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**pH-differential design and operation of electrochemical and photoelectrochemical systems
with bipolar membrane**

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Abstract:

Electrochemical and photoelectrochemical systems for hydrogen production and CO₂ reduction are regarded as prospective technologies to achieve carbon-free energy vision. Electrolytes in different pH environment is desirable for each half electrochemical reaction to optimize the electrode kinetics and reduce the cost of noble metal catalysts. The bipolar membrane provides excellent opportunities to enable pH-differential operation. However, the effect of the bipolar membrane on electrochemical performance is not clarified yet. Here, a numerical modeling framework for bipolar membrane-based cells for electrochemical and photoelectrochemical applications was presented to study the viability of using bipolar membrane in the aspect of energy loss. The model for the first time successfully integrates the water dissociation at the bipolar membrane with the rest electrode kinetics and mass transfer, by treating the interfacial layer as a virtual electrode. Based on the model, the activation loss involved in the bipolar membrane devices were identified and compared with the ones with conventional monopolar membranes. A critical current density was identified for bipolar membranes, which is determined by the water dissociation performance of the membrane. Based on the critical current, the viable operation regions of using the bipolar membrane can be clarified for the electrochemical device. It is found that the bipolar membrane-based photoelectrochemical reactor has higher energy conversion efficiency than monopolar membrane configurations. However, the advantage of bipolar membrane becomes vanishing with photocurrent rising.

Keywords: pH differential; water electrolysis; CO₂ reduction; photoelectrochemical; bipolar

membrane

1. Introduction

With the tremendous consumption of fossil fuel, the global climate change caused by greenhouse gas emission becomes increasingly challenging. The EU proposed to cut at least 40% greenhouse gas emission compared to 1990 levels and achieve a 32% share for renewable energy at least by 2030 in its ‘2030 climate and energy framework’ [1]. The UK announced its ambitious target to obtain net-zero carbon emission by 2050 [2]. China aims to reduce the CO₂ emission per unit gross domestic product (GDP) by 60%-65% by 2030 [3]. As the rigorous targets of decarbonization of the global energy system were set, the demand for more efficient and lower-cost technologies for green fuel generation continually grows.

Using sustainable energy like solar and wind power to generate hydrogen and carbon-based fuels through electrochemical and photoelectrochemical approaches is regarded as a practical way to achieve the carbon-free or carbon-neutral energy perspective. The research from Bareiß et al. indicates that up to 75% of CO₂ emission can be reduced if the electrolysis system runs on renewable energy sources [4]. According to the study of Yadav et al., the carbon emission footprint of hydrogen production from solar-assisted electrolysis can be 10%-22% of methane reforming process, and 23%-51% of chemical thermochemical cycles [5].

Recent studies suggested that the electrochemical reduction of CO₂ could be profitable in mid-term benefiting from the continuous cost reduction of renewable energy and the performance improvement of electrolyzer [6]. It is also found that higher value-added products, such as C₂-C₃

organics, are essential for CO₂ electrochemical reduction to be economically viable [7].

Membrane-based reactors are the most widely applied configuration either for fuel cell [8] or for electrolysis [9], which employed ion exchange membranes to separate catholyte and anolyte while maintaining the transport of ions through the membrane. In this architecture, monopolar membranes (MPM) like anion exchange membrane (AEM) and cation exchange membrane (CEM) can only allow the transfer of mono ions, which results in the same pH environment on both sides of the membrane. However, different pH is required for anodic and cathodic half-reactions. For example, in order to take advantage of earth-abundant oxygen reduction catalysts, an alkaline catholyte should be kept at the cathode [10]. In regard to water electrolysis, an acidic electrolyte is desirable for the cathode to fasten the kinetics of hydrogen evolution reaction (HER) and stabilize non-noble hydrogen evolution catalysts like MoS₂ [11]. As for CO₂ER, neutral catholyte is commonly used to suppress the HER and obtain a higher solubility of CO₂ [12].

Bipolar membrane (BPM) is a lamination composite of AEM and CEM, which enables water dissociation in the intermediate layer and produces acid and base simultaneously [13]. Bipolar membranes have been widely used in electrodialysis applications for water treatment [14] and resource recovery [15], and in reverse electrodialysis applications for electricity generation [16]. More than this, BPM provides opportunities to maintain a pH gradient across the membrane, which enables the utilization of low cost electrocatalysts. Moreover, the application of bipolar membrane is proved effective to inhibit undesirable crossover through the membrane [17]. Intensive researches on applying BPM in photoelectrochemical [18], electrochemical [19], electrodialysis [20], and bioelectrochemical [21] energy engineering for water splitting and CO₂ER have been

carried out recently. Experimental studies were conducted to demonstrate the ion transport in the BPM to characterize voltage-current behavior [22]. Numerical model coupling Poisson's equation and Nernst-Planck equation was developed to present the voltage and species distribution in the BPM and provide guidelines on designing and optimization of BPM [23]. It is found that the catalyst, such as graphite oxide [24] and reduced graphene oxide [25], in the intermediate layer plays a critical role in promoting the water dissociation and reduce the voltage loss caused by the membrane. A BPM with the 3D junction between CEM and AEM was demonstrated, which shows significant benefit in accelerating the transport of H^+ and OH^- in the membrane and eliminating the delamination [26]. The utility of BPM in electrochemical systems was discussed. It is suggested that the BPM is not suitable in buffered electrolytes due to high potential losses [27]. Furthermore, BPM is considered not suitable to be applied in the applications with low current density operation (about 0.5 mA cm^{-2}) because of the counterion leakage current caused by the migration of electrolyte ions through the membrane [28]. Since large membrane potential is introduced in the BPM [13], comparisons between MPM and BPM systems were performed to study the influence of BPM on the system performance and energy efficiency. In the experiments of water electrolysis conducted by Yuzer et al. [29], BPM configuration required higher bias potential than MPM ones to perform the same current because extra overpotential is needed for water dissociation. However, reverse results were also concluded for the same application. Lei et al. [30] found BPM design could enable a 30% reduction in energy consumption compared with MPM design while Ramdin et al. [31] suggested a similar and even lower performance in the BPM system than MPM one for CO_2ER .

It is clear that the BPM enables differential pH operation in electrochemical systems to improve the applicability and compatibility of catalysts. However, based on the current comparisons of performance between BPM and MPM designs, the effect of using BPM is unclear. There is a lack of knowledge based on which one can evaluate the advantages and drawbacks of deploying BPM in the electrochemical devices. In order to clarify the effect, the potential losses involved in the BPM must be identified. In this paper, we present numerical models to investigate the influence of BPM and determine the energy losses within BPM-based cells. To our best knowledge, this is the first model considering the whole BPM cell, which couples the water dissociation and mass process within the bipolar membrane with the anodic and cathodic electrode reactions. In this model, the interfacial layer in the BPM is innovatively treated as a virtual electrode, and the water dissociation reaction is treated as two half electrochemical reactions occurring on each surface of the electrode. The energy losses in BPM are categorized from the electrochemical aspect, based on which the suitability of BPM in different application scenarios was discussed. On the basis of the results, this work provides a comprehensive understanding of the overpotentials involved in BPM electrochemical cells and gives practical guidelines on designing and optimizing ion exchange membrane devices.

2. Model development

The 2D geometry of the model is shown in Fig. 1. In this work, we focus our study on the continuous flow electrolysis devices for water splitting and CO₂ER applications. The continuous flow cell configuration enables the effective removal of gaseous products and simplifies the flow

characteristics of electrolytes. Therefore, the bubble effect in the cell is neglected. The electrolyzer consists of two flow channels (1 mm in width) separated by a BPM. The BPM is formed of an AEM layer (80 μm), a CEM layer (80 μm), and an interfacial layer (10 μm). The electrolyte changes according to the configurations.

2.1 Governing equations

2.1.1 Electrochemical kinetics in BPM

In previous numerical studies, the water dissociation in BPM was modeled as an equilibrium reaction in the static electric field [23]. It is difficult to couple the water dissociation process with anode and cathode reactions. In this model, in order to integrate the electric potential gradient caused by the pH difference with the electric field of electrolyte, the interfacial layer is treated as an electrode. At the same time, the water dissociation process is split into two half electrochemical reactions that occur at each side of the interfacial layer.

Eq. 1 and 2 do not present the actual reactions taking place in the interfacial layer, and the oxygen is assumed as the intermediate generated and consumed within the BPM. The kinetics of the above two half-reactions are governed by the Butler-Volmer equation.

$$j = j_0 \left(\exp\left(\frac{\alpha_a F \eta}{RT}\right) - \exp\left(\frac{\alpha_c F \eta}{RT}\right) \right) \quad (4)$$

in which, j_0 refers to the interfacial exchange current density (mA cm^{-2}), α_a is the anodic transfer coefficient, α_c is the cathodic transfer coefficient ($\alpha_c=1-\alpha_a$), F denotes the Faradaic constant (96485 C mol^{-1}), R and T are gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and thermodynamic temperature (K), respectively. η refers to the overpotential of the electrochemical reaction.

$$\eta = \varphi - E_{eq} \quad (5)$$

where φ is the electrode potential relative to the electrolyte (V), E_{eq} is the equilibrium potential of electrochemical reaction (V).

2.1.2 Kinetics at electrode and electrolyte

In this work, both conventional electrode and photoelectrode are modeled. The kinetics of reactions that occur at conventional electrodes are also governed by the Butler-Volmer equation (Eq. 4), while the photocurrent generated at photoelectrode can be expressed using a Gärtner-Butler based equation accounting for the surface recombination effect of the electron-hole pairs[32].

$$j_{ph} = \Phi_{re,surf} eI \left[1 - \frac{\exp(-\alpha \delta_{sc})}{1 + \alpha L} \right] \quad (6)$$

in which I is the intensity of incident light ($\text{m}^{-2} \text{ s}^{-1}$), L is the diffusion distance of charge carrier (m), and α is the absorption coefficient of photoelectrode (cm^{-1}). δ_{sc} is the thickness of the space charge layer (m), which can be calculated by [33].

$$\delta_{sc} = \sqrt{\frac{2\epsilon\epsilon_0\Delta\varphi_{sc}}{eN_d}} = \sqrt{\frac{2\epsilon\epsilon_0(V - V_{fb})}{eN_d}} \quad (7)$$

where ϵ denotes the dielectric constant, ϵ_0 is the permittivity of vacuum ($\text{C V}^{-1} \text{ m}^{-1}$), $\Delta\varphi_{sc}$ refers to

the difference of potential across the space charge layer (V), V is the potential of photoanode (V), V_{fb} presents the flat band potential of semiconductor (V), e is the charge of an electron (1.6×10^{-19} C), and N_d denotes the donor density of semiconductor (m^{-3}).

The surface recombination coefficient, $\Phi_{re,surf}$, which is related to band bending can be evaluated by the following expression [34]

$$\Phi_{re,surf} = \frac{R_t}{R_t + R_r} = \frac{A \exp(B \cdot \Delta \varphi_{sc})}{1 + A \exp(B \Delta \varphi_{sc})} \quad (8)$$

in which A and B are two constants, R_t and R_r are the charge transfer resistance and recombination resistance at the surface of the semiconductor, respectively.

The decay of light intensity within the photoelectrode caused by light absorption is considered in this model. The Beer-Lambert law is used to give the distribution of light intensity.

$$\frac{I(x)}{I} = \exp(-\alpha x) \quad (9)$$

where x is the transport distance of light (cm). As a result, the photocurrent is modified to consider light absorption as follows.

$$j_{ph} = \Phi_{re,surf} e (I - I(x)) \left[1 - \frac{\exp(-\alpha \delta_{sc})}{1 + \alpha L} \right] \quad (10)$$

The charge transfer in the electrolyte and at the electrode is governed by the ohmic law.

$$j = -\sigma \nabla \varphi \quad (11)$$

in which σ is conductivity (S m^{-1}) of electrolyte and the electrode.

2.1.3 Hydrodynamics and mass transfer

The fluidic dynamics is governed by the continuity equation and conservation of momentum, which is treated as stationary.

$$\nabla \cdot (\rho U) = 0 \quad (12)$$

$$\nabla \cdot (\rho U U) = -\nabla \cdot p + \nabla \cdot \tau \quad (13)$$

where ρ is the density (kg m^{-3}), U is the velocity vector (m s^{-1}), p is the pressure (Pa), τ is the viscous stress tensor (Pa).

The mass transfer is determined by the species conservation considering diffusion, convection and migration.

$$\nabla \cdot (-D_i \nabla c_i - z_i u_i F c_i \nabla V) + U \cdot \nabla c_i = R_i \quad (14)$$

where D is the diffusion coefficient ($\text{m}^2 \text{s}^{-1}$), c is the concentration of species (mol m^{-3}), z denotes the charge number of ions, R refers to the generation or consumption rate of species ($\text{mol m}^{-3} \text{s}^{-1}$), u is the mobility of ions (mol s kg^{-1}), which can be derived from the Nernst-Einstein relation.

$$u_i = \frac{D_i}{RT} \quad (15)$$

2.2 Boundary conditions and numerical procedures

In order to solve the hydrodynamics, the inlet flow rate and outlet pressure should be set. To calculate the concentration distribution, the initial and inlet concentration of species were specified. AM 1.5G was set as the incident light for photoelectrode. The numerical model was built and solved by COMSOL Multiphysics. The computational domain was discretized with the structured grid. The key parameters inputted in the model are summarized in Table 1. Multifrontal Massively Parallel Solver (MUMPS) was used to carry out the calculation.

3. Results and discussion

3.1 Model validation

As shown in Fig. 2a, the calculated polarization curve of BPM was compared with the experimental data at the current range up to 600 mA cm^{-2} [26], which presents a good agreement. The fitted interfacial exchange current density is 90 A m^{-2} . Since the interfacial catalyst plays a critical role in accelerating the water dissociation reaction, different interfacial catalysts present different values of interfacial exchange current density, i.e., j_0 in Eq. 4. In order to further validate the model, the BPMs with various reduced graphene oxide interfacial catalysts were modeled by adjusting the interfacial exchange current density. As shown in Fig. 2b, it is found that the J-V relations are consistent with the experimental results with diverse interfacial catalysts [25]. The corresponding interfacial exchange current densities are 25 A m^{-2} , 2 A m^{-2} , 0.3 A m^{-2} , respectively. Therefore, the treatment of water dissociation reaction in BPM as two half electrochemical reactions is valid. Besides, the J-V curves of single electrodes are also validated by a BPM based water splitting experiments, as shown in Fig. 2c [20].

3.2 Energy losses in the bipolar membrane

The total potential loss involved in the BPM can be classified into two parts, i.e., ohmic loss and activation loss. The ohmic loss is related to the ion transport rates in AEM and CEM, while the activation loss is applied to drive the water dissociation. The experimental study confirmed that the commercial BPM membrane (Fumasep FBM) is capable of keeping a linear current-voltage

relation up to around 600 mA cm^{-2} , as shown in Fig. 2a [26]. At the current density of 500 mA cm^{-2} , the voltage drop across the BPM is about 1.72 V, corresponding to a membrane potential loss of 0.9 V. The ohmic loss and activation loss contribute to 0.5V and 0.4 V, respectively, as shown in Fig. 3. At the low current operation region, the activation loss is much higher than the ohmic loss, which makes the water dissociation performance-limiting step. Therefore, in this circumstance, choosing a BPM with a more efficient interfacial catalyst like reduced graphene oxide will largely reduce the potential loss of BPM [25]. In contrast, when the BPM operated under high current operation conditions (larger than 360 mA cm^{-2}), the ohmic loss exceeds the activation loss. Normally, the industrial operation of an electrolysis cell requires a current density larger than 400 mA cm^{-2} . Under such conditions, a BPM with lower ohmic loss is essential.

3.3 Use of bipolar membrane in different electrochemical and photoelectrochemical scenarios

Four electrode configurations of electrochemical and photoelectrochemical processes for water splitting are summarized in Table 2. As shown in the Table, the alkaline environment is preferred for OER in all of the configurations, either for conventional or photoelectrode. It is because alkaline environmental is required to make use of non-noble OER catalysts for conventional electrode, and enables higher performance and more stable operation of photoanode. In contrast, different pH environment is required for HER according to the type of electrode. Acid catholyte is favorable to deliver fast HER kinetics and to enable the usage of non-noble catalysts, while alkaline catholyte is required for photocathode. As for CO_2 reduction, a neutral environment is generally desirable. The feasibility of using bipolar membrane in electrochemical or photoelectrochemical

devices is summarized in Table 2.

3.4 Conventional electrochemical systems

From Table 2, it is found that both water electrolysis and CO₂ER require a pH-differential operation. In order to avoid the complex cathodic reaction in CO₂ER and focus our attention on energy loss, the water electrolysis process is investigated here. Two electrolyzers with both conventional electrodes for water electrolysis were modeled. One is equipped with MPM, in which anolyte and catholyte are in the same pH condition. The other is equipped with BPM, which enables pH-differential operation at anode and cathode. The operation conditions are summarized in Table 3. Since diverse membrane materials have been developed for both AEM and BPM with various conductivity properties, the ohmic loss of membrane was set the same in each model.

Fig. 4a shows the J-V performance of the two designs. The performance curves of MPM and BPM devices intersect together and are divided into two parts by the intersection point. When the cells operated under the current density, which is lower than the intersection point (critical point), BPM design shows higher performance. While at a higher current density region, MPM design presents better performance. The potential losses involved in each electrolyzer were analyzed to give a detailed influence of BPM on cell performance, as shown in Fig. 4b. From Fig. 4b and Fig. 4c, it can be found that the activation loss at the cathode can be reduced remarkably from 0.3 V to 0.12 V at 200 mA cm⁻², benefiting from the pH-differential operation. However, the potential loss caused by water dissociation in BPM will partially or wholly offset the improvement in cathodic kinetics. As shown in Fig. 4c, the BPM designs show lower potential losses comparing with the

MPM one at lower current density conditions. Once the current density exceeds the intersection points, at which the total potential loss in BPM cell equals the one in MPM cell, the deployment of BPM will result in a lower electrochemical performance than the MPM design. Therefore, the viable operation region of BPM depends on the critical point. BPM with more active water electrolysis catalysts leads to a higher critical current density, which extends the operation region of BPM, as well as reduces the potential loss at the membrane, as shown in Fig. 4a and Fig. 4d.

3.5 Photoelectrochemical systems combining a photoelectrode and a conventional electrode

From Table 2, BPM design is preferred in the circumstances of photoelectrochemical water splitting and photoelectrochemical CO₂ER. Although the charge carriers in photoanode are different from the ones in photocathode, the photocurrent density in both kinds of photoelectrodes can be governed by the Gärtner-Butler equation. Herein, the photoelectrochemical water splitting process was investigated. Two photoelectrochemical models with different membrane configurations were built, as summarized in Table 4.

As shown in Fig. 5a, the calculated photocurrent response of BiVO₄ is validated by comparing with experimental data [35]. Fig. 5b shows the J-V curves of individual electrodes and membranes. Since the photocurrent of BiVO₄ is at the low stage, i.e., less than 3 mA cm⁻², the total potential loss including the activation losses at cathode and membrane in the BPM design is less than 0.02 V. As for the MPM design, the HER kinetics at the cathode is more sluggish than the BPM one, the maximum cathodic activation loss is about 0.1 V, which decreases the maximum applied bias photon-to-current efficiency (ABPE) by 20%, as shown in Fig. 6a. A detailed definition of ABPE

can be found in the literature [36]. Since the current performance of photoelectrochemical devices is too low to meet the requirement of commercialization, the upscaling of current density is crucial to improve the viability of this technology. Concentrated sunlight operation is a promising way to scale up the current response of photoelectrochemical cells. Normally, the photocurrent follows a proportional relation against light intensity under 2-3 suns. However, a power function relation is detected in the highly concentrated region [37]. Here, an ideal photocurrent response against concentrated sunlight, i.e., proportional relationship, is assumed. The ABPE profiles of both cells at various scale-up conditions were plotted in Fig. 6b and Fig. 6c. Since the potential losses at cathode and BPM rise with current performance increasing, the ABPE of both BPM and MPM cells drops. When the photocurrent is upscaled by 20 times, the MPM design only presents 66% of the maximum ABPE in BPM cell. However, with further improvement in photocurrent, the influence of activation losses at cathode and membrane in the BPM cell becomes more and more significant. As shown in Fig. 6c, the ABPE performance of MPM has surpassed BPM cell when the photocurrent is upscaled by 50 times.

4. Conclusions

This paper presents a numerical study of bipolar electrochemical and photoelectrochemical devices and discusses the suitability of applying pH-differential operation from the aspect of energy loss. For the first time, this model successfully integrates the water dissociation and mass transfer within the bipolar membrane with the anodic and cathodic electrochemical reactions, by creatively treating the interfacial layer as a virtual electrode. At the same time, the water dissociation reaction

is treated as two half-reactions occurring on each side of the virtual electrode. Therefore, the potential losses involved in the bipolar membrane can be categorized into two types, i.e., activation loss for water dissociation and ohmic loss. The potential losses in bipolar membrane-based devices were compared with monopolar membrane-based devices. For electrochemical applications, the bipolar membrane device presents lower potential loss than the monopolar membrane one when the operating current is less than the critical current point, while the bipolar membrane shows higher potential loss at the high current region because of the rising dissociate activation loss. The bipolar membrane, which has more active dissociation performance and higher critical current, can extend the viable operation region for the bipolar membrane. For the photoelectrochemical scenario, the bipolar membrane configuration presents less potential loss and higher applied bias photon-to-current efficiency compared with the monopolar membrane designs. However, with the scaling up of the current performance under concentrated sunlight, the advantage brought by the bipolar membrane descends due to the increased activation loss for water dissociation. In practice, for electrochemical cells, it is important to make sure the critical current point of the bipolar membrane is larger than the working current region to make the whole cell fall into the viable region. In line with the photoelectrochemical cell, suitable light intensity should be identified first to eliminate the activation loss. This work not only gives mechanistic understandings of pH-differential devices from the aspect of energy loss, but also provides clear practical guidelines of using the bipolar membrane.

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List of tables:

Table 1. Key input parameters of the model.

Table 2. Electrochemical and photoelectrochemical scenarios for water splitting and CO₂ER.

Table 3. The electrode configurations of electrolyzers for water electrolysis.

Table 4. The electrode configurations of photoelectrochemical cells for water electrolysis.

Table 1. Key input parameters of the model.

Parameters	Unit	Value	Ref.
α_a at AEM, CEM	-	0.5	-
α_a of OER at NiFe	-	0.99 (pH=14)	[38]
j_0 of OER at NiFe	A m ⁻²	9.04×10 ⁻² (pH=14)	[38]
α_a of HER at Pt	-	0.44 (pH=0)	[39]
j_0 of HER at Pt	A m ⁻²	160 (pH=0)	[39]
D_{OH^-} in electrolyte	m ² s ⁻¹	5.3×10 ⁻⁹	[23]
D_{OH^-} in AEM	m ² s ⁻¹	2.8×10 ⁻¹¹	[23]
D_{H^+} in electrolyte	m ² s ⁻¹	9.3×10 ⁻⁹	[23]
D_{H^+} in CEM	m ² s ⁻¹	5×10 ⁻¹¹	[23]
σ_l of electrolyte	S m ⁻¹	20	Assumed
σ_l of BPM	S m ⁻¹	1	Assumed
α	cm ⁻¹	Derived from data	[35]
V_{fb}	V	0.2V vs RHE	[35]
ε	-	68	[35]
N_d	cm ⁻³	17.3×10 ¹⁷	[35]
L	m	6×10 ⁻⁷	Fitted
A	-	0.025	Fitted
B	-	6.2	Fitted

Table 2. Electrochemical and photoelectrochemical scenarios for water splitting and CO₂ER

Electrode configuration	Conventional anode and cathode	Photoanode with conventional cathode	Conventional anode with photocathode	Photoanode with photocathode
OER	Alkaline	Neutral/Alkaline	Alkaline	Neutral/Alkaline
HER (*)	Acid (Y)	Acid (Y)	Neutral/Alkaline (N)	Neutral/Alkaline (N)
CO ₂ ER (*)	Neutral (Y)	Neutral (N)	Neutral (Y)	Neutral (N)

* Use of bipolar membrane: Y- Yes; N-No.

Table 3. The electrode configurations of electrolyzers for water electrolysis

No.	Membrane	Anode	Cathode	Anolyte pH	Catholyte pH
1	AEM	NiFe	Pt	14	14
2	BPM	NiFe	Pt	14	0

Table 4. The electrode configurations of photoelectrochemical cells for water electrolysis

No.	Membrane	Anode	Cathode	Anolyte pH	Catholyte pH
3	AEM	BiVO ₄	Pt	9.3	9.3
4	BPM	BiVO ₄	Pt	9.3	0

List of figures:

Figure 1. Schematic of a BPM based device for electrochemical water splitting.

Figure 2. Comparison of experimental data and simulation results for (a) commercial BPM; (b) in-house BPM with various intermediate catalysts. The corresponding interfacial exchange current densities are 25 A m^{-2} , 2 A m^{-2} , 0.3 A m^{-2} for yellow, green, and blue lines, respectively; (c) anodic and cathodic performance.

Figure 3. The energy losses involved in the BPM, consisting of ohmic loss and activation loss.

Figure 4. (a) The total potential loss of water electrolysis in MPM based device and BPM based devices with various water dissociation exchange current density, i.e., $100, 200, 500 \text{ mA cm}^{-2}$; (b) the potential losses in MPM device; (c) the potential losses in BPM device with water dissociation exchange current density of 100 mA cm^{-2} ; (d) the potential losses in BPM device with water dissociation exchange current density of 200 mA cm^{-2} .

Figure 5. (a) The comparison between experimental data and simulation results of BiVO_4 photoanode; (b) the potential loss caused by membrane, HER in BPM, and MPM based photoelectrochemical cells.

Figure 6. The ABPE profiles of photoelectrochemical cells based on BPM and MPM designs under (a) original current density operation; (b) 20 folds current density operation; (c) 50 folds current density operation.

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