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# Mathematical modelling of a photoelectrochemical anion exchange membrane electrolyser for sustainable hydrogen production

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### ABSTRACT

Solar hydrogen production using a photoelectrochemical anion exchange membrane reactor is vital to reduce our dependence on fossil fuels. Anion exchange membranes use electrocatalysts based on low-cost earth metals. This paper provides a mathematical model to understand the influence of operating parameters on a photoelectrochemical anion exchange membrane reactor using Engineering Equation Solver (EES). It is used to estimate the performance of a reactor with hydrogen mass flow rate, energy and exergy efficiency. The results indicate the highest hydrogen production of 75.92  $\mu$ g/s at a solar irradiation flux of 600 W/m<sup>2</sup>. Overall energy efficiency decreases as the photocathode illumination area increases while the mass flow rate of hydrogen increases. Moreover, with the change in illuminated area from 0.04 to 0.08 m<sup>2</sup>, the overall efficiency decreases from 12.32% to 10.76%. Mathematical modelling indicates that the mass flow rate of hydrogen is directly proportional to the solar irradiation flux, illuminated area and quantum efficiency.

### 1. Introduction

Energy plays a vital role in our daily lives, affecting the economy and our growing population. Global energy demand and costs have risen dramatically due to geopolitical instability, energy demand mismatch and our reliance on fossil fuels [1]. As countries develop, so does the demand for energy to power daily activities [2]. Global energy consumption increases the concentration of carbon dioxide, which is associated with fossil fuel use [3,4]. To reduce the impact of greenhouse gas emissions, there is a persistent need to transition to renewable energy sources [5]. They can assist in gradually phasing out carbon-intensive fossil fuels and mitigate climate change by lowering the emissions [6, 7]. Renewable technology advancements and energy efficiency measures can help to ensure a more sustainable energy future [8]. In the following years, renewable energy is envisaged to grow. Solar energy is expected to account for 60% of future renewable growth due to its ease of access. Furthermore, maintaining a consistent energy supply will accelerate the transition to a lower carbon economy, resulting in emission reductions to meet the goals of the Paris Agreement [9].

Solar-based hydrogen production technologies offer a compelling

possibility for a sustainable energy future [10]. Hydrogen has a high heating value (141.9 MJ/kg) and emits no direct CO<sub>2</sub> emissions [11]. Currently, the standard method of hydrogen generation is from fossil fuels using steam methane reforming (SMR) [12]. Solar-based hydrogen production technologies use solar irradiation to split water molecules into oxygen and hydrogen fuel [13]. These technologies are roughly classified into three main types: photocatalysis (PC), photoelectrochemical (PEC) and PV-connected electrolyser (PV-EC) [14]. In PC, water-splitting semiconductor particles are dispersed in an aqueous solution. These semiconductor particles (like TiO<sub>2</sub> and SrTiO<sub>3</sub>) absorb sunlight to generate charge carriers. These carriers then migrate to the semiconductor's surface and undergo water reduction or oxidation reactions [15]. However, certain wide band-gap semiconductors have a narrow absorption range for light wavelengths [13]. This characteristic results in poor light utilisation efficiency, which reduces solar-to-hydrogen (STH) efficiency. Another complication is the necessity to effectively separate the produced H<sub>2</sub> and O<sub>2</sub> in the same colloidal suspension [16]. However, PV-EC water splitting has a higher STH efficiency. Commercial PV modules and electrolysers can be coupled into a system to generate H<sub>2</sub> [17]. While scaling up PV-electrolysis for water

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splitting is straightforward, the economic viability of hydrogen production is uncertain when compared to SMR, owing to the high costs involved with PV modules and electrolysers [13].

Despite immense advances in solar-based water splitting, a significant barrier remains to develop an affordable integrated device with comparable solar-to-hydrogen (STH) efficiency [18]. Photoelectrochemical (PEC) systems are composed of absorbers with catalysts and use solar radiation to activate the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) [19]. Using solar energy, the absorber semiconductor generates an electron-hole pair. In addition, the band bending at the electrolyte semiconductor contact causes the segregation of charge carriers [14]. Under standard conditions, water splitting requires a potential of 1.23 eV/electron or an energy  $\Delta g_0$  of +237 (kJ/mol) [19]. A PEC device can utilise a single photoanode, a single photocathode and multiple photoabsorbers (tandem) [15]. Membranes are also an essential component in the PEC reactors because they allow the selective transport of ions. They enable the electrochemical reactions to proceed efficiently, maximising hydrogen generation and minimising recombination reaction [20]. Significant advances in anion exchange membranes (AEM) have effectively overcome the limits of proton and alkaline exchange membranes. AEM reduces the possibility of gas crossover and differential pressure between the electrodes [21]. It also has lower ohmic overvoltage due to the reduced thickness. It is compatible with low-alkalinity electrolytes or deionised water [22]. Due to low alkalinity, utilising less expensive metal catalysts other than platinum is advantageous [23]. The AEM membranes are based on quaternary ammonia cation, which is highly stable and economical in alkaline environments [24,25]. Furthermore, it is predicted that only 10% of efficient photoelectrochemical (PEC) cells are spread over 1% of the earth's surface. It is expected to provide 36 TW of energy to meet the estimated world energy demand in 2050 [17].

Numerous studies have been conducted to enhance the performance of PEC reactors [13,15]. They are primarily concerned with semiconductor materials for optimal use of the solar radiation spectrum [17], membranes, electrolytes [26], and catalysts used in photoelectrodes [14]. As a result, developing an integrated system with enhanced STH and optimising the components can pave the way for a green and clean hydrogen production process [18]. Karaca et al. [27] investigated novel conic electrodes with a proton exchange membrane (Nafion) for photoelectrochemical hydrogen production. The anode was coated with TiO<sub>2</sub>, the cathode with Cu<sub>2</sub>O, and both electrodes submerged in 0.1 M KOH solution. Under illumination, the greatest hydrogen mass flow rate of 4.5 µg/s and maximum STH of 1.82% was achieved at a current density of 1.81 mA/cm<sup>2</sup>. Qureshy et al. [28] analysed the PEC hydrogen reactor using electrochemical modelling and fluid flow simulation techniques. The photocathode was dome-shaped and coated with Cu<sub>2</sub>O on grade 2 titanium, whereas the anode was made of SS304 and coated with TiO2. A Nafion 117 membrane (PEM) was placed between the electrodes. The overall energy efficiency was 4.9%, with a hydrogen production rate of 42.1 µg/s. Bicer et al. [29] assessed the environmental impact of ammonia synthesis using photoelectrochemical PEM assembly to produce hydrogen. The findings revealed that this technique might significantly reduce the overall environmental impact, equivalent to around half of current steam methane reforming-based ammonia manufacture technologies. Acar et al. [20] investigated the performance of a hybrid photoelectrochemical chloralkali reactor. The reactor converted industrial by-products into hydrogen, sodium hydroxide, and chlorine hydroxide. Moreover, the reaction produced 295 mL/h of hydrogen at 80 °C with an irradiation intensity of 1200 W/m<sup>2</sup>. A tandem photoelectrochemical cell with a Cu<sub>2</sub>O cathode and a Mo-doped BiVO<sub>4</sub> anode was investigated by Pan et al. [30]. This configuration attained an unassisted STH efficiency of 3%, the highest among oxide tandem cells. Li et al. [31] investigated a PEC tandem cell to drive unbiased water splitting using a TiO<sub>2</sub> nanorod array as a photoanode in combination with a nanotextured CuBi<sub>2</sub>O<sub>4</sub> photocathode. An STH efficiency of 1.23% was demonstrated for the PEC tandem cell. Jang et al. [32] studied the

development of a solution-based regrowth technique to reduce surface disorders in hematite photoanode. A Fe<sub>2</sub>O<sub>3</sub> photoanode with an a-Si photocathode in a tandem cell could attain an unbiased STH efficiency of 0.91%. Bedoya-Lora et al. [33] investigated a 2D Multiphysics model for a new PEC cell to examine photoelectrode materials under concentrated irradiation. They concluded that kinetic rates and charge transfer can be improved due to concentrated solar flux. Modestino et al. [18] studied the overall integration of components for photoelectrochemical water-splitting devices. They demonstrated that for stable, practical, sustainable and inexpensive PEC solar hydrogen generation, an amalgamation of modelling-based design guidelines, life cycle analysis, and techno economics is required. Kim et al. [34] conducted a technoeconomic analysis of AEM electrolysis for sustainable and green hydrogen production. They compared the catalyst and stack cost to be less expensive than proton exchange membranes. Also, the technology will be desirable if the AEM stack lifetime is equivalent to PEM. Karaca et al. [35] conducted an electrochemical investigation using PEM-based mathematical modelling of a PEC reactor. Their innovative design enables conical photoelectrodes to capture sunlight efficiently all day. With an energy efficiency of 6.3% and an exergy efficiency of 6.38%, they discovered that the rate of hydrogen synthesis was 47.1 µg/s. Qureshy et al. [28] also conducted a multicomponent mathematical modelling and simulation of a unique PEC reactor with PEM with a hemispherical-shaped photocathode. Energy efficiency of 4.9% was achieved with a hydrogen mass flow rate of 42.1 µg/s.

The literature indicates that substantial studies have been conducted on conventional anion exchange membrane electrolysers that are not photoelectrochemical. Also, the mathematical models for photoelectrochemical proton exchange membrane electrolysers for hydrogen production are well understood. However, mathematical modelling of photoelectrochemical anion exchange membrane electrolysers is relatively scarce in the open literature. This research focuses on photoelectrochemical anion exchange membrane reactors, which introduce complications like light absorption, charge carrier dynamics, and photocatalytic processes, as detailed in section 2.5. As a result, mathematical modelling is used to understand photoelectrochemical anion exchange membrane reactors better and contribute to creating a scalable and successful renewable energy system.

The objectives of the study are:

- To develop a mathematical model for a photoelectrochemical anion exchange membrane reactor.
- To understand the influence of operating parameters on the hydrogen mass flow rate and efficiency of the reactor.

### 2. System overview

The suggested model considers the primary physicochemical phenomena occurring in the PEC AEM reactor. This involves analysing how the components interact. The primary components of a reactor are photoanode, photocathode, AEM membrane, water feed, and electrolyte, as described in Fig. 1. The operating pressure and temperature in the current study have been set to ambient conditions. The fundamental equations include the Nernst equation, which describes the system's thermodynamics; the electrochemical reaction kinetics, given by the Butler-Volmer equation; and Ohm's law, which represents the electrical losses in the reactor. A few assumptions are considered in this model:

- i) Steady-state with constant system properties and isothermal conditions with uniform temperature distribution,
- ii) The electrolyte is considered as an ideal solution,
- iii) A homogeneous catalyst layer is assumed with uniform distribution across its entirety, facilitating the occurrence of no gas crossover between hydrogen and oxygen,
- iv) The reaction happens at the boundary between the catalyst and liquid gas diffusion layers.





We have used EES software, a widely used software package, to solve n nonlinear equations for n unknowns. The thermodynamic and electrochemical equations are solved using this software package, along with assumptions and inputs for the variables as described (Table 1).

# 2.1. Thermodynamic factors

Electrochemical reactions take place simultaneously at both anode and cathode electrodes [36]:

At anode:

$$2OH^{-}_{(aq)} \leftrightarrow H_2O + \frac{1}{2}O_{2(g)} + 2e^{-} \quad E_{0a} = 1.229V \quad [298K]$$
 1

At cathode:

$$2H_2O + 2e^- \leftrightarrow 2H_{2(g)} + 2OH^-_{(aq)}$$
  $E_{0c} = 0V$  [298K] 2

Table 1

PEC AEM geometry with physical and chemical parameters for modelling.

Faraday constant, [C mol <sup>-1</sup> ]	96 500
Universal gas constant, [J mol <sup>-1</sup> K <sup>-1</sup> ]	8.3145
Density of water, [kg/m <sup>3</sup> ]	1000
Viscosity of water, [Pa-s]	0.0011
Molar mass of water, [kg/mol]	0.018
Molar mass of hydrogen, [kg/mol]	0.002
Molar mass of oxygen, [kg/mol]	0.032
Diffusion coefficient of water [m <sup>2</sup> /s]	0.128
Operating temperature [K]	333
Operating pressure [Pa]	1.013*10^ (5)
Partial pressure of hydrogen [Pa]	0.5
Partial pressure of oxygen [Pa]	0.2
Partial pressure of water [Pa]	1
Membrane active area, A <sub>m</sub> [m <sup>2</sup> ]	0.005
Avogadro's number, NA [1/mol]	6.022*10^ (23)
Planck's constant, h [J-s]	6.626*10^ (-34)
Speed of light, c [m/s]	3*10^ (8)
Lower heating value of hydrogen, LHV <sub>H2</sub> [J/kg]	120.1*10^ (6)
Solar irradiance flux, Ir [W/m <sup>2</sup> ]	600
Quantum efficiency, φ	0.20
Incident wavelength, $\lambda_i$ [m]	500*10^ (-9)
Illumination area, A <sub>i</sub> [m <sup>2</sup> ]	0.08
Sun's temperature, T <sub>s</sub> [K]	5778
Ambient temperature, T <sub>0</sub> [K]	298
Chemical exergy of hydrogen, $ex_{ch}^{H_2}$ [kJ/mol]	236.249

The overall reaction is:

$$H_2O_{(l)} \leftrightarrow 2H_{2(g)} + \frac{1}{2}O_{2(g)}E_{rev}^0 = 1.229V$$
 [298K] 3

The net water electrolysis process involves a phase transition, where the liquid water molecules change state to form gaseous hydrogen and oxygen products [37]. The thermodynamic potential  $E_{rev}$  represents the thermodynamic component of the electrochemical reaction. It is affected by several factors, including water activity, operational temperature, and the partial pressures of the resulting gaseous products within the electrolyte solution. The Nernst equation is expressed as follows [28]

$$E_{rev} = E_{rev}^{0} + \frac{RT}{nF} ln \left( p_{H_2} \frac{p_{O_2}^{1/2}}{p_{H_2O}} \right)$$

where F Faraday's constant [96 500 As/mol], *R* is the universal gas constant [8.314 J/(mol-K)], *T* is the temperature [K], and *n* is the number of electrons involved. The equation accounts for a phase transition, where the reactants in the liquid state are converted into gaseous products.  $E_{rev}^0$  the minimum voltage required for an electrochemical process of water splitting is known as the reversible potential. It is described by the following equation [38]

$$E_{rev}^0 = 1.229 - 0.9 \times 10^{-3} (T - 298)$$

The following equation is used to evaluate the voltage loss in the electrolysis process [39]:

$$E_{cell} = E_{rev} + \eta_{act} + V_{ohm} + \eta_{diff}$$

where  $V_{ohm}$  total ohmic loss,  $\eta_{act}$  is the activation overpotential, and  $\eta_{diff}$  is the overpotential due to diffusion.

### 2.2. Kinetic effects

Based on reaction kinetics, the energy needed to overcome the activation energies of the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) is known as the activation overpotential or  $\eta_{act}$  [37]. The kinetic effect of water electrolysis is given by the Butler-Volmer equation and is represented by [39]

$$\eta_{act} = \frac{RT}{\alpha_a F} \arcsin h\left(\frac{j}{2j_{0,a}}\right) + \frac{RT}{\alpha_c F} \arcsin h\left(\frac{j}{2j_{0,c}}\right)$$

The following equation is used to describe the charge transfer coefficients [37].

$$\alpha_a = 0.0675 + 0.00095T$$
8

$$\alpha_c = 0.1175 + 0.00095T$$

# 2.3. Effects of resistance

The ohmic resistances in a PEC AEM reactor cell arise from the electrical resistances within the reactor components. These resistances can be described using Ohm's law. The total ohmic loss, represented by the voltage drop  $V_{ohm}$ , is expressed as a function of the current flowing through the cell and the effective resistance of the cell components [40]

$$V_{ohm} = (r_{KOH} + r_{mem})i$$

Where  $r_{mem}$  is the AEM membrane separator resistance [ $\Omega$ ],  $r_{KOH}$  is the resistance of dilute KOH electrolyte, and *i* is the current [A].

The resistance contribution from the electrolyte solution, which in this case is a dilute potassium hydroxide (KOH) feed solution, can be expressed as follows [37]:

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$$r_{KOH} = \frac{1}{\sigma_{KOH}} \left( \frac{d_{am}}{S_a} + \frac{d_{cm}}{S_c} \right)$$
 11

The ionic conductivity of the electrolyte is obtained from the modified correlation given by Ref. [41], which influences both the molar concentration  $m \pmod{m^3}$  and temperature T [K] of the electrolyte.

$$\sigma_{KOH} = \left(-2.04m - 0.0027m^2 + 0.005332mT + 207.2rac{m}{T} + 0.00105m^3 - 0.000004m^2T^2
ight)$$

The resistance of the anion exchange membrane (AEM) accounts for a significant portion of the total ohmic loss in AEM water electrolysis. The membrane resistance can be determined using the subsequent equation [28]:

$$r_{mem} = \left(\frac{\delta_m}{A_m \sigma_m}\right)$$
 13

In the given expression,  $\delta_m$  represents thickness [m] of the AEM,  $A_m$  denotes the total surface area of the membrane [m<sup>2</sup>], and symbolises conductivity of the membrane material, expressed in (S/m).

The conductivity of the membrane is influenced by both the degree of humidification and the operating temperature. A higher degree of humidification  $\lambda[mol_{H_2O} / mol_{SO_3}]$  and higher operating temperature T[K] generally lead to improved membrane conductivity and is given by Ref. [37]:

$$\sigma_m = (0.524\lambda - 0.318)e^{\left(1270 \times \left(\frac{1}{303}, \frac{1}{T}\right)\right)}$$
14

The membrane is regarded as completely hydrated in this model. For such cases, the humidification degree, represented by  $\lambda$ , is typically assumed to be within the range of 14–21. In this model, the value of  $\lambda$  is set to 18, which lies within the expected range for a fully hydrated AEM membrane.

### 2.4. Mass transfer dynamics

The diffusion overpotential addresses the management of mass transport constraints in PEC AEM  $\eta_{diff}$ . The electrochemical reaction in the water electrolysis process necessitates a constant source of water entering the system and the elimination of hydrogen and oxygen. However, at elevated current densities, the removal rate of H<sub>2</sub> and O<sub>2</sub> lags behind their production, leading to an accumulation that obstructs reaction sites [37], reducing the process's kinetics and efficiency. The Nernst equation may be used to quantitatively explain the phenomena, which represents a substantial mass transport constraint that is determined by the concentration of species at the membrane and electrode interface [42]:

$$\eta_{diff} = \frac{RT}{4F} ln \left( \frac{C_{O_2,mem}}{C_{O_2,mem,0}} \right) + \frac{RT}{2F} ln \left( \frac{C_{H_2,mem}}{C_{H_2,mem,0}} \right)$$
15

where  $C_{O_2,mem}$  and  $C_{H_2,mem}$  are the concentration of oxygen and hydrogen at the membrane electrolyte interface [mol/m<sup>3</sup>], and the subscript 0 indicates a reference working condition.

Because diffusion controls mass flow, Fick's Law may be used to predict the gas concentration at the electrolyte/membrane contact. This yields the following correlation [42]:

$$C_{O_2,mem} = \frac{p_a \left(\frac{\dot{n}_{O_2}}{\dot{n}_{O_2} + \dot{n}_{H_2O_a}}\right)}{RT_a} + \frac{\delta_a \dot{n}_{O_2}}{D_{eff,O_2/H_2O}}$$
16

$$C_{H_2,mem} = \frac{p_c \left(\frac{\dot{n}_{H_2}}{\bar{n}_{H_2} + \bar{n}_{H_2 o_c}}\right)}{RT_c} + \frac{\delta_c \dot{n}_{H_2}}{D_{eff,H_2/H_2 O}}$$
17

Here,  $T_c \& T_a$  and denote the temperatures at the cathode & anode [K],  $p_c \& p_a$  indicate the pressures at the cathode and anode [Pa],  $\delta_c$  and  $\delta_a$  refer to the thicknesses of the cathode and anode [m],  $\dot{n}_{H_2}$ ,  $\dot{n}_{O_2} \& \dot{n}_{H_2O}$  represent the molar flow rate per unit area [mol/(s-m<sup>2</sup>)], and  $D_{eff}$  stands for effective binary diffusion coefficient [m<sup>2</sup>/s].

 $D_{eff,O_2/H_2O}$  and  $D_{eff,H_2/H_2O}$ , represent the O<sub>2</sub>/H<sub>2</sub>O and H<sub>2</sub>/H<sub>2</sub>O effective binary coefficients within the electrodes. The porosity adjustment can be applied to the binary coefficient that has been computed in to determine these coefficients [43]:

$$D_{eff,H_2/H_2O} = D_{H_2/H_2O} \cdot \varepsilon \cdot \left(\frac{\varepsilon - \varepsilon_p}{1 - \varepsilon}\right)^{\alpha}$$
18

$$D_{\text{eff},O_2/H_2O} = D_{O_2/H_2O} \cdot \varepsilon \cdot \left(\frac{\varepsilon - \varepsilon_p}{1 - \varepsilon}\right)^{\alpha}$$
19

where  $\varepsilon$  is the electrode porosity,  $\varepsilon_p$  is the percolation threshold,  $\alpha$  is an empirical coefficient [0.75] [37] and  $D_{H_2/H_2O}$ ,  $D_{O_2/H_2O}$  are the mixture diffusion coefficient and it can be estimated as,

$$D_{H_2/H_2O} = \frac{1}{P} a \left( \frac{T}{\sqrt{T_{crH_2} \cdot T_{crH2O}}} \right)^b (p_{crH_2} \cdot p_{crH2O})^{1/3} (T_{crH_2} \cdot T_{crH2O})^{5/12} \\ \left( \frac{1}{M_{m,H_2}} + \frac{1}{M_{m,H2O}} \right)^{0.5}$$
20

$$D_{O_2/H_2O} = \frac{1}{p} a \left( \frac{T}{\sqrt{T_{crO_2} \cdot T_{crH2O}}} \right)^5 (p_{crO_2} \cdot p_{crH2O})^{1/3} (T_{crO_2} \cdot T_{crH2O})^{5/12} \\ \left( \frac{1}{M_{m,O_2}} + \frac{1}{M_{m,H2O}} \right)^{0.5}$$
21

where *T* represents temperature [K]; *P* denotes electrode pressure [atm];  $T_{crH_2}$ ,  $T_{crO_2}$  and  $T_{crH2O}$  signify the critical temperatures of hydrogen, oxygen and water components; and  $M_{m,H_2}$ ,  $M_{m,O_2}$  and  $M_{m,H2O}$  stand for the molar masses hydrogen, oxygen and water [g/mol]. The dimensionless empirical coefficients, a [3.640 × 10<sup>-4</sup>] and b [2.34]. The calculated  $D_{O_2/H_2O}$  and  $D_{H_2/H_2O}$  value is in units of cm<sup>2</sup> s<sup>-1</sup>.

The molar flow of the gaseous is given by using the Faradays Law's:

$$\dot{N}_{O_2}^{\text{prod}} = \frac{i}{4F}$$
 22

$$\dot{N}_{H_2}^{\text{prod}} = \frac{i}{2F}$$
 23

The rate of molar flow per unit area of ( $\dot{n}_{O_2} \& \dot{n}_{H_2}$ ) O<sub>2</sub> and H<sub>2</sub> across the porous electrode can be established by applying Faraday's Law [37]:

$$\dot{n}_{O_2} = \frac{\dot{N}_{O_2}^{\text{prod}}}{A_m} = \frac{i}{4FA_m}$$
 24

$$\dot{n}_{H_2} = \frac{\dot{N}_{H_2}^{prod}}{A_m} = \frac{i}{2FA_m}$$
 25

In the given context,  $\dot{N}_{H_2}^{prod}$  &  $\dot{N}_{O_2}^{prod}$  represents the molar flow of hydrogen and oxygen gas generated at the electrode [mol/s], *i* denotes the electric current [A], and  $A_m$  signifies the active area of the AEM [m<sup>2</sup>].

 $\dot{W}_e$  represent solar photovoltaic power and is described by the equation [28]:

$$W_e = E_{cell} j A_m$$
 26

Here, *j* is the current density  $[A/m^2]$ .

## 2.5. Photoelectrochemical effects

Following equations are used for photoelectrochemical analysis of the reactor. The hydrogen mass flow rate (kg/s) produced is given by

$$\dot{m}_{PEC,H_2} = \frac{\dot{n}_{PEC,H_2} M_{H_2}}{10^3}$$
 27

where,  $M_{H_2}$  (2.0156 g/mol) is the hydrogen molar mass and  $n_{PEC,H_2}$  is the molar flow rate of hydrogen (mol/s).

The molar flow rate of hydrogen produced from is given by [44].

$$\dot{n}_{PEC,H_2} = \frac{I_r A_i \phi}{2N_A} \left[ \frac{\lambda_i}{hc} \right]$$
28

 $N_A$  is Avogadro's constant,  $\phi$  is the quantum efficiency,  $I_r$  is the incident light intensity,  $A_i$  is the illumination area,  $\lambda_i$  is the incident wavelength, h is Planck's constant, and c is the speed of light.

The Solar-to-Hydrogen efficiency of the PEC AEM reactor is defined as [45].

$$\eta_{STH} = \left(\frac{\dot{m}_{PEC,H_2}LHV_{H_2}}{I_r A_i}\right)$$
29

where  $LHV_{H_2}$  is the lower heating value of hydrogen,  $\dot{m}_{PEC,H_2}$  is the mass flow of hydrogen produced photoelectrochemically. Incident light intensity  $I_r$  times illumination area  $A_i$  gives the solar power input to the reactor.

The overall energy efficiency of the reactor is defined as [28]:

$$\eta_{overall} = \frac{(\dot{m}_{PEC,H_2} + \dot{m}_{AEM,H_2})LHV_{H_2}}{I_r A_i + \dot{W}_e}$$
 30

where,  $\dot{m}_{AEM,H_2}$  is the hydrogen mass flow rate from the electricity input  $\dot{W}_e$ , using a PV panel.

The overall exergetic efficiency can be determined by Ref. [28]:

$$\psi_{overall} = \frac{\left(\dot{m}_{PEC,H_2} + \dot{m}_{AEM,H_2}\right)ex_{ch}^{H_2}}{I_r A_i \left(1 - \frac{T_0}{T_s}\right) + \dot{W}_e}$$
31

where  $ex_{ch}^{H_2}$  is the chemical exergy of hydrogen,  $T_0$  is the ambient temperature and  $T_s$  is the temperature of the sun.

#### 3. Results and discussion

This study aims to investigate the performance of a PEC AEM reactor by developing a mathematical model as described in the system overview section. This mathematical model simulates charge transport, reactions occurring during electrochemical processes, mass transport, and photoelectrochemical effects occurring in photoelectrochemical anion exchange membrane reactor. The model parameters primarily depend on the membrane, photoelectrochemical reactions, photoelectrode nature and fluid dynamics. The initial operating conditions are presented in Table 1. The impacts of varying solar irradiation flux, quantum efficiency, and photoelectrode area on the reactor performance are described in this section.

# 3.1. Impact of varying solar irradiation flux on the performance of PEC AEM reactor

The variation of solar incidence on the overall energy efficiency and the resulting mass flow rate of hydrogen are illustrated in Fig. 2. Higher solar irradiance flux leads to an enhanced hydrogen evolution rate but at the expense of reduced total energy efficiency. As seen from equation (28), the H<sub>2</sub> flow rate rises as the irradiation flux increases because more electron-hole pairs are generated, increasing the kinetics of HER. However, the increase in solar irradiation flux leads to a decrease in overall energy efficiency, attributed to the increased output energy of the generated hydrogen ( $\dot{m}_{PEC,H_2} \times LHV_{H_2}$ ), which cannot compensate for the energy input from the solar irradiation flux (*I<sub>r</sub>A<sub>i</sub>*). The increase in



Fig. 2. Variation in the irradiance flux and its impact on the overall energy efficiency and the hydrogen mass flow rate.

irradiation flux can cause saturation of photon absorption and increased heat loss due to overexcitation and electrochemical losses. The graph exhibited similar trends to previous studies [28,46]. Increasing the irradiation flux decreases total energy efficiency from 11.86% to 11.17%. Concurrently, the H<sub>2</sub> mass flow rate increases from 38.66  $\mu$ g/s to 72.55  $\mu$ g/s. These changes occur under 20% quantum efficiency and an illuminated photoelectrode area of 0.08 m<sup>2</sup>.

# 3.2. Effect of quantum efficiency on the performance of PEC AEM reactor

The effect of varying the quantum efficiency with hydrogen mass flow rate and reactor performance is described in Fig. 3. By increasing quantum efficiency, overall energy efficiency and hydrogen flow rates increase. This indicates that a more significant proportion of incident photons are successfully converted into electrons, which can be used to drive the hydrogen production reaction. More electrons are generated



Fig. 3. A graphical representation depicting how variations in quantum efficiency affect both the hydrogen mass flow rate and the overall energy efficiency.

for the same amount of incoming sunlight, increasing hydrogen production. As seen from equation (28), the molar hydrogen flow rate is directly independent of the quantum efficiency. A higher quantum efficiency increases the overall energy efficiency by maximising the efficiency of photon-to-electron conversion and decreasing the non-radiative losses. Moreover, with the increase in the mass flow rate of hydrogen, the output power increases, which eventually increases the overall energy efficiency. Therefore, enhancing quantum efficiency in PEC systems is a crucial strategy for improving their overall performance and the feasibility of renewable hydrogen production. By altering the quantum efficiency from 0.1 to 0.2, the overall efficiency improves from 6.25% to 11.23%. Simultaneously, the hydrogen mass flow rate experiences a significant doubling from 25.39  $\mu$ g/s to 45.60  $\mu$ g/s, respectively, under an irradiation flux of 600 W/m<sup>2</sup> and a photoarea of 0.08 m<sup>2</sup>.

# 3.3. Impact of photoelectrode illuminated area on the performance of PEC AEM reactor

The increased illuminated area in the reactor increases the mass flow rate of hydrogen due to enhanced photon absorption and energy conversion. The larger area allows more sunlight to be captured, increasing the photons available at reaction sites for hydrogen production. Consequently, increasing the illuminated area impacts the efficiency and performance of the hydrogen production process. Fig. 4 demonstrates the impact of changing the photoelectrode illuminated area on the overall energy efficiency and the hydrogen mass flow rates. The overall energy efficiency decreases as the photocathode illumination area increases while the mass flow rate of hydrogen increases. When altering the illuminated area from 0.04 to 0.08 m<sup>2</sup>, the overall efficiency decreases from 12.32% to 10.76%. Meanwhile, the mass flow rate of H<sub>2</sub> increases significantly, from 25.39  $\mu$ g/s to 75.92  $\mu$ g/s, respectively, under an irradiation flux of 600 W/m<sup>2</sup> and a quantum efficiency of 20%.

# 3.4. Impact of solar irradiation flux variation on the overall exergy efficiency of PEC AEM reactor

The overall exergy efficiency and the rate of hydrogen produced with the change in solar irradiation flux are described in Fig. 5. The solar irradiation flux increases the rate of electrochemical reactions, which enhances the rate of hydrogen production. However, the increased thermal losses and reduced charge separation efficiency decrease the



Fig. 4. A graphical depiction illustrates the effect of varying the illuminated area on the hydrogen mass flow rate and the overall energy efficiency.



**Fig. 5.** Variation of solar irradiation flux on the hydrogen mass flow rate and the overall exergy efficiency.

overall exergy efficiency. Under varying solar irradiation, the bargain between the exergy efficiency and hydrogen mass flow rate must be carefully considered when optimising the PEC reactor operation. The total exergy efficiency decreases from 11.86% to 11.17% with the increase in irradiation flux from 500 W/m<sup>2</sup> to 1000 W/m<sup>2</sup>. Simultaneously, it increases the mass flow rate of H<sub>2</sub> from 38.86 µg/s to 72.55 µg/s, respectively, under 20% quantum efficiency and an area of 0.08 m<sup>2</sup>.

# 3.5. Effect of varying the photoelectrode area on the mass flow rate of hydrogen under artificial and no light conditions

The effect of varying photoelectrode area on the hydrogen mass flow rate under artificial (PEC) and no light conditions (AEM) are shown in Fig. 6. The hydrogen mass flow rate due to the photoelectrochemical effect increases with the increase in illuminated area, as evident from Fig. 6. With the increase in the illuminated area, the light absorption



Fig. 6. The variation of hydrogen mass flow rate with artificial (PEC) and no light conditions (AEM) with change in the illuminated area.

increases the generation of electron-hole pairs, which increases the electron flux for the HER reaction. Moreover, a greater area provides active sites for catalytic efficiency, increasing the hydrogen production rate. The hydrogen mass flow rate remains constant with 5.18 µg/s produced with no light conditions. With the increased illuminated area, the H<sub>2</sub> mass flow rate increases from 20.21 µg/s to 70.73 µg/s with an illuminated area increase from 0.04 m<sup>2</sup> to 0.14 m<sup>2</sup>, respectively.

#### 4. Conclusions

A mathematical model is developed to investigate the performance of the PEC AEM reactor under various operating conditions using Engineering Equation Solver (EES). The study looks at the governing equations of PEC modelling to determine the rate of hydrogen generation and the solar-to-hydrogen (STH) efficiency. The electrochemical calculations indicate that the overall energy efficiency and hydrogen mass production rate are 11.23% and 45.60 µg/s, respectively, at the solar incident flux of 600  $W/m^2$  and 20% quantum efficiency. The results also show that the hydrogen production rate increases with the photoelectrode area, quantum efficiency, and incoming flux of solar irradiation. It is observed that the overall energy efficiency decreases with the increase in the solar incident flux. With an increase in the active area of the photoelectrode, there is an increase in the generation of holes and electrons. Accordingly, the hydrogen mass production rate is enhanced. Based on the findings of the parametric analysis, the most significant amount of hydrogen production was 75.92 µg/s at a solar radiation flux of 600  $W/m^2$  with an illuminated area of 0.08  $m^2$  and quantum efficiency of 0.20. Increasing the illuminated area from 0.04 to 0.08 m<sup>2</sup> reduces total efficiency from 12.32% to 10.76%. Furthermore, the mass flow rate of H<sub>2</sub> increases significantly, from 25.39  $\mu$ g/s to 75.92  $\mu$ g/s. Consequently, the overall energy efficiency also increases alongside the hydrogen production rate.

### CRediT authorship contribution statement

Altaf Hasan Tarique: Writing – original draft, Software, Conceptualization. Vivek Prasad: Writing – review & editing, Writing – original draft, Validation, Software, Investigation, Conceptualization. Sher Afghan Khan: Writing – review & editing, Supervision. Farrukh Khalid: Writing – review & editing, Supervision, Project administration. Muhammad Hanafi Bin Azami: Writing – review & editing, Supervision, Conceptualization.

### Declaration of competing interest

The authors have declared that they have no competing financial interest.

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# Nomenclature

 $A_i$ : illumination area, m<sup>2</sup>

- $A_m$ : total area of the membrane, m<sup>2</sup>
- $C_{O_2,mem}$ : oxygen concentration at the membrane/electrolyte interface, mol m<sup>-3</sup>  $C_{H_2,mem}$ : hydrogen concentration at the membrane/electrolyte interface, mol m<sup>-3</sup>  $D_{eff,O_2/H_2O}$ : effective binary coefficient of  $O_2/H_2O$  in the porous electrodes, m<sup>2</sup> s<sup>-1</sup>  $D_{eff,H_2/H_2O}$ : effective binary coefficient of H<sub>2</sub>/H<sub>2</sub>O in the porous electrodes, m<sup>2</sup> s<sup>-1</sup>
- $D_{0_2/H_20}$ : mixture diffusion coefficient of  $O_2/H_2O$ , m<sup>2</sup> s<sup>-</sup>
- $D_{H_2/H_2O}$ : mixture diffusion coefficient of H<sub>2</sub>/H<sub>2</sub>O, m<sup>2</sup> s<sup>-1</sup>
- dam: distances between the anode and the membrane, m
- $d_{cm}$ : distances between the cathode and the membrane, m
- $E_{0a}$ : anodic water dissociation potential, V
- $E_{0c}$ : cathodic water dissociation potential, V
- Ecell: cell voltage, V
- Erev: reversible potential, V
- $E_{rev}^0$ : minimum reversible potential, V

- ex<sup>H2</sup>: Chemical exergy of hydrogen, kJ/kmol
- F: Faraday constant, 96 485 C mol<sup>-1</sup>
- *i*: cell current. A
- Ir: Solar irradiation flux, Wm<sup>-2</sup>
- *j*: operating current density, A cm<sup>-2</sup>
- $j_{0,a}$ : anodic exchange current density, A cm<sup>-2</sup>
- $j_{0,c}$ : cathodic exchange current density, A cm<sup>-2</sup>
- LHVH2: Lower heating value of hydrogen, MJ/Kg
- m: molar concentration, mol/m3

 $\dot{m}_{PEC,H_2}$ : Photoelectrochemical hydrogen mass flow rate, kg/s

 $\dot{m}_{AEM,H_2}$ : Anion exchange membrane electrolysis hydrogen mass flow rate, kg/s

- $M_{m,H_2}$ : molar masses of hydrogen, kg mol<sup>-1</sup>
- $M_{m,O_2}$ : molar masses of oxygen, kg mol<sup>-1</sup>
- M<sub>m.H2O</sub>: water molar mass, g mol
- $\dot{N}_{O_2}^{prod}$ : molar flow of oxygen at the electrode, mol s<sup>-1</sup>
- $\dot{N}_{H_2}^{prod}$ : the molar flow of hydrogen at the electrode, mol s<sup>-1</sup>
- *n*: number of electrons involved in the reaction
- $\dot{n}_{O_2}$ : oxygen molar flow per unit area in the electrodes, mol s<sup>-1</sup> m<sup>-2</sup>
- $\dot{n}_{H_2}$ : hydrogen molar flow per unit area in the electrodes, mol s<sup>-1</sup> m<sup>-2</sup>
- $n_{H_2O,c}$ : water flows per unit area in the cathode, mol s<sup>-1</sup> m<sup>-2</sup>  $n_{H_2O,c}$ : water flows per unit area in the anode, mol s<sup>-1</sup> m<sup>-2</sup>
- $n_{PEC,H_2}$ : the photoelectrochemical molar flow rate of hydrogen per unit area in the elec-
- trodes, mol s<sup>-1</sup>
- $p_a$ : anode pressures, Pa
- $p_c$ : cathode pressures, Pa
- $p_{H_2}$ : the partial pressure of hydrogen, Pa
- $p_{O_2}$ : the partial pressure of oxygen, Pa
- $p_{H_2O}$ : the partial pressure of water vapour, Pa
- $p_{crH_2}$ : critical pressure of hydrogen, Pa
- $p_{crO_2}$ : critical pressure of oxygen, Pa
- $p_{crH2O}$ : critical pressure of water vapour, Pa *R*: universal gas constant, 8.3145 J mol<sup>-1</sup> K<sup>-1</sup>
- $r_{KOH}$ : resistance of the electrolyte (KOH),  $\Omega$
- $r_{mem}$ : resistance of the membrane,  $\Omega$

 $S_a$ : anode cross-section area, m<sup>2</sup>

 $S_c$ : cathode cross-section area, m<sup>2</sup>

- T: temperature, K
- $T_0$ : ambient temperature, K
- $T_s$ : sun's temperature. K
- $T_{crcH_2}$ : critical temperatures of hydrogen, K
- $T_{crO_2}$ : critical temperatures of oxygen, K
- $T_{crH2O}$ : critical temperatures of water, K
- Vohm: voltage loss (ohmic losses), V
- We: Electric work input from photovoltaic panel, W

#### Greek symbols

 $\alpha_a$ : anodic charge transfer coefficient  $\alpha_c$ : cathodic charge transfer coefficient  $\eta_{overall}$ : overall energy efficiency  $\eta_{act}$ : activation overpotential, V  $\eta_{diff}$ : concentration overpotential, V  $\eta_{STH}$ : Solar to hydrogen efficiency  $\phi$ : quantum efficiency  $\delta_m$ : membrane thickness, m  $\varepsilon$ : electrode porosity  $\varepsilon_p$ : percolation threshold  $\eta_{act}$ : activation over potential, V  $\eta_{diff}$ : diffusion over potential, V  $\lambda$ : humidification degree  $\lambda_i$ : incident wavelength  $\sigma_m$ : membrane conductivity, S m<sup>-1</sup>  $\sigma_{KOH}$ : ionic conductivity, S cm  $\psi_{overall}$ : exergetic efficiency