditions and other supporting equations mentioned in the result.

Conclusion

We went across some basic electrochemical processes like copper electrowinning and fuel cells. We also discussed a discretisation model to smooth out our computation. In between, we briefed some state-of-the-art technologies used in the field. A conclusion can be drawn that the voltage versus current graph of an electrochemical system comprises three significant segregations which occur due to activation polarisation, ohmic losses polarisation and concentration polarisation. The produced results of the simulations mimic the natural response of all the systems included in our study. Finally, an optimal way of running the CO_2 reduction reaction is discussed using Copper-membrane electrode assemblies. The results help us solve the problem of net carbon neutrality while producing certain organic compounds. We still need to simulate the results in this paper, and we hope that we will get a good chance later on to complete it.

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