Global warming presents an ever-rising challenge to humans today, caused by an unprecedented rise in the carbon dioxide levels in the atmosphere over the past decade. This study proposes a way to fix this problem in a sustainable way using sunlight to convert CO₂ into useful fuels through a novel device. A Simulink model of photo-voltaic cell, CO₂ electrochemical reduction and photo-electrochemical reduction cell is developed and integrated together to model the device. The photo-voltaic cell model calculates the voltage required to operate the CO₂ reduction cell. The CO₂ photo-electrochemical reduction cell calculates product flow rates and voltage required to operate the cell using continuity, charge balance and Butler-Volmer equations. The model of the integrated device calculates i-V characteristics of the photovoltaic, electrochemical reduction and photo-electrochemical reduction cell under different environmental conditions, the product flow rates, contribution of various cell over-voltages. The model developed predicts photo-electrochemical route to be more energy and area efficient as compared to the electrochemical route.

Conversion is achieved at low temperatures and pressures; unlike the other two processes viz. RWGS and reaction of CO₂ with hydrocarbons. Photosynthesis, electro-chemical and photo-electro-chemical reduction of CO₂ seem to be three of the most effective methods for the processing and recovery of carbon dioxide. Both electro-chemical and photo-electro-chemical reductions of carbon dioxide have been studied in detail and experiments conducted confirm their feasibility.

Electrochemical reduction (ECR) of carbon dioxide involves addition of protons and electrons to carbon dioxide resulting formation of hydrocarbons through the application of suitable voltage. Various possible CO₂ reduction reactions are shown in Table I. In this study, we have considered the reaction (Eq. 1) mentioned below, producing formic acid, for which there is a growing market demand and can be produced with greater selectivity as compared to other products.

The redox reaction occurring in the cell is:

$$H_2O + CO_2 → 0.5O_2 + HCOOH \quad E_0 = -1.429 \text{ V} \quad [1]$$

Depending on cathode potential, catalyst and electrolyte used, the products of the above reaction may vary (Table I). Jitaru discussed thermodynamic considerations and possible mechanisms for carbon dioxide reduction to a variety of end products and summarizes key methods for CO₂ reduction on metallic cathodes in aqueous and non-aqueous mediums. Chaplin and Wragg and N Kumari et al. gave reaction pathways for CO₂ reduction and effect of choice of electro-catalyst, electrolyte and process conditions on end products. Recently, Garg and Basu studied stability of Cu/CuO₂ cathode toward conversion of CO₂ in proton exchange membrane (PEM) based CO₂ electrolysis cell. Further the effect of support material, e.g., ZSM5 and γ-alumina on CO₂ electro-reduction has been

Table I. Equilibrium potentials for various CO₂ electro-reduction reactions

| Reduction Reaction |  \( E^0 / V \) |
|--------------------|-----------------|
| \( 2CO_2 + 2e^- + 2H^+ \rightarrow H_2C_2O_4 \) | -0.475 V |
| \( CO_2 + 2e^- + 2H^+ \rightarrow HCOOH \) | -0.199 V |
| \( CO_2 + 2e^- + 2H^+ \rightarrow CO + H_2O \) | -0.109 V |
| \( CO_2 + 4e^- + 4H^+ \rightarrow HCHO + H_2O \) | -0.071 V |
| \( CO_2 + 6e^- + 6H^+ \rightarrow CH_4OH + H_2O \) | +0.03 V |
| \( CO_2 + 8e^- + 8H^+ \rightarrow CH_4 + 2H_2O \) | +0.169 V |

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investigated to show that non-conducting support material results in catalyst stability but percolation limit of metal catalyst needs to be reached in creating conducting pathways. Theoretical models for PEM water electrolyser (similar to CO₂ electro-reduction) have been presented but no work exists on modeling of CO₂ electro-reduction to the best of our knowledge.

The electrochemical reduction (ECR) and photo-electrochemical reduction (PECR) of carbon dioxide requires application of potential difference across the electrodes, which is generally obtained from a renewable energy source to be sustainable. Just as plants receive sunlight, and industrial effluents, CO₂, for generating important hydrocarbons by using a novel photo-electrochemical approach. Recently, several attempts have been made to replicate photosynthesis through the external circuit, constituting current for the reduction of carbon dioxide, lowering down the energy required (from photovoltaic cell) to bring about the dissociation of water and reduction of CO₂. As such, this integrated device is expected to provide greater efficiency than simple electrochemical reduction method.

Convincingly enough, implementation of this concept will not only reduce the levels of CO₂ in the atmosphere but at the same time transform it into liquid fuels, which can be stored, transported and used. The hydrocarbons produced can alternatively be also used as chemical feedstock. The photo-electrochemical (PEC) reactor is a strong step toward achieving energy sustainability.

**Theoretical Model**

Theoretical modeling in this study has been covered in three modules, namely the solar photo-voltaic cell (PV cell), electro-chemical reduction and photo-electro-chemical reduction of carbon dioxide.

**Solar Photovoltaic Cell.**—For modeling, poly-crystalline Si solar cell has been chosen which is studied experimentally as a part of Solarex MSX60 PV module. While Gow and Manning discussed double diode model in great detail, in the present study single diode model of Chenni et al. is considered for its simplicity and fairly good accuracy in prediction. Similar models have also been given in other studies. The equivalent circuit (Fig. 2) of a solar cell is a current source in parallel with a diode. An ideal solar cell has a non-linear I-V relationship, dependent on solar irradiation, temperature, water-splitting, semi-conductor material, geometry. Various 3/4/5-parameter models have been used for modeling solar cells, using electrical circuits comprising diodes, resistors and current sources. Gow and Manning discussed double diode model and gave an analytical equation through curve fitting of experimentally recorded data. However, single diode models have also been shown to emulate solar cell fairly accurately.

In this study, an attempt is made to develop a theoretical model of an integrated device to convert easily available natural resources, sunlight, and industrial effluents, CO₂, for generating important hydrocarbons by using enzymes. However, no significant literature and experimental work are available on devices that perform artificial photosynthesis based on photo-voltaic and electro-chemical or photo-voltaic and photo-electrochemical cells. This novel device works similar to that of additional to photovoltaic cell, sunlight is utilized by reduction cell (see dotted line) by employing a photo-anode.

![Figure 1. Schematics of device: Sunlight incident onto a photo-voltaic cell. The photo-current reduces CO₂ in the reduction cell. In alternate arrangement, in addition to photovoltaic cell, sunlight is utilized by reduction cell (see dotted line) by employing a photo-anode.](image)

Support this electro-chemical reaction, a CO₂ reducing catalyst (e.g., In, Sn, Hg, Pb) is present at the cathode and a water splitting (oxygen evolution reaction) catalyst (Hematite/TiO₂) exists at the anode. In an alternate arrangement (Fig. 2), we have proposed photo-electrochemical assisted reduction of CO₂. In this arrangement, anode is covered with a layer of semiconductor nano-sized catalyst that ejects electrons when exposed to sunlight. These electrons travel to cathode through the external circuit, constituting current for the reduction of carbon dioxide, lowering down the energy required (from photovoltaic cell) to bring about the dissociation of water and reduction of CO₂. As such, this integrated device is expected to provide greater efficiency than simple electrochemical reduction method.

In this study, an attempt is made to develop a theoretical model of an integrated device to convert easily available natural resources, sunlight, and industrial effluents, CO₂, for generating important hydrocarbons by using enzymes. However, no significant literature and experimental work are available on devices that perform artificial photosynthesis based on photo-voltaic and electro-chemical or photo-voltaic and photo-electrochemical cells. This novel device works similar to that of additional to photovoltaic cell, sunlight is utilized by reduction cell (see dotted line) by employing a photo-anode.

![Figure 2. Single-diode electric-circuit model for PV cell.](image)
below: 28, 35

\[ I_{ph} = I_{ph}(T_s) + \sigma (T_c - T_s) \]  [4]

\[ V = V(T_s) + \zeta (T_c - T_s) \]  [5]

\[ I_{ph} = I_{SC}(T_s) \frac{G}{G_s} \]  [6]

\( I_{ph}(T_s) \) denotes value of \( I_{ph} \) calculated at \( T_s \), similarly for others. Equations 4 and 6 take the variation of photo-current with temperature and irradiance respectively. Equation 5 accounts for the variation of voltage with temperature. Here, \( T_s, G_s \) are defined at standard test condition (STC). Subscript ‘s’ stands for solar cell performance under standard test condition (STC), which is defined as follows: air mass ratio (AM) 1.5, irradiance (\( G_s \)) as 1000 W/m\(^2\) and cell temperature (\( T_s \)) as 25 °C, \( \sigma \) and \( \zeta \) are current and voltage temperature coefficients respectively, calculated using experimental observations recorded. 32 The reverse saturation current is given as: 35

\[ I_0 = I_0(T_s) \left( \frac{T_s}{T_c} \right)^{n} \left( e^{\frac{-qV_{OC}}{m_k B T_s}} - 1 \right) \]  [7]

\( I_0(T_s) \) is given by: 29

\[ I_0(T_s) = \frac{I_{SC}(T_s)}{e^{\frac{qV_{OC}}{m_k B T_s}} - 1} \]  [8]

where, \( I_{SC} \) is the short-circuit current and \( V_{OC} \), denotes open-circuit voltage of the cell. The resistance \( R_s \) can be incorporated by using the relation given by Gow and Manning. 28

\[ R_s = \frac{dV}{dI_{VOC}} - \frac{1}{X_V} \]  [9]

Equation 9 is obtained by differentiating Eq.3 w.r.t. \( V \) evaluated at \( V = V_{OC} \), where, \( X_V \) can be calculated from: 28

\[ X_V + \frac{1}{X_V} = I_0(T_s) \frac{q}{m_k B T_s} e^{\frac{qV_{OC}}{m_k B T_s}} \]  [10]

It is important to note that the cell temperature (\( T_c \)) differs from the ambient temperature (\( T_s \)) and can be treated as a function of incident solar irradiation. It can be estimated by using an approximate relation given by Ross 38 as:

\[ T_c = T_e + \left( \frac{T_{NOCT} - 20}{800} \right) G \]  [11]

More sophisticated relations are available for different geometries and environmental conditions (solar irradiation, wind speed, humidity, etc.), given by Skolplaki and Palyvos. 39 In Eq. 11, \( T_{NOCT} \) is the nominal operating cell temperature and is defined for open-circuit solar cells at the following conditions: \( T_e = 20 \, ^\circ\text{C}, \, \text{AM} = 1.5, \, G = 800 \, \text{W/m}^2 \) and wind velocity \( \sim 1 \, \text{m/s} \). For calculation purposes, \( T_{NOCT} \) has been assumed \( 50 \, ^\circ\text{C} \). Similarly, irradiance value of 1000 W/m\(^2\) is seldom received at the earth’s surface owing to low intensity of sunlight during morning and evening hours and dispersion due to clouds and dust particles. An irradiance value of 400 W/m\(^2\) has been assumed for calculation purposes. 40 \( T_e \) is calculated to be 35 °C. Equation 3 has been solved by employing an iterative procedure by using Newton-Raphson method in Matlab-Simulink.

For characterizing the PV cell, following parameters have been used:

i. Maximum power point: It is that point in i-V curve at which power delivered by the cell becomes maximum (\( P_{max} \)).

ii. Efficiency: It is defined as the percentage of incident energy converted. It is the ratio of maximum power to incident energy.

\[ \text{Eff} = \frac{P_{max}}{A G} \]

The theoretical maximum efficiency limit of a PV cell using a p-n junction is given by the Shockley-Queisser limit or detailed balance limit. The limit indicates maximum conversion efficiency \( \sim 33\% \) for a single p-n junction with a bandgap of 1.1 eV (for Si). 40, 41, 42

iii. Fill factor: It is defined as the ratio of maximum power to the product of open-circuit voltage and short-circuit current. A fill factor greater than 0.7 is an indication of good commercial cells. 41

\[ \text{FF} = \frac{P_{max}}{V_{OC} I_{SC}} \]

The model parameters have been provided in Table II. Eqs. 2–11 have been solved in Matlab Simulink as per the model configuration depicted in Fig. 3.

**Carbon Dioxide Electrochemical Reduction Cell**—Modeling of CO\(_2\) reduction cell (Fig. 4) has been categorized into three ancillaries: anode, cathode and voltage ancillary. The reduction cell has been modeled on ‘voltage mode’ i.e. the reduction cell withdraws a particular amount of current on application of voltage from solar cells. Water is oxidized at anode and carbon dioxide is reduced at cathode. Anode ancillary gives oxygen flow rate, cathode ancillary gives formic acid production rate and voltage ancillary calculates the voltage bias required to operate the cell. The cathode and anode ancillaries are

| Parameter | Value |
|-----------|-------|
| \( q \)     | \( 1.6 \times 10^{-19} \) C |
| \( m \)     | 1.3 |
| \( k_B \)   | \( 1.38 \times 10^{-23} \) JK\(^{-1}\) |
| \( T_e \)   | 296 K |
| \( G_s \)   | 1000 Wm\(^{-2}\) |
| \( V_{OC} \)| 1.12 V |
| \( T_{NOCT} \)| 293 K |
| \( V_{sc} \)| 323 K |
| \( A_s \)   | 100 cm\(^2\) |
| \( F \)     | 96487 Cmol\(^{-1}\) |
| \( R \)     | 8.314 Jmol\(^{-1}\)K\(^{-1}\) |
| \( k_{ao} \)| 0.5 mols\(^{-1}\)Pa\(^{-1}\) |
| \( k_{co} \)| 0.35 mols\(^{-1}\)Pa\(^{-1}\) |
| \( k \)     | 1 \([\text{mg}]\) |
| \( V_a \)   | 16 cm\(^3\) |
| \( V_c \)   | 16 cm\(^3\) |
| \( P_o \)   | 101325 Pa |
| \( E_{H2O/O2} \)| −1.23 V |
| \( E_{CO2/HCOOH} \)| −0.199 V |
| \( E_0 \)   | −1.429 V |
| \( E_{CB} \)| −0.5 V |
| \( E_F \)   | −0.52 V |
| \( E_{fb} \)| −0.43 V |
| \( E_{Vb} \)| 1.7 V |
| \( E_{qs} \)| 2 V |
| \( t_w \)   | 0.0051 cm\(^{19}\) |
| \( D_{abs} \)| 4.07 \( \times 10^{4} \) cm\(^{2}\)s\(^{-1}\) |
| \( D_{w} \)  | 1.25 \( \times 10^{-10} \) m\(^{2}\)s\(^{-48}\) |
| \( L \)     | 63 nm |
| \( b \)     | 1 cm\(^{-1}\) |
| \( \eta_{h,i} \)| 0.91 (ft) |
| \( \beta_{abs} \)| 8.5 \( \times 10^{1} \) cm\(^{-122}\) |
| \( I_0 \)   | 1.5 \( \times 10^{17} \) cm\(^{-2}\)s\(^{-122}\) |
| \( h \)     | 6.626 \( \times 10^{-4} \) m\(^{3}\)kg\(^{-1}\) |
| \( \alpha \) | 0.22 m\(^{2}\) |
| \( \eta_{PEC} \)| 0.25 (ft) |
| \( \eta_{dilute} \)| 50 cm\(^{2}\) |
| \( I_0 \)   | 10\(^{-7}\) Acm\(^{-2}\) |
connected to each other through proton conducting membrane electrolyte (Fig 5). Membrane electrolyte facilitates proton transport for CO₂ electro-reduction. In this study, we shall modify the model given by Gorgun for modeling the ECR cell.

Reaction scheme is as follows:

At anode : \( H_2O \rightarrow 2H^+ + 0.5O_2 + 2e^- \) \( E_{H_2O/O_2} = -1.23 \text{ V} \) \[12\]

At cathode : \( CO_2 + 2e^- + 2H^+ \rightarrow HCOOH \) \( E_{CO_2/HCOOH} = -0.199 \text{ V} \) \[13\]

\( H_2O + CO_2 \rightarrow 0.5O_2 + HCOOH \) \( E_o = -1.429 \text{ V} \) \[14\]

**Anode Ancillary.**—At anode, water is oxidized to oxygen (Eq. 12). Hence, mass balance equations can be written for water and oxygen.

\[
\frac{dN_{H_2O}}{dt} = F_{H_2O} - F_{H_2O,anode} + G_{H_2O}
\]

\[15\]

\[
\frac{dN_{O_2}}{dt} = F_{O_2} - F_{O_2,anode} + G_{O_2}
\]

\[16\]

where, \( N_{O_2} \) and \( N_{H_2O} \) represent moles of \( O_2 \) and \( H_2O \) respectively. \( F_{O_2}, F_{H_2O}, F_{H_2O,anode}, F_{H_2O,anode} \) are the inlet and outlet molar flow rates of oxygen and water respectively. \( F_{H_2O,anode} \) and \( F_{H_2O,anode} \) are the electro-osmotic drag and diffusion flows. \( G_{O_2} \) is the rate of \( O_2 \) generation. \( F_{H_2O,anode} \) accounts for water transport along with \( H^+ \) ions that travel toward cathode through the proton conducting membrane electrolyte while \( F_{H_2O,anode} \) denotes flow of water due to concentration difference across the membrane electrolyte. Here, \( F_{O_2,anode} \) is zero, since there is no oxygen inflow at anode. \( F_{H_2O,anode} \) is given by:

\[
F_{H_2O,anode} = \frac{kI}{F}
\]

\[17\]

where, \( I \) is the cell current, \( F \) is Faraday’s constant and \( k \) is the electro-osmotic drag coefficient. \( k \) is given by:

\[
k = 0.0029 \lambda_m^2 + 0.05 \lambda_m - 3.4 \times 10^{-19}
\]

\[18\]

where, \( \lambda_m \) is the water content of the membrane electrolyte and can be calculated using the relation:²¹

\[
\lambda_m = 0.43 + 17.81\alpha_{H_2O} - 39.85\alpha_{H_2O}^2 + 36\alpha_{H_2O}^3 \quad \alpha_{H_2O} > 1
\]

\[19\]

\[
\alpha_{H_2O} = 14 + 1.4 (a_{H_2O} - 1) \quad a_{H_2O} \leq 1
\]

\[20\]

\( a_{H_2O} \) is the activity of water in Eq. 19 and 20 above.

A small amount of water also diffuses through the PEM to the cathode side because of concentration difference between the two sides of the membrane electrolyte. \( F_{H_2O,anode} \) is given by Fick’s law of diffusion as:

\[
F_{H_2O,anode} = \frac{AD_w}{t_w} \left( C_{m,cathode} - C_{m,anode} \right)
\]

\[21\]
where, \( \eta_F \) is the faraday’s efficiency. Total anode pressure (\( P_a \)) can be written as \( P_a = p_{O_2} + p_{H_2O} \), where \( p_{O_2} \) and \( p_{H_2O} \) are the partial pressures of \( O_2 \) and \( H_2O \) respectively given by \( p_{O_2} = \frac{N_{O_2}RT}{V_\text{act}} \) and \( p_{H_2O} = \frac{N_{H_2O}RT}{V_\text{act}} \), \( V_\text{act} \) being the anode volume, \( R \) the universal gas constant and \( T \) the reduction cell temperature. Mole fraction of oxygen (\( y_{O_2} \)) can be calculated by \( \frac{p_{O_2}}{P_a} \). Anode outflows can be written as:

\[
F_{\text{total,ao}} = F_{O_2o} + F_{H_2Oo}
\]

where, \( F_{\text{total,ao}}, F_{O_2o} \) and \( F_{H_2Oo} \) are the total, oxygen and water outflows at anode respectively. \( F_{\text{total,ao}} \) is given by:

\[
F_{\text{total,ao}} = k_{ao}(P_a - P_o)
\]

where, \( k_{ao} \) is the anode outflow coefficient and \( P_o \) is the ambient pressure at exit. Equation 15 can be integrated over time and \( F_{O_2o} \) is calculated using the above equations.

**Cathode Ancillary**.—At cathode, carbon dioxide is reduced into hydrocarbons using protons (Eq. 13) that travel from anode to cathode via PEM electrolyte and electrons supplied by the external voltage bias. For simplifying our calculations, it is assumed that formic acid is the only product formed during reduction of carbon dioxide and that there is no side-reaction. Two chemical entities involved at cathode side are HCOOH and CO\(_2\). Their mass balance equations are as follows:

\[
\frac{dN_{\text{HCOOH}}}{dt} = F_{\text{HCOOH}} - F_{\text{HCOOH}} + G_{\text{HCOOH}}
\]

\[
\frac{dN_{\text{CO}_2}}{dt} = F_{\text{CO}_2} - F_{\text{CO}_2} - R_{\text{CO}_2}
\]

where \( N_{\text{HCOOH}} \) and \( N_{\text{CO}_2} \), represent moles of \( \text{HCOOH} \) and \( \text{CO}_2 \) respectively. \( F_{\text{HCOOH}}, F_{\text{HCOOH}}, \) and \( F_{\text{CO}_2}, F_{\text{CO}_2} \), refer to inlet and outlet flow rates for HCOOH and \( \text{CO}_2 \) respectively. \( G_{\text{HCOOH}} \) is rate of formic acid production at cathode when current is passed. \( R_{\text{CO}_2} \) is rate of \( \text{CO}_2 \) consumption in the reaction. Here, \( F_{\text{HCOOH}} \) is zero as no formic acid is sent into the cathode side. The rate of formic acid generation is given by Faraday’s law:

\[
G_{\text{HCOOH}} = \frac{I}{4F}\eta_F
\]

The partial pressures of HCOOH and \( \text{CO}_2 \) are given by:

\[p_{\text{HCOOH}} = \frac{N_{\text{HCOOH}}RT}{V_c}\]

\[p_{\text{CO}_2} = \frac{N_{\text{CO}_2}RT}{V_c}\]

where \( V_c \) is the cathode volume. Total cathode pressure is given as:

\[P_c = p_{\text{CO}_2} + p_{\text{HCOOH}}\]

Mole fraction of formic acid (\( y_{\text{HCOOH}} \)) can be calculated by \( \frac{F_{\text{HCOOH}}}{P_c} \). Cathode outflows are given by:

\[
F_{\text{total,co}} = F_{\text{CO}_2o} + F_{\text{HCOOH}o}
\]

where, \( F_{\text{total,co}}, F_{\text{CO}_2o} \) and \( F_{\text{HCOOH}o} \) are the total, \( \text{CO}_2 \) and formic acid outflows at cathode respectively.

\[
F_{\text{HCOOH}o} = y_{\text{HCOOH}}F_{\text{co}}
\]

\[
F_{\text{CO}_2o} = k_{co}(P_c - P_o)
\]

where, \( k_{co} \) is the cathode outflow coefficient and \( P_o \) is the ambient pressure at exit. Equation 26 can be integrated over time and \( F_{\text{HCOOH}o} \) is calculated using the above equations.

**Voltage Ancillary**.—Voltage is applied to \( \text{CO}_2 \) reduction cell and depends on the operating conditions; the cell draws a current from the source and attains a steady state value. The operating voltage of the cell is given by adding open circuit voltage and losses, namely, ohmic, concentration and activation. For calculation purposes, concentration loss has been neglected. Thus, the operating voltage (\( V_T \)) is given by:

\[V_T = V_{oc} + V_{act} + V_{ohmic}\]
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where, \( V_{OC} \) is the open-circuit voltage, \( V_{act} \) is the activation overpotential and \( V_{ohmic} \) is the ohmic voltage loss. \( V_{OC} \) is given by the Nernst equation for the reaction shown by Eq. 14:

\[
V_{OC} = E_0 + \frac{RT}{2F} \ln \left( \frac{a_{HCOOH}a_{O_2}^{0.5}}{a_{H_2}a_{PcO_2}} \right) \tag{33}
\]

where, \( E_0 \) is the standard redox potential for the reaction in Eq. 14, \( a_{HCOOH} \) and \( a_{O_2} \) are the activities for formic acid and water respectively. \( E_0 \) is taken from literature or may be calculated as: \( E_0 = \frac{\Delta G}{2F} \), where, \( \Delta G \) is the Gibbs free energy for the reaction (Eq. 14). \( V_{act} \) can be calculated as: \( V_{act} = \frac{RT}{2 \alpha F} \ln \left( \frac{i}{i_0} \right) \) \tag{34}

where, \( \alpha \) is the charge transfer coefficient, \( i \) is the cell current density and \( i_0 \) is the exchange current density. Ohmic loss can be calculated as:

\[
V_{ohmic} = iR_{ohm} \tag{35}
\]

where, \( R_{ohm} = \frac{\sigma}{h} \), and \( R_{ohm} \) is the ohmic resistance between the two electrodes, \( t_m \) is the thickness of the membrane electrolyte and \( \sigma_m \) is the conductivity of the membrane electrolyte which is given as:\( \sigma_m = (0.00514 \lambda_m - 0.00326) e^{(1268(\frac{1}{\lambda_m} - \frac{1}{\lambda})}} \) \tag{36}

where, \( \lambda_m \) is the water content of the membrane electrolyte discussed earlier. Adding Eq. 33, 34 and 35, the total external voltage bias, \( V_T \) is calculated.

Now, as discussed earlier, voltage for the ECR cell is provided by the PV cells in series together. The two systems (PV cell and ECR cell) need to be integrated together, which is performed by connecting PV system block to ECR cell block by the current signal arm. The input ports to the complete system block are solar irradiation and \( \nu \) are the input powers to the ECR cell. The output power ratio of the ECR cell to the PV cell is given as:

\[
\eta_{ECR} = \frac{P_{ECR}}{P_{PV}} \]

where, \( P_{ECR} \) is the power generated by the ECR cell and \( P_{PV} \) is the power generated by the PV cell. The efficiency of the ECR cell is given as:

\[
\eta_{ECR} = \frac{P_{ECR}}{P_{ECR} + P_{PV}} \]

where, \( P_{ECR} \) is the power generated by the ECR cell and \( P_{PV} \) is the power generated by the PV cell. The efficiency of the ECR cell is given as:

\[
\eta_{ECR} = \frac{P_{ECR}}{P_{ECR} + P_{PV}} \]

The semiconductor catalysts can be either n-type/p-type or a combination of both. The choice of semi-conductor should be made carefully. Nakabayashi et al.\(^{48}\) first reported hydrogen evolution through photo-electrochemical reduction of water on TiO\(_2\) surface. Hematite and TiO\(_2\) both have shown promising results for water splitting.\(^{48-52}\) Hematite offers advantages in the form of suitable band-gap energy (2.0 eV), can use a large part of available spectrum and is chemically stable and resistant to photo-corrosion. Moreover, it is a low cost material and abundantly available. Hematite suffers from high loss due to electron-hole recombination and there are ways, such as thermal oxidation, to mitigate the problem by producing high aspect, nano-structured iron oxide electrodes.\(^{44}\) On the other hand, bandgap of TiO\(_2\) is 3.2 eV for which only UV radiation is suitable for electron-hole pair creation. UV radiation accounts for just 4% of the solar radiation energy while visible light contributes \( \sim 50\% \).\(^{47}\) TiO\(_2\) suffers from rapid recombination of electron-hole and dominant backward reaction. For the aforementioned reasons, hematite is considered as electrode for modeling of PECR in this study.

The photo-electrochemical water splitting model given by Andrade et al.\(^{53}\) has been modified for modeling PECR cell. Operating photo-electrochemical cell for CO\(_2\) reduction is governed by the kinetics of charge carriers and reactions, which take place at the two electrodes. Photons with energy greater than the bandgap (\( h\nu > V_F \)) generate electron hole pairs in the semiconductor (SC).

\[
2h\nu + SC \rightarrow SC (2e^- + 2h^+) \tag{37}
\]

Holes oxidize water to oxygen at the semiconductor-electrolyte interface (anode):

\[
2h^+ + H_2O \rightarrow 2H^+ + 0.5O_2 \tag{38}
\]

The photo-generated electrons transported to cathode reduce carbon dioxide to formic acid. Side reaction is ignored here for modeling purposes.

\[
CO_2 + 2e^- + 2H^+ \rightarrow HCOOH \tag{39}
\]

**Photo-electrochemical Reduction Cell.**—The photo-electrochemical reduction of CO\(_2\) consists of a semiconductor such as iron oxide (Fe\(_2\)O\(_3\))-hematite or TiO\(_2\)\(^{45-50}\) for water photo-oxidation and a counter electrode for CO\(_2\) reduction (e.g. In/Sn/Hg). The two electrodes are placed in an aqueous electrolyte. When exposed to sunlight, the semiconductor absorbs photons with energy (\( h\nu \)) larger than the band-gap (\( V_F \)) generating electron-hole pairs (Fig. 7). The holes have oxidation potential and oxidize water to oxygen and protons, while the electrons are routed through the external circuit to reduce carbon dioxide to formic acid with the help of photons (Fig. 7).

The semiconductor catalysts can be either n-type/p-type or a combination of both. The choice of semiconductor should be made carefully. Nakabayashi et al.\(^{48}\) first reported hydrogen evolution through photo-electrochemical reduction of water on TiO\(_2\) surface. Hematite and TiO\(_2\) both have shown promising results for water splitting.\(^{48-52}\) Hematite offers advantages in the form of suitable band-gap energy (2.0 eV), can use a large part of available spectrum and is chemically stable and resistant to photo-corrosion. Moreover, it is a low cost material and abundantly available. Hematite suffers from high loss due to electron-hole recombination and there are ways, such as thermal oxidation, to mitigate the problem by producing high aspect, nano-structured iron oxide electrodes.\(^{44}\) On the other hand, bandgap of TiO\(_2\) is 3.2 eV for which only UV radiation is suitable for electron-hole pair creation. UV radiation accounts for just 4% of the solar radiation energy while visible light contributes \( \sim 50\% \).\(^{47}\) TiO\(_2\) suffers from rapid recombination of electron-hole and dominant backward reaction. For the aforementioned reasons, hematite is considered as electrode for modeling of PECR in this study.

The photo-electrochemical water splitting model given by Andrade et al.\(^{53}\) has been modified for modeling PECR cell. Operating photo-electrochemical cell for CO\(_2\) reduction is governed by the kinetics of charge carriers and reactions, which take place at the two electrodes. Photons with energy greater than the bandgap (\( h\nu > V_F \)) generate electron hole pairs in the semiconductor (SC).

\[
2h\nu + SC \rightarrow SC (2e^- + 2h^+) \tag{37}
\]

Holes oxidize water to oxygen at the semiconductor-electrolyte interface (anode):

\[
2h^+ + H_2O \rightarrow 2H^+ + 0.5O_2 \tag{38}
\]

The photo-generated electrons transported to cathode reduce carbon dioxide to formic acid. Side reaction is ignored here for modeling purposes.

\[
CO_2 + 2e^- + 2H^+ \rightarrow HCOOH \tag{39}
\]

**Figure 6.** Matlab Simulink model for CO\(_2\) electro-reduction cell in integration with solar cells in series.

**Figure 7.** Schematic representation of photo-electrochemical cell used in modeling. Semiconductor-conductive support interface, at \( x = 0 \), and Hg electrode, at \( x = b \), define the limits of the PECR cell. Semi-conductor/photo-catalyst exists from \( x = 0 \) to L. Electrolyte fills the gap between \( x = L \) and \( x = b \). \( V_{bias} \) is provided from solar photovoltaic cells.
Electrons traveling through the external circuit constitute the cell current. If current-voltage characteristics can be modeled for PECR, we can use the model developed for electro-reduction cell to calculate the formic acid production rate from PECR of CO₂.

Flux of electrons arising out of the semiconductor layer (Fig. 7) constitutes the electric current. Here, area of interest is the region from \( x = 0 \) to \( L \), where the semiconductor substrate lies. Continuity equation for electrons in this region is given by:

\[
-\frac{\partial j_e}{\partial x} + G_e (x) - R_e (x) = \frac{\delta n_e}{\delta t}
\]

[40]

where, \( j_e \) is the flux of electrons in the \( x \) direction, \( G_e \) and \( R_e \) are the generation and relaxation rates of electrons respectively and \( n_e \) is the electronic density. Relaxation term is taken to account for recombination of electrons with holes. The flux of electrons is governed by both diffusion and macroscopic electric field (\( E \)) existing in the cell. Thus,

\[
j_e = -D_e \frac{\delta n_e}{\delta x} - \mu_e n_e E
\]

[41]

where, \( D_e \) is the electronic diffusion coefficient and \( \mu_e \) is the electronic mobility. First term on the R.H.S in Eq. 41 governs transport under electric field.

In Eq. 42, \( \eta_{inj} \) is the electron injection efficiency, \( \beta_{phabs} \) is the photon absorption coefficient and \( \eta_{phabs} \) is the photon intensity. \( \eta_{inj} \) gives the number of electrons generated per absorbed photon with energy \( h\nu > V_e \). \( \beta_{phabs} \) determines how far sunlight penetrates the semiconductor material. Higher value of \( \beta_{phabs} \) denotes greater solar radiation absorption. In Eq. 43, \( k_e \) is the relaxation constant and \( \Delta n_e = n_e - n_{eq} \), where \( n_{eq} \) is the dark equilibrium electron density.

\[
n_{eq} = N_{CB} \left( e^{-\left( E_{CB} - E_{F}\right) / k_B T} \right)
\]

[44]

where,

\[
N_{CB} = \frac{2 \pi m_e^{3/2} k_B T}{h^2}
\]

[45]

In Eq. 44, \( N_{CB} \) is the effective density of states in the conduction band, \( k_B \) is the Boltzmann constant, \( E_{CB} \) is the conduction band potential and \( E_{RED\text{OX}} \) is the redox potential. In Eq. 45, \( m_e^{*} \) is the effective mass of electron and \( h \) is the Planck’s constant. Substituting Eq. 45, 44 in 43, and then plugging Eq. 41, 42 and 43 in Eq. 42, one may obtain:

\[
-\frac{D_e}{\varepsilon_0} \frac{\partial^2 n_e}{\partial x^2} + \mu_e E \frac{\partial n_e}{\partial x} + \mu_n \epsilon \frac{dE}{dx} + \eta_{inj} \beta_{phabs} I_0 \left(e^{-\beta_{phabs} x} \right)
\]

\[\frac{\delta n_e}{\delta t} = \frac{\delta n_e}{\delta t}
\]

[46]

where, \( \beta_{phabs} \) being the mean time before electron recombine with holes. For solving Eq. 46, steady state condition is assumed resulting \( \frac{\delta n_e}{\delta t} \to 0 \). Here, one needs the value of \( E \) and \( \frac{dE}{dx} \) and boundary conditions at \( x = 0 \) and \( x = L \). \( E \) is related to charge carrier density by Poisson’s equation:

\[
d\frac{d^2 \phi}{dx^2} = \frac{q n_{int}}{\varepsilon_0} \left( \frac{q \phi}{k_B T} \right)
\]

[47]

where,

\[
n_{int} = (N_{CB} N_{VB})^{0.5} e^{\frac{q \phi}{k_B T}}
\]

[48]

Here, \( n_{int} \) is the intrinsic carrier concentration, \( \epsilon \) is the relative permittivity and \( \epsilon_0 \) is the dielectric constant. In Eq. 47, \( N_{VB} \) is the effective density of states in the valence band. \( E_f \) is the semi-conductor bandgap energy. Equation 47 can be solved numerically by discretization, which involves solving the given equation for a finite number of numerical values at regular intervals in the given function domain. It is assumed that \( E = 0 \) outside the cell, i.e., \( E = 0 \ at \ x = 0 \ and \ x = b \). Thus, discretizing Eq. 47 in the range, \( x = 0 \ and \ x = b \), one can extract the values of \( E \) and \( \frac{dE}{dx} \) at regular intervals between, \( x = 0 \ and \ x = L \). Now, boundary conditions for Eq. 46 can be given as:

\[
j_e^e = j_e^c at \ x = 0
\]

[49]

\[
\delta n_e / \delta x = 0 at \ x = L
\]

[50]

In Eq. 49 above, \( j_e^e \) and \( j_e^c \) denote electron flux just to left and just to right of \( x = 0 \) and this boundary condition ensures continuity of electronic flux where,

\[
j_e^c = j_e^e at \ x = 0^-
\]

[51]

\[
j_e^c = -D_e \frac{\delta n_e}{\delta x} - \mu_e n_e E at \ x = 0^+
\]

[52]

In Eq. 51, \( J_{cell} \) is the net cell current density and can be found by writing Butler-Volmer equation for half-cell reaction at cathode. Equation 51 represents balance of photo-generated charge carriers and electrons supplied by the external voltage since at steady-state, Eq. 51 corresponds to the net cell current density, \( J_{cell} \). Equation 52 is same as Eq. 41 evaluated at \( x = 0^+ \). Equation 50 accounts for the fact that there is no flow of electrons from the semiconductor to the electrolyte at the interface. Now \( J_{cell} \) is given by the Butler-Volmer equation for cathode:

\[
J_{cell} = J_0 \left(e^{\frac{n_{int} - (1-\alpha) \eta_{PH}}{n_F}} - e^{\frac{1-\alpha - \eta_{PH}}{n_F}} \right)
\]

[53]

where, \( J_0 \) is exchange current density, \( \alpha \) is the transfer coefficient, \( n \) is the number of electrons in the redox reaction (\( n = 2 \)) and \( \eta_{PH} \) is the activation over-potential at cathode. Activation over-potential is the extra voltage required to be supplied so that the reaction can proceed at a desired rate, \( \eta_{PH} \) can be found out by writing an energy balance for the complete cell as:

\[
E_{Bias} + E_f - E_{E_f} - \Delta E_{F} = \frac{\Delta G}{n_F} + \eta_{c} + \eta_{ohmic}
\]

[54]

where, \( E_{Bias} \) is the external voltage bias applied, \( E_f \) is the semiconductor band-gap, \( E_{E_f} \) is the band bending potential and \( \Delta E_{F} \) is the variation in the Fermi level potential. \( \frac{\Delta G}{n_F} \) is the standard redox potential, \( \eta_{c} \) is the activation over-potential at anode, \( \eta_{ohmic} \) is the ohmic voltage loss. As mentioned earlier, we have neglected the concentration loss here. \( E_f \) arises because some energy is lost when electrons travel from the generation point in the semiconductor to the electrode. \( \Delta E_f \) arises from difference between the conduction band edge energy in the bulk and in the Fermi level. \( E_f \) can be found out by:

\[
E_f = E_f (x = 0) - E_{fb}
\]

[55]

Here, \( E_f \) is the Fermi energy level and \( E_{fb} \) is the flatband potential.

\[
\Delta E_{F} = E_f (x = 0) - E_{CB}
\]

[56]

Anodic overpotential is given by:

\[
\eta_{a} = E_{VB} - E_{H_{2}O} (O_2)
\]

[57]

In Eq. 57, \( E_{VB} \) is the valence band potential and \( E_{H_{2}O} (O_2) \) is the water reduction potential. Lastly, ohmic losses can be accommodated by:

\[
\eta_{ohmic} = J_{cell} A_{PEC} R_{ohmic}
\]

[58]
Eq. 58 in Eq. 54, we can solve for \( \eta_e \) in terms of \( J_{cell} \). Equation 53 is solved by using an iterative procedure employing Newton-Raphson Method.

Once \( J_{cell} \) is known to us, we can solve Eq. 46 by using Eq. 49, 50, 51 and (52) by using shooting method.

Total system integration for second configuration is achieved by integrating PV cell block with PECR cell block in a similar fashion as done earlier for ECR cell.

### Results and Discussion

**Solar photovoltaic cell.**—Solar photovoltaic current-voltage (i-V) characteristics for polycrystalline Si cells simulated in MATLAB/Simulink as described through Fig. 3, match closely with the results obtained in literature. At STC, the open circuit voltage is recorded as \( \sim 0.585 \) V and short circuit current to be \( \sim 3.8 \) A as shown in Fig. 8. The data predicted closely matches with the technical specifications provided in literature and by various manufactures for Solarex MSX60 PV panel. Though the single-diode model employed in the modeling is relatively simpler as compared to other sophisticated models available in literature, its verification through data provided by the manufacturers makes it robust and trustworthy. Figure 9 explains the variation of power delivered by the solar module with voltage at different values of solar irradiation. It can be seen that at \( T = 308 \) K, the power extracted from the cell varies before achieving a maxima at 1.668 W (\( G = 1000 \) W/m\(^2\)). The \( V_{MPP} \) obtained is 0.475 \( V \) and \( I_{MPP} \) 3.51 A, which are close to the reference values taken for modeling. Peak efficiency of the cell obtained is \( \sim 16.68\% \) which falls within the experimentally reported range. Fill factor calculated is \( \sim 0.74 \) (STC), which is acceptable for commercially available solar cells. These values obtained further substantiate the findings and the model employed. Though the power derived from the solar cell falls with decreasing solar irradiation, its efficiency remains almost constant, as the simulated data show.

Model validation has been done at STC but it holds across a range of solar irradiation values and temperatures. The amount of solar irradiation received is \( \sim 1366 \) W/m\(^2\) (solar constant) at the periphery of the earth’s atmosphere. On a clear day when the sunlight falls perpendicular to the surface of the photo-voltaic module, the irradiation received is \( \sim 1000 \) W/m\(^2\). However, taking into account light absorption, diffusion, lower intensity of sunlight in the morning and evening, the irradiation is close to 400 W/m\(^2\) on a daily average basis. Moreover, the temperature of the module is not constant as all the incident light is not spent into generating photo-current. Heat is also generated in the solar cell. Therefore, it is important to study i-V characteristics over a range solar irradiation values and temperatures (Fig. 10, 11). It can be seen from Fig. 10 that the current obtained for a particular voltage falls as the solar irradiation received decreases. Thus, it is expected that lower current values and lower power is generated on a cloudy day as compared to STC. This is important for devising practical use for solar modules since performance falls considerably with irradiation.

At higher temperatures, the conductivity of semi-conductor material increases i.e., bandgap shrinks. The electric field at the junction is reduced because the available charge is balanced within the material. This leads to charge separation which further leads to lower voltages across the cell. The effect of temperature on i-V characteristics is shown in Fig. 11. While the current value slightly increases owing to increase in electronic mobility, voltage falls due to charge separation. Since the fall in voltage is more than the rise in current value, this leads to lower power produced from the solar module at higher temperatures. The power versus voltage curves are shown in Fig. 12. Thus, it is important to keep temperature in control to extract maximum power.

![Figure 8. i-V characteristics of a PV cell at G = 1000 W/m\(^2\) and 298 K (STC).](image)

![Figure 10. i-V characteristics for PV cell at G = 1000 W/m\(^2\) and 308 K.](image)
Figure 12. Power-voltage characteristics for a PV cell at different temperatures and irradiance 1000 W/m².

Figure 13. i-V characteristics for a PV cell at G = 400 W/m² and 308 K.

Figure 14. i-V characteristics for CO₂ ECR cell at various temperatures.

Figure 15. Contribution of various overvoltages to cell polarization at different current values passing through the CO₂ ECR cell.

Figure 16. HCOOH production rate from ECR cell with temperature at different irradiance.

In this study, i-V characteristics at G = 400 W/m² and 308 K is considered (Eq. 11) accommodating real-time weather conditions. Figure 13 shows i-V characteristics for such kind of condition.

**CO₂ Electro-chemical Reduction Cell.—** CO₂ reduction cell Equations 12–36 have been modeled in Simulink (Fig. 5). Power output from solar cell is input into a CO₂ electro-reduction cell, integrated together as shown in (Fig. 6). The modeling calculation of CO₂ ECR shows that electro-chemical splitting of water and reduction of CO₂ requires an external bias of ∼1.9 V. Figure 14 shows the effect of temperature on ECR cell voltage and current. The increase in cell temperature results in cell performance enhancement due to decrease in cell voltage for a given value of cell current. This leads to less consumption of power from solar cells for a given rate of formic acid production. This is because of lower ohmic overvoltage at higher temperature.

A comparison of contribution of various overpotentials to total cell voltage is shown in Fig. 15. It is seen that the contribution of ohmic overvoltage almost doubles, while, contribution of activation overvoltage does not change much with the increase in current. Therefore, choice of membrane electrolyte material becomes extremely important to keep $V_{\text{ohmic}}$ low.

Solar cells in series provide power to CO₂ ECR reduction cell and the amount of formic acid produced is plotted against solar irradiation and temperature in Fig. 16 and 17, respectively. Formic acid production rate falls with increasing temperature at constant solar irradiation. This is due to lower power production in the solar cells. However, at power from the cell.
a particular temperature, formic acid production increases with increasing solar irradiation, due to higher power production from solar cells.

**Photo-electrochemical Reduction Cell.**—The photo-electrochemical assisted reduction of CO₂ receives energy from two sources: one, directly from sun and the second from solar cells in the form of externally applied bias. The i-V curve for the cell is shown in Fig. 18. Initially, at low voltages, there is negligible current which rises abruptly and almost linearly with voltage there-on. The charge transfer coefficient (α) plays a crucial role in governing the i-V characteristics as seen in Fig. 19. The current density decreases with decrease in α values at given voltage. Hence, proper choice of electrode material, electrolyte, pH, catalyst should be made since α has a drastic impact on the i-V curve. However, the role of temperature is insignificant as seen in Fig. 20.

**Electrochemical Reduction Cell and Photo-ElectroChemical Reduction cell.**—Comparison of ECR and PECR of carbon dioxide is done by plotting formic acid production rate in each with number of PV cells in series to provide the required voltage. Calculations show that operating the PECR cell at an external bias of 1.425 V produces formic acid at the same rate as ECR cell operated at 1.92 V but requires 30% less area. This is due to less number of solar cells required and less area of PECR cell. Hence, PECR cell would result in compact devices. Figure 21 shows HCOOH production and area required for both ECR and PECR for same number of solar cells employed in each. Since voltage requirement in PECR is less than ECR, HCOOH production is equal or greater for PECR. For same HCOOH production, area requirement for PECR is up to 30% less. This confirms the hypothesis that PECR should be more efficient than ECR of CO₂.

**Conclusions**

The model developed here predicts the behavior of PV, ECR and PECR cell under different environment conditions. The PV model successfully incorporates variation of cell current and voltage and predicts their values with changing solar irradiation and temperature. Power delivered by the PV cell decreases with decreasing solar irradiation and increasing temperature. CO₂ ECR cell performance decreases with increasing temperature, as voltage applied to sustain a current flow in the cell increases with decreasing temperature. Formic acid production rate increases with increasing solar irradiation and decreasing temperature of the PV cell. The i-V characteristics of the PECR cell show similar behavior as ECR cell, with voltage rising sharply after a certain voltage. Though temperature has minimal effect, transfer coefficient plays a dominant role in deciding i-V characteristics of ECR and PECR. PECR cell is more energy and area efficient than ECR cell, producing same amount of formic acid at a less voltage applied. The Simulink model developed in this study successfully predicts the dynamic behavior of this novel device, which holds the key for closing the CO₂ cycle in a sustainable way.
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List of Symbols

\[ A \] Electro-reduction cell area
\[ A_c \] Solar cell area
\[ A_{PEC} \] Area of the photo-electrochemical reduction cell
\[ a_i \] Activity of \( i \), where \( i = \) water, formic acid
\[ C_{m, anode} \] Concentration of water at anode surface of membrane electrolyte
\[ C_{m, cathode} \] Concentration of water at cathode surface of membrane electrolyte
\[ D_e \] Diffusivity of electron
\[ D_w \] Diffusivity of water in membrane electrolyte
\[ E_0 \] Standard redox potential
\[ E_B \] Band bending potential
\[ E_{Bias} \] External voltage bias
\[ E_{CB} \] Conduction band potential
\[ E_{CO_2/HCOOH} \] Standard reduction potential of \( CO_2 \) to formic acid
\[ E_F \] Fermi energy level
\[ \Delta E_F \] Variation in the Fermi level potential
\[ E_{fb} \] Flat band potential
\[ E_{ff} \] Efficiency
\[ E_{g} \] Semi-conductor bandgap energy
\[ E_{H_2O/O_2} \] Standard reduction potential of water
\[ E_{REDOX} \] Redox potential
\[ E_{VB} \] Valance band potential
\[ F \] Faraday’s constant
\[ F_F \] Fill factor
\[ F_{CO_2} \] Flow rate of \( CO_2 \) in cathode
\[ F_{CO_2} \] Flow rate of \( CO_2 \) out of cathode
\[ F_{HCOOH} \] Flow rate of formic acid out of cathode
\[ F_{HCOOH} \] Flow rate of formic acid in cathode
\[ F_{H_2O, out} \] Flow rate of water due to diffusion
\[ F_{H_2O, in} \] Flow rate of water due to electro-osmotic drag
\[ F_{H_2O, in} \] Flow rate of water in anode
\[ F_{H_2O, out} \] Flow rate of water out of anode
\[ F_{O_2} \] Flow rate of oxygen in anode
\[ F_{O_2} \] Flow rate of oxygen out of anode
\[ F_{total, co} \] Total molar flow rate out of cathode
\[ F_{total, oo} \] Total molar flow rate out of anode
\[ G \] Solar irradiation
\[ G_e \] Change in Gibbs free energy
\[ G_{HCOOH} \] Generation rate of formic acid
\[ G_{O_2} \] Generation rate of oxygen at anode
\[ h \] Planck’s constant
\[ h \] Holes in valance band of semi-conductor
\[ h \] Energy of the photon
\[ I \] CO\(_2\) electro-chemical reduction cell current
\[ I_0 \] Diode saturation current
\[ I_c \] Net current from the PV cell
\[ I_D \] Diode current
\[ I_{ph} \] Photo-current in the PV cell
\[ I_{SC} \] Short-circuit current in the PV cell
\[ i \] Electro-chemical reduction (ECR) cell current density
\[ i_0 \] Exchange current density
\[ J_{cell} \] Net current density
\[ J_e \] Flux of electrons
\[ k \] Electo-osmotic drag coefficient
\[ k_{an} \] Anode outflow coefficient
\[ k_{bo} \] Boltzmann constant
\[ k_{co} \] Cathode outflow coefficient
\[ k_e \] Relaxation constant
\[ m \] Diode quality factor of PV cell
\[ m_e ^* \] Effective mass of electron
\[ N_{CB} \] Effective density of states in the conduction band.
\[ N_i \] Moles of \( i \), where \( i = \) HCOOH, \( CO_2 \), \( H_2O \)
\[ N_{VB} \] Effective density of states in the valence band
\[ n_e \] Concentration of electrons in SC
\[ n_{eq} \] Dark equilibrium electron density
\[ n_{lat} \] Intrinsic carrier concentration
\[ P_0 \] Ambient pressure
\[ P_E \] Total pressure at anode
\[ P_T \] Total pressure at cathode
\[ P_{max} \] Maximum power generated in solar cell
\[ p_i \] Partial pressure of \( i = \) HCOOH, \( CO_2 \), \( H_2O \)
\[ q \] Charge
\[ R \] Gas constant
\[ R_e \] Relaxation rate of electrons
\[ R_{CO_2} \] Rate of \( CO_2 \) consumption in the reaction
\[ R_{ohmic} \] Resistance across the two electrodes in the ECR cell
\[ R_{ohmic} \] ohmic resistance across the two electrodes in the ECR cell
\[ R_S \] Series resistance in PV cell
\[ SC \] Semiconductor
\[ T \] \( CO_2 \) reduction cell temperature
\[ T_a \] Ambient temperature
\[ T_e \] Cathode temperature
\[ T_i \] Standard temperature
\[ T_{NOCT} \] Nominal operating cell temperature
\[ t \] Time
\[ t_m \] Thickness of the membrane electrolyte
\[ V \] Voltage across the solar cell
\[ V_a \] Anode voltage
\[ V_{act} \] Activation overpotential of ECR cell
\[ V_{Cathode} \] Cathode voltage
\[ V_f \] Semi-conductor band-gap
\[ V_{ohmic} \] Voltage across the \( CO_2 \) electro-reduction cell
\[ V_{ohmic} \] ohmic voltage loss in ECR cell
\[ V_{VC} \] Open-circuit voltage of ECR cell
\[ V_{VC} \] Open-circuit voltage of the PV cell
\[ V_T \] Voltage across the \( CO_2 \) electro-reduction cell
\[ X_0 \] Photon intensity
\[ Y_i \] Mole fraction of \( i \), where \( i = \) HCOOH, \( O_2 \)

Greek

\[ \lambda \] Water content of the membrane electrolyte
\[ \sigma \] Conductivity of the membrane electrolyte
\[ \mu \] Electronic mobility
\[ \eta_{inj} \] Electron injection efficiency
\[ \rho_{abs} \] Photon absorption coefficient
\[ \xi \] Mean time before electronic recombination
\[ \varepsilon \] Relative permeability
\[ \varepsilon_0 \] Dielectric constant
\[ \eta_0 \] Activation overpotential at anode
\[ \eta_c \] Activation overpotential at cathode
\[ \eta_{ohmic} \] ohmic voltage loss
\[ \xi \] Voltage temperature coefficient of the PV cell
\[ \sigma \] Current temperature coefficient of the PV cell

References

1. S. Ritter, Chem. Eng. News, 85, 11 (2007).
2. D. Rowe, New Sci., 2645, 32 (2008).
3. G. Centi and S. Perathoner, Catal. Today, 148, 191 (2009).
4. International Energy Agency (IEA), World Energy Outlook, (2016).
5. G. Centi and S. Perathoner, Stud. Surf. Sci. Catal., 153, 1 (2004).
6. C. Song, W. Zhang, Y. Pei, G. Fan, and G. Xu, Atmos. Environ., 40, 1957 (2006).
7. D. Cassada, Y. Zhang, D. Snow, and R. Spalding, Anal. Chem., 72, 4654 (2000).
8. M. Itar, J. Univ. Chem. Technol. Metall., 191 (2007).
9. D. DaBos, Encycl. Electrochem., 7A, 202 (2006).
10. M. Gattrell, N. Gupta, and A. Co, J. Electroanal. Chem., 594, 1 (2006).
11. Hori, Handle Fuel Cells, 2, 720 (2003).
12. G. Centi, S. Perathoner, G. Wine, and M. Gangeri, Green Chem., 9, 671 (2007).
13. G. Centi and S. Perathoner, Top. Catal., 52, 948 (2009).
14. O. Varghese, M. Paulose, T. LaTempa, and C. Grimes, Nano Lett., 9, 731 (2009).
C. Genovese, C. Ampelli, S. Perathoner, and G. Centi, Chem. Eng. Trans., 32, 289 (2013).

16. H. Flaisher, R. Tenne, and M. Halmann, J. Electroanal. Chem., 402, 97 (1996).

17. R. Chaplin and A. Wrugg, J. Appl. Electrochem., 33, 1107 (2003).

18. Neetu Kumari, M. Ali Haider, and Suddhasatwa Basu, Mechanism of Catalytic and Electrocatalytic CO2 Reduction to Fuels and Chemicals (Ch 6) in Electrochemical Reduction of Carbon Dioxide, Fundamentals and Technologies, Ed. Jinli Qiao, Yuyu Liu, and Jiujun Zhang, page 267, CRC Press 2016.

19. Garima Gag and Suddhasatwa Basu, Electrochimica Acta, 177, 359 (2015).

20. Suddhasatwa Basu, Debasish Biswal, and Amol Shegonkar, J CO2 Utilization, 18, 80 (2017).

21. M. Blas, J. Torres, E. Prieto, and A. Garcia, Renewable Energy, 25, 371 (2002).

22. F. Marangio, M. Santarelli, and M. Cali, Int. J. Hydrogen Energy, 31, 29 (2006).

23. S. Khan and J. Bockris, J. Phys. Chem., 88, 2504 (1984).

24. A. Bard, J. Phys. Chem., 86, 172 (1982).

25. L. Andrade, T. Lopes, H. Ribeiro, and A. Mendes, Int. J. Hydrogen Energy, 36, 175 (2011).

26. K. Takahisa, T. Kojima, K. Nakamura, T. Koyanagi, and T. Yanagisawa, Sol. Energy Mater. Sol. cells, 49, 179 (1997).

27. B. Parida, S. Iniyan, and R. Goic, Renewable and Sustainable Energy Rev, 15, 1625 (2011).

28. J. Gow and C. Manning, IEEE Proceedings of Electric Power Applications, 146, 193 (1999).

29. W. Xiao, W. Danford, and A. Capel, 55th Annual IEEE Power Electronics Specialists Conference, 1950 (2004).

30. R. Chenni, M. Makhfouf, T. Kerbach, and A. Bouzid, Energy, 32, 1724 (2007).

31. A. Celik and N. Acikgoz, Appl. Energy, 84, 1 (2007).

32. F. Longatt, 2DO Congreso iberoamericano de estudiantes de ingeniería eléctrica, electrónica y computación, (2009).