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Article

Mass Transport Limitations in Electrochemical Conversion of CO₂ to Formic Acid at High Pressure

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Abstract: Mass transport of different species plays a crucial role in electrochemical conversion of CO₂ due to the solubility limit of CO₂ in aqueous electrolytes. In this study, we investigate the transport of CO₂ and other ionic species through the electrolyte and the membrane, and its impact on the scale-up process of HCOO[−] / HCOOH formation. The mass transport of ions to the electrode and the membrane is modelled at constant current density. The mass transport limitations of CO₂ on the formation of HCOO[−] / HCOOH is investigated at different pressures ranges from 5–40 bar. The maximum achievable partial current density of formate/formic acid is increased with increasing CO₂ pressure. We use an ion exchange membrane model to understand the ion transport behaviour for both the monopolar and bipolar membranes. The cation exchange (CEM) and anion exchange membrane (AEM) model show that ion transport is limited by the electrolyte salt concentrations. For 0.1 M KHCO₃, the AEM reaches the limiting current density more quickly than the CEM. For the BPM model, ion transport across the diffusion layer on either side of the BPM is also included to understand the concentration polarization across the BPM. The model revealed that the polarization losses across the bipolar membrane depend on the pH of the electrolyte used for the CO₂ reduction reaction (CO₂RR). The polarization loss on the anolyte side decreases with an increasing pH, while, on the cathode side, it increases with increasing catholyte pH. With this combined model for the electrode reactions and the membrane transport, we are able to account for the various factors influencing the polarization losses in the CO₂ electrolyzer. To complete the analysis, we simulated the full cell polarization curve and fitted with the experimental data.

Keywords: CO₂ electrolyzer; mass transport; modelling

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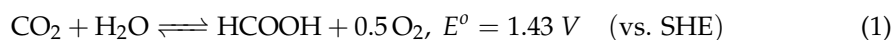


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1. Introduction

The effects of global warming have already reached an alarming level [1]. The scientific community and the industry have been trying to reduce the emission of greenhouse gases from the atmosphere, especially CO₂. There are several methods being developed to store and sequester emitted CO₂ gas to reduce CO₂ concentrations in the atmosphere [2–4]. One of the ways to reduce CO₂ emissions is to electrochemically convert CO₂ into valuable chemicals [5–13]. The electrochemical method is a green process that only requires electricity that can be generated from renewable sources like solar and wind [14]. The main issue with the electrochemical conversion method is the need of an electrocatalyst that can produce desirable chemicals with a reasonable Faradaic efficiency [15–17]. Recently, considerable efforts have been made to produce CO and HCOOH from CO₂ [18–20]. Electrochemical reduction of CO₂ produces various products depending on the electrocatalyst used [16,21–26]. When tin metal (Sn) is used as electrocatalyst, formate/formic acid is identified as the main product of the CO₂ reduction reaction (CO₂RR) along with small quantities of CO [18–20,22,27,28]. The formate/formic acid can also be formed by direct reduction of bicarbonate anions [29–31]. In addition to the CO₂RR, reduction of water also occurs. The CO₂RR is carried out at the cathode in an electrochemical cell in combination

with the oxygen evolution reaction (OER) at the anode. The overall reaction, which involves formate/formic acid formation and oxygen evolution is as follows:



where E° is the standard reduction potential, and SHE stands for Standard Hydrogen Electrode. The Faradaic efficiency for formic acid formation depends on the electrolyte concentration, pressure, and the applied potential. The Faradaic efficiency ranges from 65–90% as reported in literature [16,23,27]. One of the crucial factors that causes mass transport limitations is the low solubility of CO_2 in aqueous electrolytes [32–35]. Increasing the CO_2 pressure is one way to improve the mass transport of CO_2 to the electrode surface. Another way is to feed gaseous CO_2 (g) directly to the catalyst surface using a gas diffusion electrode (GDE). A high concentration of formic acid is reported using GDEs [36,37]. The depletion of CO_2 at the electrode surface forms a concentration gradient of specific thickness that defines the rate of CO_2 transfer to the electrode. This diffusion layer thickness also determines the maximum achievable current density. It is also possible to suppress the effect of mass transport limitations by operating the CO_2 RR at low current density [38]. At this lower current density, the CO_2 surface concentration is not different from the bulk concentration, so there are more CO_2 molecules available for reduction. There is also another way in which the CO_2 RR is carried out under controlled mass transport limitations in which the electrode is rotated at certain speed. It is reported that the rotation speed of 450 rpm is sufficient to maintain the surface concentration equal to bulk concentration [39]. There are several reports that investigated the effect of mass transport limitations experimentally [40,41]. In those studies, the rotating disc electrode was used to maintain the well-defined mass transport that allowed them to study the kinetics of CO_2 RR without any mass transport complications. One of the interesting experimental results related to the mass transport limitation has been reported by Dunwell et al. [39]. These authors used surface enhanced infrared spectroscopy to study the impact of mass transport limitations on the electrochemical reduction of CO_2 . Interestingly, these authors correlated the mass transport effects with the concentration overpotential and its influence on the electrode kinetics of CO_2 RR. However, the measurements were performed using a half-cell configuration. These experimental conditions are not possible to implement in the industrial scale CO_2 electrolyzers where high current density and large electrodes are used. However, the effect of ion transport through the membrane on performance of the CO_2 electrolyzers was clearly missing from these studies.

In CO_2 electrolyzers, the role of ion exchange membrane is crucial as it prevents the products from reaching the anode surface. The membrane also plays a role in maintaining the pH, since electrolytes with different pH are required at the cathode and anode sides to facilitate CO_2 RR and OER reactions at low overpotential. In addition, the CO_2 RR and OER reactions also produce OH^- and H^+ . Typically, KHCO_3 is used as a catholyte for the CO_2 RR, and alkaline electrolyte (KOH) is used as an anolyte for the OER. Bipolar membranes (BPM) have attracted much attention because of their ability to maintain the pH and high permeability and low cross-over. It facilitates the usage of electrolytes with different pH at the cathode and anode compartment. This application is very useful, especially for the CO_2 electrolyzer, where neutral pH is beneficial for CO_2 reduction (CO_2 RR), and an alkaline anolyte is needed for the oxygen evolution reaction (OER). In a BPM, the cation exchange membrane (CEM) and anion exchange membrane (AEM) are sandwiched together to form a single sheet of a membrane [42,43]. When a BPM is operated under reverse bias mode, water molecules present at the interface undergo dissociation, and H^+ and OH^- ions are produced which are transported through the CEMs and AEMs to the catholyte and anolyte compartments, respectively. It is widely accepted that the water dissociation reaction at the interface is greatly influenced by the electric field effect according to the second Wien effect [44–48]. However, an electric field enhanced water dissociated model showed similar dissociation rate enhancement for an CEM and an AEM, but this cannot explain why water dissociation is only observed in

AEM [44,49]. Simon et al. [42,49,50] have proposed a chemical reaction model based on the acid–base reaction of a weak basic group surrounded by water molecules. Both the electric field effect and the chemical reaction model are combined to calculate the enhanced rate dissociation constant for water dissociation at the interfacial region. It is also shown by Simon et al. [50] that the presence of catalysts at the interfacial region enhances the water-splitting reaction. The weak ion exchange groups present as a fixed charge on the polymer backbone that catalyzes the water dissociation reaction. Recently, Yan et al. [51] prepared a BPM with graphene oxide as a catalyst, and it was shown that the presence of the catalyst decreases the electric field intensity and at the same time the reversible protonation of weak basic group is catalyzed. However, there are fewer studies that describe the transport of H^+ and OH^- ions inside the BPM and the adjacent diffusion boundary layer (DBL) [46,51,52]. Yan et al. [51] developed a numerical simulation model to describe ion transport and electric field enhanced water dissociation reaction. Recently, Mareev et al. [46] have developed a comprehensive model to describe the transport of salt ions, and the effect of a catalyst on the interfacial region. To the best of our knowledge, there is no study available to systematically understand the role of the BPM in the electrochemical conversion of CO_2 to formate/formic acid. Given this background, we developed a full-cell model to understand the role of mass transport through the electrolytes and the membrane. This may provide valuable parameters for the scale up of formate/formic acid production.

Several models have been reported for CO_2 electrolyzers [33,34,53–56]. Most of them are based on diffusion–reaction models to describe the transport of CO_2 to the cathode surface [33,34,54]. The Butler–Volmer equation [34,53,57] is generally used to obtain the current density from the model. Few reports discussed the effect of the anode and the membrane [33]. Although the ion exchange membrane plays a critical role in the CO_2 electrolyzer, there are not many studies that investigate the role of the membrane on the performance of CO_2 electrolyzers. The focus of this study is to investigate the effect of ion transport through the membrane and its effect on the CO_2 electrochemical conversion. A diffusion layer is included in the membrane model to analyze the role of electrolyte concentration and the limiting current density.

In this paper, we analyze the effect of CO_2 pressure on the concentration of different ionic species produced during the homogeneous reactions of CO_2 (g) in the bulk of the $KHCO_3$ electrolyte. The mass transport limited current density is modelled using a diffusion–reaction model. The limiting current density of the oxygen reduction reaction (ORR) on the Ir/IrO₂ electrode is also modelled to explore the limitation of anode reactions. Subsequently, the transport of ions in the monopolar membrane, and the bipolar membrane is modelled. The membrane model also includes the diffusion layer on either side of the membrane. The correlation between the electrolyte concentration and limiting current density is established. We will show that, at a low electrolyte concentration (<0.1 M), the CO_2 electrochemical conversion with the monopolar membrane is limited by the ion transport through the membrane. In the case of a BPM, the pH of the catholyte and anolyte plays an important role in reducing the polarization losses at the membrane/electrolyte interface. Finally, the contribution of different elements involved in the polarization losses is modelled. These parameters are used to model the full cell voltage and polarization curve.

2. Modelling

A schematic representation of the electrochemical cell used for this study is shown in Figure 1. The model electrochemical cell consists of Sn metal as cathode, Ir/IrO₂ as anode and the ion exchange membrane. The electrolyte on both sides of the membrane is considered well stirred. The model system is also comparable to the flow cell configurations with a constant flow rate. We used a diffusion–reaction model to investigate the mass transport of CO_2 to the cathode surface and the oxygen evolution at the anode surface. The concentration of dissolved CO_2 at different pressures is used as input to investigate the transport of CO_2 . The mass transfer rate of major charge carriers to the membrane is defined using a mass transfer coefficient and a Donnan equilibrium constant. The concentration of

the counter ions at the membrane surface is calculated by assuming that the concentration is equal to the fixed membrane charges (1M).

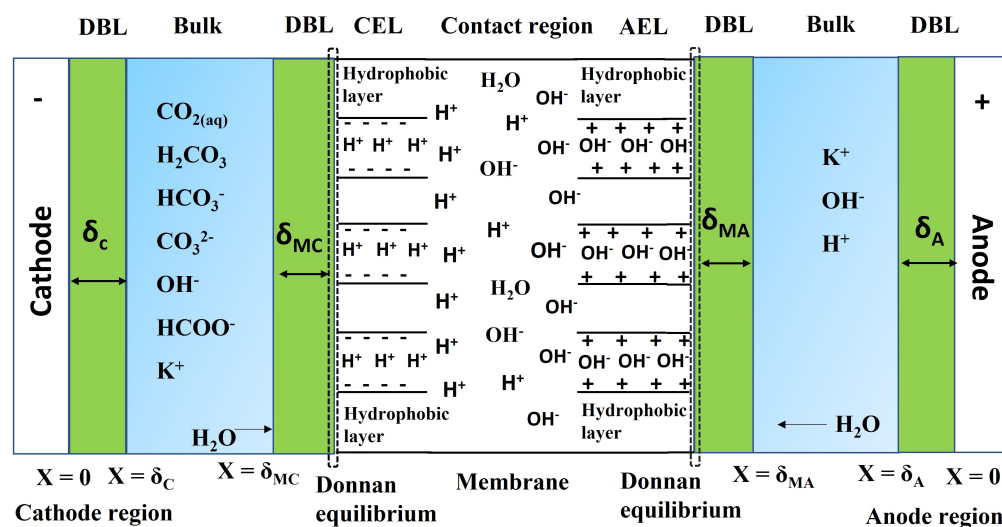


Figure 1. Schematic representation of the simulated electrochemical cell. The boxes in the figure do not represent the actual dimensions. The figure consists of a cathode, anode and the bipolar membrane regions. To explain the water dissociation reactions at the interphase, the box containing the membrane region is shown larger than the other regions. The dotted line indicates the Donnan equilibrium at the membrane–electrolyte interphase. The following abbreviations are used in the figure: DBL is the diffusion layer, CEL is cation exchange layer, AEL is anion exchange layer, δ is the diffusion layer thickness, δ_C and δ_A represent the diffusion layer at the cathode and anode, respectively. δ_{MC} and δ_{MA} represent the diffusion boundary layer at the cathode and anode side membranes, respectively.

2.1. Transport of the Species to the Electrode Surface

The transport of CO_2 and other ionic species in the electrolyte is governed by the Nernst–Planck equation [57], which considers diffusion, migration and convection transport phenomena:

$$N_i = -z_i u_i F C_i \nabla \Phi + C_i V - D_i \nabla C_i \quad (2)$$

where N_i is the flux, C_i is the concentration of species i (CO_2 , HCO_3^- , CO_3^{2-} , OH^-), z_i is the charge number of the species, u_i is the mobility of the ions related to the diffusion coefficient by the Nernst–Einstein equation, F is Faraday’s constant, D_i is the diffusion coefficient, and $\nabla \phi$ is the electrolyte potential. In Equation (2), the left side first term represents the migration, the second term represents the convection, and the third term represents the diffusion transport process. We assumed that the transport of CO_2 (a neutral reactive species) takes place due to a change of concentration near the electrode surface. The influence of migration and convection phenomena to describe the transport of species to the electrode surface is neglected. By neglecting this, the Nernst–Planck equation becomes similar to Fick’s diffusion equation:

$$\frac{d[C_i]}{dt} = D_i \frac{d^2[C_i]}{dx^2} + r_i \quad (3)$$

In this equation, r_i is the net rate of formation and consumption of species i involved. As CO_2 reacts with water, it is important to consider all the ionic species formed in these reactions. This is written out in Appendix A. The set of transport equations for CO_2 , HCO_3^- , OH^- and CO_3^{2-} are solved numerically using the following initial and boundary conditions. Initially, the concentration of species near the electrode is equal to the bulk of the electrolyte i.e., concentrations are the same everywhere at $t = 0$ (Figure 2). When the current is applied,

a diffusion layer is formed near the electrode due to the concentration gradient. Two boundary conditions need to be defined, one at the boundary between diffusion layer ($X = \delta$) and the bulk of the electrolyte, another one at the electrode surface ($X = 0$). At $X = \delta$, the concentration of the various species equals their bulk values. The boundary condition at the electrode surface ($X = 0$) is defined by the flux term. The fluxes are calculated using the partial current density obtained from the Butler–Volmer equation:

$$I = i_{0,i} k_i C_i \exp \left[-\frac{\alpha_i n F \eta_i}{RT} \right] \quad (4)$$

in which $i = \text{HCOO}^-$, CO , H_2 . In this equation, i_0 is an exchange current density, k is the rate constant, C_i is the concentration of electroactive species (CO_2 for CO_2RR , and H_2O for HER), α is the charge transfer coefficient, F is the Faraday constant, η is the overpotential, R is the gas constant, and T is the temperature.

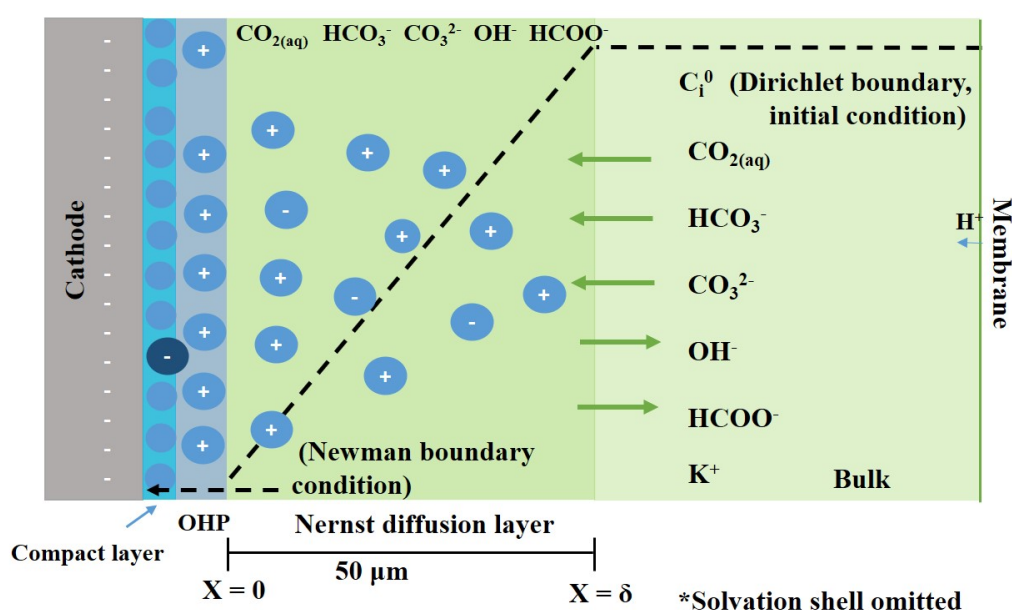


Figure 2. Schematic representation of the cathode diffusion–reaction model. It consists of a bulk electrolyte, diffusion layer and electrode surface. The diffusion layer contains two boundaries, one at the bulk of the electrolyte, and another one at the electrode surface. The dotted line indicates the concentration profile of the species inside the Nernst diffusion layer. The diffusion of ions in and out of the diffusion layer is represented by arrows. The solvation shell is omitted. OHP denotes the outer Helmholtz plane.

The reactions at the anode surface are considered non-limiting. To understand the behaviour of the full electrochemical cell, information from the anode electrode is needed. As the cell voltage and the polarization loss of the CO_2 electrolyzer are influenced by the anodic reactions, it is important to model the anode reactions as well. The anode side is modelled in the same way as the cathode side, and the anolyte concentration (0.5 M KOH) is directly taken as the concentration of the electroactive species. The Nernst–Planck equation is used for the anode as well. No source term (r_i) is added to the transport equation, as no chemical reaction occurs in the anolyte. At the anode, the oxygen evolution reaction (OER) occurs at the Ir/IrO₂ coated Ti electrode. The reaction is carried out in alkaline pH, and 0.5 M KOH is used as anolyte. The OH^- ion is the only reactive species in the OER reaction; hence, the electrolyte concentration is directly taken as the initial and boundary condition (Dirichlet). For the boundary condition at the electrode surface ($X = 0$), the anodic flux is

calculated from total current density obtained from the cathode model. The total current density is the summation of the partial current densities of CO₂RR and HER:

$$I_{\text{tot}} = I_{\text{HCOO}^-} + I_{\text{CO}} + I_{\text{H}_2} \quad (5)$$

$$D \frac{d[\text{OH}^-]}{dx} = [\text{OH}^-] \text{ consumption} = -\left(\frac{I_{\text{tot}}}{nF}\right) \quad (6)$$

where I_{tot} is the total current density which is calculated using Equation (4). Kinetic parameters for the Butler–Volmer equation given in Equation (4) are obtained from experimental data of Kuo et al. and Kai et al. as shown in Table 1 [58,59].

Table 1. Kinetic parameters for the CO₂RR and the oxygen evolution reaction taken from Refs. [42,43]

Kinetic Parameter	CO ₂ RR	OER	Units
Tafel slope	120	40–45	mV
Exchange current density	5.97×10^{-8}	5.75×10^{-10}	A.cm ⁻²
Charge transfer coefficient	0.236	0.246	—
Rate constant	9.38×10^{-12}	2.98×10^{-15}	cm.s ⁻¹

2.2. Transport of Species through the Membrane

The monopolar and the bipolar membranes are modelled assuming 1 M of fixed charge groups, which is equivalent to 1 meq.g⁻¹. Our membrane model considers the membrane as a homogeneous mixture containing polymers with ion exchange groups and the electrolyte solution. The oppositely charged mobile ions are called “counter ions”, and the mobile ions with the same charge as the fixed ion exchange groups are called “co-ions”. These ionic species are transported across the membrane under the influence of the electric field. The mobility of the ionic species within the polymer differs from that of the aqueous solution due to the electrostatic forces and tortuosity of the polymer chains. To account for differences in the mobility, the diffusion coefficient of the counter ions is reduced by one order of magnitude, and the co-ions are reduced by two orders of magnitude as reported earlier in literature [33]. The following additional assumptions are made for the membrane model:

1. The ionic charges present in the membrane are larger than the charges present in the electrolyte.
2. The bulk of the electrolyte on either side of the membrane is well stirred; hence, the concentration of the mobile ions is constant at all times in the bulk electrolyte. There is an unstirred layer (Nernst layer) that is formed on both sides of the electrolyte–membrane interface (Figure 3). The thickness of the Nernst layer or diffusion layer is assumed to be same for the cathode and anode.
3. The concentration of the counter ions inside the membrane is equal to the concentration of fixed charge groups. The electroneutrality approximation is valid inside the membrane and also in the diffusion layer. The Donnan equilibrium is present at the solution–membrane interface.
4. At the junction of the bipolar membrane, the water dissociation reaction is catalyzed by an acid–base reaction of the weakly basic group present in the membrane. Donnan equilibrium is assumed to be present at the interface between CEM-AEM.
5. In the BPM, the current is carried only by water ions (H⁺ and OH⁻). Therefore, the electrolyte salt ion transport from the interface is not included.
6. It is assumed that the membrane has a high permeability, and hence the transport of co-ions is negligible. The membrane is assumed to have a zero crossover for other molecules; hence, the transport of HCOOH/HCOO⁻ ion through the membrane is negligible. However, in practice, it is difficult to produce a membrane with exactly zero crossover.

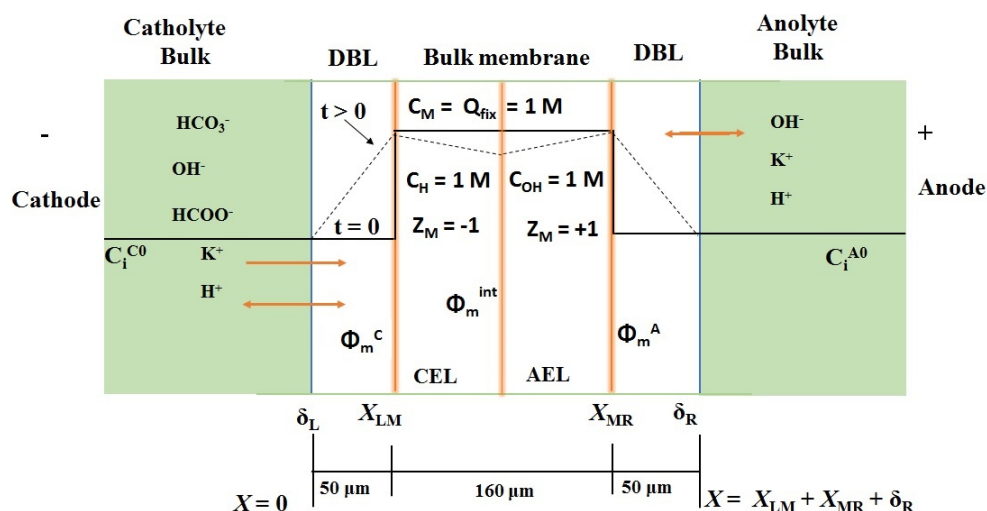


Figure 3. Ion transport through a BPM in reverse bias mode. C_i^{C0} , C_i^{A0} are the initial concentration of mobile ionic species in the catholyte and anolyte, respectively. C_M is the concentration of fixed charge groups on the membrane. C_H , C_{OH} are the concentrations of H^+ and OH^- ions in respective CEL and AEL. ϕ_m^C , ϕ_m^A is a Donnan potential at the interface between catholyte–membrane and membrane–anolyte, respectively. X_{ML} , X_{MR} represent the electrolyte–membrane interface near catholyte and anolyte bulk. The black bold line represents concentration in the diffusion layer and inside the membrane at $t = 0$, and dotted lines indicate the concentration changes in the diffusion layer and inside the membrane at $t > 0$.

To understand the transport of species through the membrane, the number of mobile ions that carries current needs to be defined. The electrolyte salt ($KHCO_3$) used as catholyte consists of K^+ and HCO_3^- ions. The CO_2 dissolution reactions produce H_2CO_3 , HCO_3^- and CO_3^{2-} ions. In Appendix A, it is shown that the concentration of H_2CO_3 is very low and always in equilibrium with CO_2 (aq). Therefore, we consider that H_2CO_3 is not transported through the membrane. Similarly, CO_3^{2-} reacts with H^+ at the diffusion boundary layer (near the cathode side of the membrane) to form HCO_3^- . For this reason, we also assumed that CO_3^{2-} is not transported through the membrane. The CO_2 RR produces $HCOO^-$, which is also present in the electrolyte along with H^+ and OH^- ions produced due to water dissociation. Overall, we have five mobile ions: K^+ , HCO_3^- , H^+ , $HCOO^-$ and OH^- that are present in the catholyte. At the other side of the membrane, i.e., in the anolyte, we have three mobile ions K^+ , OH^- and H^+ . Since we assumed that the membrane has a high permeability and zero crossover, no co-ions and $HCOOH/HCOO^-$ ions are transported through the membrane. Therefore, for the BPM model, the transport of K^+ and H^+ ions (counter ions for the CEL layer) in the catholyte side and OH^- ions (counter ion for the AEL layer) at the anolyte side is considered. For the monopolar membrane, K^+ is transported through CEM from the anolyte side to the catholyte side. For the AEM, HCO_3^- is transported from the catholyte side to the anolyte side.

The model for the monopolar membrane is extensively discussed in the literature [52,60–64]; however, the influence of the diffusion layer adjacent to the membrane is considered by only a limited number of studies. Fila and Bouzek et al. [61,62,64,65] explicitly investigated the influence of the concentration gradient in the diffusion layer on the ion transport through the membrane. A similar model was used to analyze the ion transport through the membrane in the CO_2 electrolyzer. In this model, the thickness of the diffusion layer (DBL) is an important parameter that needs to be determined. The DBL thickness, in general, is calculated using the mass transfer coefficient as:

$$k_m = \frac{D_e}{\delta}, \quad (7)$$

where k_m is the mass transfer coefficient, D_e is the effective diffusion coefficient and δ is the diffusion layer thickness. For a well stirred electrolyte, the thickness of the stagnant layer at the electrode and the membrane is the same. Therefore, we assumed that the diffusion layer thickness adjacent to the membrane is the same as for the cathode diffusion layer. The Nernst–Planck equation is used to describe the electro migration of ionic species through the membrane;

$$\frac{d[C_i]}{dt} = D_i \frac{d^2[C_i]}{dx^2} + z_i F [C_i] \left(\frac{D_i}{RT} \right) \nabla \phi \quad (8)$$

where i represents K^+ for the CEM and HCO_3^- for the AEM, respectively. z_i is the charge number of the species, F is the Faraday's constant, C_i is the concentration of the ionic species, D_i is the diffusion coefficient and ϕ is the electrolyte potential. The current carried by the ions through the membrane is calculated using

$$I = F \sum z_i N_i \quad (9)$$

The potential gradient ($\nabla \phi$) in Equation (8) is obtained by substituting Equation (8) into Equation (9), and subsequent rearrangement leads to

$$\nabla \phi = \frac{\left(\frac{I}{F} \right) + D_i \nabla C_i}{z_i^2 \left(\frac{D_i}{RT} \right) F C_i} = \frac{I + F D_i \nabla C_i}{k} \quad (10)$$

in which k is the electrolyte conductivity. Charge neutrality is assumed in the electrolyte and also in the membrane bulk

$$\sum z_i C_i = 0, \text{ (diffusion layer)} \quad (11)$$

$$\sum z_i C_i + \sum z_M C_M = 0, \text{ (membrane bulk)} \quad (12)$$

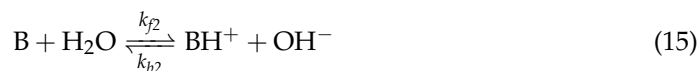
where z_M and z_i are the charge number of the fixed charge group and the concentration of the counter ion, respectively. C_M , C_i are the concentration of the fixed charge group and the concentration of the counter ion inside the membrane bulk. These equations are also applicable for the BPM. However, in sharp contrast to the monopolar membrane, in the BPM, the current is carried by water ions generated from water dissociation reactions occurring at the interface of the CEM and AEM contact region:



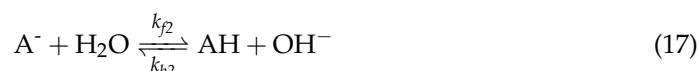
In literature, there are two models to explain the nature of the interface or transition layer between the CEM-AEM. The abrupt junction model which is the analogy of p-n junction in semiconductors, assumes the existence of the depletion layer due to the presence of uncompensated fixed charge groups at the interface [45,66]. The neutral layer model assumes a neutral layer between CEM and AEM, where the contact surface of the CEM and AEM contains a thin layer of water molecules and the unbalanced fixed charge groups are balanced by an electrical double layer at the junction [42]. The thickness of this region depends on the resistance of the interface layer. Recently, Yan et al. [51] have used electrochemical impedance spectroscopy to measure the thickness of the interface layer in the BPM. It was found that the thickness of this layer equals 3 nm. The reported value is similar to the theoretical value predicted by Strathmann et al. [44]. To investigate the transport of the water ions through the BPM, a source term is added to the NP equation to account for the water dissociation reaction at the interface of the BPM. The source term defines the rate of water dissociation reaction that includes the catalytic effect and electric field effect enhanced water dissociation rate constant k_d . The rate of generation and recombination of H^+ and OH^- ions is obtained from

$$R_{H^+} = R_{OH^-} = k_d [H_2O] - k_b [H_3O^+][OH^-] \quad (14)$$

In this equation, R_i is the generation and recombination rate of water ions produced at the interphase layer. The rate constant k_d is obtained by considering the base catalysed water dissociation reaction and the electric field effect according to the second Wien effect. The proton transfer reaction catalyzed by a neutral base in AEM can be written as



Similarly, the acid catalyzed proton transfer reaction in CEM is written as



where B is the weak base, BH^+ the conjugate acid of the weak base, AH is a weak acid, and A^- is the conjugate base of the weak acid. k_{f2} , k_{f3} are the forward rate constants and k_{b2} , k_{b3} are the rate constants for the backward reaction. The ability of the fixed charge groups to undergo protonation and deprotonation reactions with water molecules depends on the pK_b value of that group. If pK_b (or pK_a for the CEM) is low, the reaction rate for the protonation reaction k_{f2} is higher, and all groups are in the protonated form. If the pK_b is lower than 7, then $k_{f2} > k_{b2}$ that means that the protonation step is faster than the deprotonation, and hence the deprotonation reaction is the rate determining step. When $pK_b = 7$, the protonation and deprotonation reactions occur at the same rate. By assuming that the reactions of Equations (16) and (17) are in equilibrium, we are able to calculate the rate constants k_{f2} and k_{f3} . For instance, the rate constant k_{f2} can be calculated as follows:

$$\frac{k_{f2}}{k_{b2}} = \frac{[BH^+][OH^-]}{[B]} \quad (19)$$

$$k_{f2} = k_{b2} \times K_b \quad (20)$$

By using the relation between K_b and pK_b , the pK_b dependent rate constant is obtained:

$$k_{f2} = k_{b2} \times 10^{-pK_b} \quad (21)$$

Similarly, k_{f3} can be calculated as

$$k_{f3} = k_{b3} \times 10^{-(14-pK_b)} \quad (22)$$

The electric field enhanced water dissociation constant was calculated using the Onsager equation for the dissociation of weak electrolytes under the electric field [67]

$$\frac{k_d(E)}{k(0)} = 1 + b + \frac{b^2}{3} + \frac{b^3}{18} + \frac{b^4}{180} + \frac{b^5}{2700} + \frac{b^6}{56700} \quad (23)$$

According to this equation, the dissociation rate constant of weak electrolytes under the electric field can be computed from the parameter b given by

$$b = 0.09636 \frac{E}{\epsilon T^2} \quad (24)$$

where E is the electric field, ϵ is the dielectric constant of the electrolyte, and T is the temperature. The value of the b is directly proportional to the electric field intensity. For

the derivation of this parameter, it was considered that the molecule is dissociated into the respective ions through the ion-pair formation (molecule \rightleftharpoons ion-pair \rightleftharpoons ions). The recombination of ion-pair to molecule occurs at a faster rate, and the rate of this molecule formation is considered independent of the electric field. The dissociation reaction of ion-pair to individual ions occurs slowly. This interaction is depending on the electric field as it is influenced by the coulombic forces between the ions. The field effect and the electrostatic forces between the ions are combined with the equation for Brownian motion to describe the enhancement of dissociation constant under the electric field [67].

The concentrations of the ionic species in the catholyte and anolyte are used as initial and boundary conditions for the catholyte (left) and anolyte (right) sides of the membrane (Figure 3). For the concentration inside the membrane bulk, we can write

$$C_i^M = [Q]_{\text{fix}} \quad (25)$$

where C_i^M is the concentration of the counter ion inside the membrane. Q_{fix} is the concentration of fixed charge groups. The concentration of the ions at the electrolyte/membrane interface is defined using Donnan equilibrium constants:

$$\Delta\phi_m^C = \frac{RT}{zF} \log \frac{[C_i^C]}{[C_M]} \quad (26)$$

$$\Delta\phi_m^A = \frac{RT}{zF} \log \frac{[C_i^A]}{[C_M]} \quad (27)$$

where C_i^C , C_M is the concentration of the ions in the catholyte bulk and inside the membrane bulk, respectively. ϕ_m^C and ϕ_m^A are the Donnan potentials at the catholyte–membrane and anolyte–membrane interface, respectively. The concentration of the ions at the solution side of the electrolyte/membrane interface is calculated using

$$C_C^{\text{int}} = \frac{C_m^i}{K_C} \quad (28)$$

where C_C^{int} is the concentration of counter ion at the solution side of the interface. K_C is the Donnan equilibrium constant that is obtained by rearranging Equations (27) and (28) as follows:

$$\frac{[C_M]}{[C_i^C]} = \exp \left[-\frac{zF\Delta\phi_m^C}{RT} \right] = K_C \quad (29)$$

where M represents the concentration of the counter ion species i (K^+ , HCO_3^- , H^+ , OH^-) inside the membrane. For the monopolar membrane, i represents the K^+ (CEM), HCO_3^- concentrations (AEM) and the bipolar membrane H^+ for the CEM layer, and OH^- for the AEM layer. Q_{fix} is the fixed charge group concentration, which is equivalent to ion exchange capacity of 1 meq/g (1M). Similar to Equations (28) and (29), the concentration of the ions at the anolyte side of the interface can be calculated.

The model discussed above is also applicable to study the transport of salt ions through the CEM and AEM in bipolar membranes. There are two limiting current regions observed in the BPM. At low current density, the current is carried by salt ions present in the interface layer. When the applied voltage is high enough, all salt ions are removed from the interface and the resistance of the membrane increases. Further increase in the voltage results in the dissociation of water, and the current will be solely be carried by H_3O^+ and OH^- . The rate constant k_d for the forward dissociation reaction determined the limit of the current that can be carried by the water ions.

2.3. Total Cell Voltage and Polarization Loss

The cell voltage of the electrolyzer consists of the following polarization losses:

$$E_T = E_{equ} + (E_C + E_a) + (E_{iR} + E_m) \quad (30)$$

where E_{equ} represents the equilibrium potential of the respective cathode and anode reactions. E_C and E_a represent the cathode and anode over potentials. E_{iR} is the contribution of the ohmic drop due to electrolyte and membrane components inside the cell. The contribution of concentration polarization is given by E_m . Concentration polarization occurs due to mass transport limitation of the active species to the electrode surface. The standard equilibrium potential for the electrochemical conversion of CO_2 to formic acid is 1.03 V (corresponding to pH = 7 for the cathode and pH = 13 for the anode) [18]. In practice, higher voltages are required to perform the reaction. The contribution of the voltage losses to the cell voltage is modelled by combining the equilibrium potential (E_{equ}), the overpotential of the cathode and anode reactions (E_η) and ohmic losses (E_{iR}). The ohmic losses are calculated from electrolyte and the membrane conductivity. The voltage loss in the BPM is due to the combined resistance of the ion exchange membrane (CEM and AEM) and the interfacial layer. The main contribution for the voltage drop at the interfacial region is the voltage needed to split water to produce H^+ and OH^- ions, which is equal to 0.8 V [68–70]. Furthermore, there is an additional resistance contribution due to the concentration loss at the electrolyte–membrane interface. If 1 M (pH = 1) of acid and 1 M alkaline (pH = 14) electrolyte is used as catholyte and anolyte, there will be zero voltage loss as there is no pH gradient at the interface. However, the pH range of the catholyte used for CO_2 reduction is >7 . Therefore, there will be an additional voltage loss due to the pH gradient at the electrolyte–membrane interface. For a change of one pH unit, there will be a potential loss of 59 mV [57,68]:

$$\Delta\phi = \phi_m^C + \phi_m^{\text{int}} + \phi_m^A \quad (31)$$

where ϕ_m^C , ϕ_m^{int} and ϕ_m^A are the Donnan potentials at the catholyte–CEL, CEL–AEL and AEL–anolyte interface, respectively. The Nernst-like equation can be expressed to calculate the Donnan potential for each interface and also across the membrane as follows:

$$\Delta\phi = \frac{RT}{F} \log \frac{[\text{H}^+_{\text{anolyte}}]}{[\text{H}^+_{\text{catholyte}}]} \quad (32)$$

The polarization curve simulated using Equation (30) is fitted to the experimental data. For the experimental data, a flow cell with a Sn cathode, Ir/IrO₂ anode, and bipolar membrane (160 μm thickness, purchased from Fumasep FBM-PK, Fumatech), was fabricated. At the cathode compartment, 0.5 M KHCO_3^- catholyte was used, and 0.5 M KOH anolyte was used at the anode compartment. The applied voltage was varied from 1 V to 4 V, and current was measured at each applied potential for 10 min. Before the experiments, KHCO_3 electrolyte was purged with CO_2 gas. More details of the experimental setup can be found in our previous work [35].

3. Results and Discussion

The concentration of CO_2 at different KHCO_3 concentration at different pressures is taken from Morrison et al. [34]. These authors calculated the CO_2 concentration in a KHCO_3 electrolyte assuming that HCO_3^- has a similar salt effect as that of chloride ions, as reported by Tang et al [71]. To calculate the concentration of the species present in the bulk of the electrolyte at different CO_2 pressures, the concentration dependent CO_2 solubility is taken into account [34]. Since the composition of the species dissolved in the electrolytes are pH dependent, the distribution of the carbon species at different pH is modelled as shown in Figure 4. At a pH lower than 5, CO_2 and H^+ are the dominant species. The availability of protons at low pH reduces the polarization loss of the cell. This is beneficial for the conversion of CO_2 to formic acid. However, a high H^+ concentration promotes

the H_2 evolution reaction on the formic acid producing electrodes that will impact the Faradaic efficiency of $\text{HCOO}^-/\text{HCOOH}$ formation. At $\text{pH} > 5$, the concentration of HCO_3^- is increasing and reaches the solubility limit around $\text{pH} 9$. Further increase in pH results in equilibrium shifting towards the CO_3^{2-} formation. For $\text{pH} > 12$, CO_3^{2-} is the dominant species present in the electrolyte. However, the information about the CO_2 concentration at different pH is significant for CO_2RR . We can observe that, at $\text{pH} > 7$, the CO_2 concentration is decreasing and completely converted into HCO_3^- and CO_3^{2-} at alkaline pH . Though only a small amount of CO_2 is involved in the homogeneous reaction, we have a plenty of CO_2 available for the CO_2RR reaction. Figure 4a shows the charge balance calculated for 0.5 M KHCO_3 at 5 bar CO_2 pressure. It reveals important information about the pH of the electrolyte (dashed line in Figure 4a). It also shows the relation between CO_2 concentration and the electrolyte pH . For instance, the CO_2 concentration is 33 mM for the $\text{pH} 7.6$. This value corresponds to CO_2 concentration in 0.5 M KHCO_3 at atmospheric pressure. The effect of pressure on the pH of the KHCO_3 electrolyte at different concentrations is another important parameter modelled here to calculate the distribution of the reactive species in the bulk, which is shown in Figure 4b. The results showed that, at high pressure, the electrolyte pH is dropped significantly and still acidic even at 1 M KHCO_3 . At atmospheric pressure, the pH stays neutral to slightly basic for all the KHCO_3 concentrations used here.

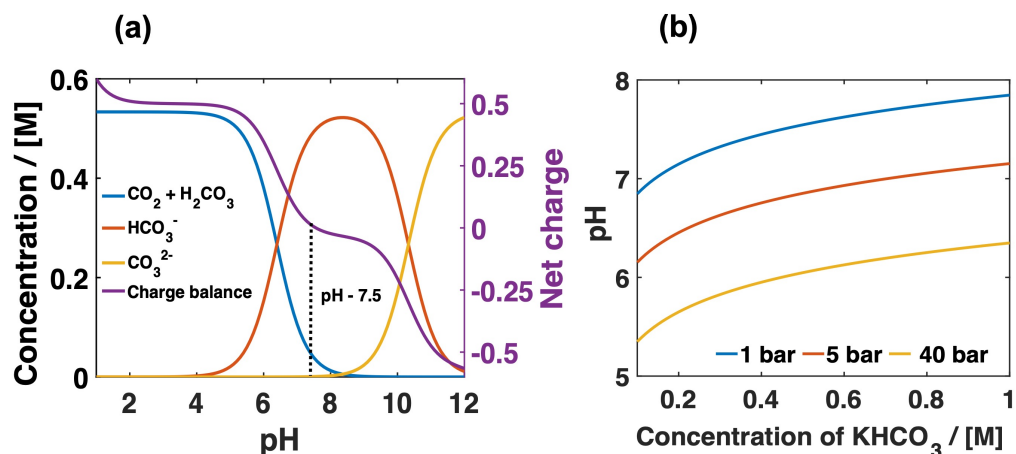


Figure 4. (a) The distribution of carbon species in 0.5 M KHCO_3 electrolyte at fixed CO_2 concentration and pH values, at 1 bar. The dashed line indicates the pH value at which the CO_2 dissolution reaction reaches equilibrium at 1 bar. This pH value changes with respect to CO_2 pressure and electrolyte salt concentration, (b). The effect of electrolyte concentration on the pH of bulk electrolyte at CO_2 pressures of 1, 5 and 40 bar, respectively. Details of these calculations can be found in Appendix A.

At the electrode surface, CO_2 is reduced and converted to formic acid. At $t = 0$, the concentration of CO_2 at the surface is equal to the bulk concentration. At $t > 0$, when an external voltage is applied, CO_2 is consumed that leads to a concentration gradient near the electrode surface. At a certain voltage, all the CO_2 molecules are reduced, and the concentration becomes negligible. At this point, the reaction is limited by the mass transport of CO_2 to the electrode surface. One of the effects of high pressure is the enhanced CO_2 mass transport. The CO_2 concentration at atmospheric pressure is 33 mM while at 40 bar the concentration is close to 1 M. Since there is a 10-fold jump in CO_2 concentration in 0.5 M KHCO_3 solution, we could also expect a similar increment in limiting current density at high pressure. We can correlate this limiting current density with the diffusion layer thickness that defines the rate of mass transport resistance to the electrode surface. In general, diffusion layer thickness is calculated using experimentally observed limiting current density data or based on theoretical methods. Here, we used the diffusion layer thickness that was fitted to the experimentally observed limiting current density data of Todoroki et al. [32]. The kinetic parameters obtained from the fitting process used to simulate voltage dependent current density for CO_2RR and HER using the Butler–Volmer

equation as shown in Figure 5. The kinetic parameters used for the calculation are listed in Table 1 [32,34]. To show the effect of CO_2 concentration polarization across the $50\ \mu\text{M}$ diffusion layer, the current density is simulated with and without mass transfer effects (Figure 5a). The limiting current density of $30\ \text{mA}\cdot\text{cm}^{-2}$ is obtained for mass transport limited CO_2RR in atmospheric pressure (33mM). The effect of CO_2 partial pressure on the current density is shown in Figure 5b. We can clearly see that the CO_2 limiting current density is increasing with increasing CO_2 partial pressure. The predicted limiting current density is $200\ \text{mA}\cdot\text{cm}^{-2}$ at 40 bar, which is nearly seven times higher compared to atmospheric CO_2 pressure.

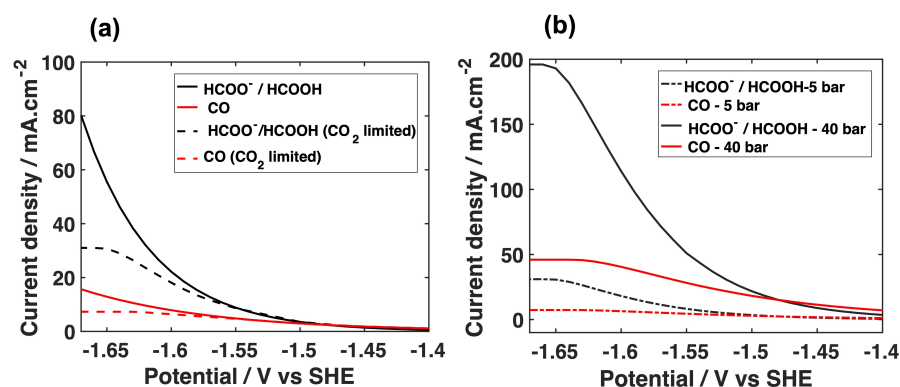


Figure 5. (a) The potential dependent partial current density of formate/formic acid and CO formation with and without applying CO_2 mass transport resistance. The current density without mass transfer resistance is calculated assuming that the CO_2 concentration at the electrode surface is equal to bulk at all voltage. For the mass transfer affected current density, the surface concentration is updated for every applied potential; (b) effect of CO_2 pressure on maximum achievable current density for formate/formic acid and CO at 5 and 40 bar, respectively.

Mass Transport Limitations in Monopolar and Bipolar Membranes

In MEA configured CO_2 electrolyzers, the role of ion selective membrane is crucial to determine the performance of CO_2RR . Since CEM is permeable to positively charged ions, it transports not only H^+ ions but also allows transport of K^+ ions. However, the concentration of K^+ is much higher in the catholyte than that of H^+ ions. Thus, the dominant charge carrier for the CEM membrane is K^+ ions. Figure 6 shows the concentration profile of K^+ ions across the cation exchange membrane and the diffusion layer adjacent to the CEM/electrolyte interface. When the current is applied, the K^+ ions transported from the anolyte compartment to the catholyte compartment where it becomes concentrated. The flux of K^+ ions enters the membrane is equal to the flux of CO_2 and H_2O consumed at the cathode surface. The concentration change of K^+ ions across the anolyte/CEM interface and within CEM at $100\ \text{mA}\cdot\text{cm}^{-2}$ is shown in Figure 6b. As expected, the concentration of K^+ is depleted at the anolyte side of the membrane as a result of migration into the membrane. The concentration changes within either side of the membrane are also evident from Figure 6b, which indicates ion transport across the membrane. One of the implications of the constant pumping of K^+ ions from anolyte to catholyte is that, after a certain period of time (depending on the concentration of KHCO_3), the depletion of K^+ ion starts limiting the cell performance. This transport limitations of K^+ ion leads to increased cell voltage and decreased Faradaic efficiency. After the complete transport of K^+ ions, the current will be carried by H^+ ion. This transition of H^+ ions being the main charge carrier, after the K^+ ions transport ceased, has important consequences for the total cell voltage. This behavior was experimentally observed by Vermaas et al. [72]. These authors showed a nearly 700 mV increase in the cell voltage due to the K^+ depletion. The increased H^+ concentration led to a change in 4 pH unit. Another effect of steady increases in the K^+ concentration in the CEM is the decreased CO_2 solubility due to salting-out effects at high catholyte concentration. It was observed in the previous studies that,

at high salt concentration (>1 M, KHCO_3), the CO_2 solubility was decreased due to the salting-out effect [34].

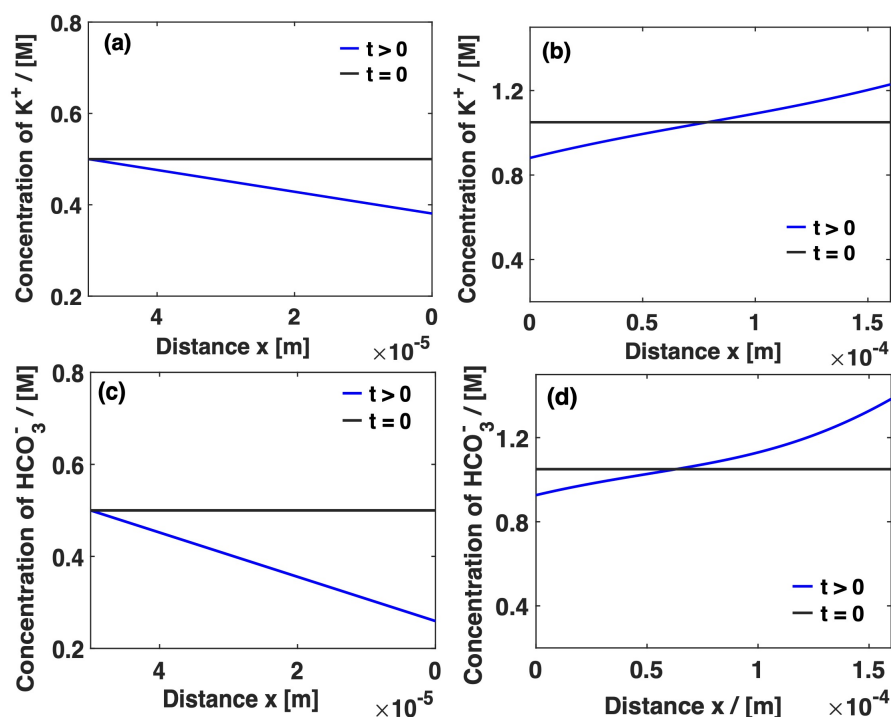


Figure 6. The transport of the ionic species through the diffusion layer (depleted side) and the bulk of the membrane at $t = 0$ (black line) and $t > 0$ (blue line). (a) the steady state concentration of K^+ at the depleted side of the CEM (blue line) and (b) inside the bulk of CEM (blue line); (c) the steady state concentration of HCO_3^- at the depleted side of the AEM (blue line) and the concentration change of HCO_3^- inside the bulk of AEM ((d), blue line). The equal concentration of 0.5 M KHCO_3 is assumed for catholyte and anolyte, respectively. The thickness of the bulk membrane is 160 μm , and the diffusion layer thickness on either side of the membrane is 50 μm .

Similarly, for AEM, the transport of HCO_3^- ions from the catholyte to the anolyte is modelled. Though AEM is permeable to other anions like CO_3^{2-} and OH^- , the concentration of these minority carriers is very low compared to the HCO_3^- ions and contributes little towards the total current density. Therefore, we limit our discussion to the transport of HCO_3^- only. The concentration changes within the diffusion layer and the bulk of the AEM are shown in Figure 6c,d for the 0.1 M KHCO_3 /0.1 M KHCO_3 system. When the HCO_3^- ions are transported, a concentration gradient is formed at the catholyte/AEM interface as shown in Figure 6c. The limiting current density is reached at $30 \text{ mA}\cdot\text{cm}^{-2}$ for 0.1 M HCO_3^- catholyte, which is lower than the limiting current achieved for CEM. Since we have a limited amount of HCO_3^- ions for a given volume of catholyte, the continuous transport of HCO_3^- completely depletes the catholyte of HCO_3^- ion. At this point, the pH of the catholyte bulk starts to increase as a result of the increased OH^- concentration and reduced buffering capacity of the catholyte. This increased catholyte pH favors the $\text{HCO}_3^-/\text{CO}_3^{2-}$ formation through homogeneous reaction of dissolved CO_2 . This pH effect can be clearly understood from Figure 4. At the anolyte side, concentrated $\text{HCO}_3^-/\text{CO}_3^{2-}$ ions react with H^+ ions (formed during OER at the anode) to form CO_2 . Therefore, under the limitation of HCO_3^- ion, the CO_2 will be transported to an anolyte compartment through $\text{HCO}_3^-/\text{CO}_3^{2-}$ formation. This is explained in a sequence of reactions in Figure 7. In addition, formate ions would also be transported to an anolyte compartment, where it oxidizes at the anode to form CO_2 . These complications in AEM assembled cells can be avoided by periodically replenishing the catholyte. In this way HCO_3^- is always available for transport and will

not limit the CO₂RR. Another important parameter extracted from the membrane model is the voltage drop across the membrane. Figure 8 shows the potential drop obtained for CEM and AEM. The potential drop across the AEM is higher than for the CEM; this means that the resistance of the AEM is higher than that of the CEM. The trend is expected since the concentration polarization is deeper for AEM compared to CEM (Figure 6). We can attribute this behaviour to the differences in diffusivity of HCO₃[−] ions.

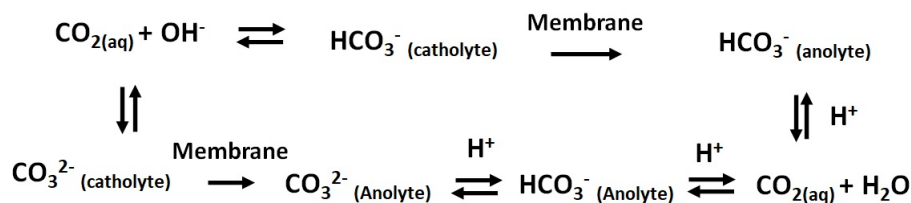


Figure 7. AEM ion transport mechanism; Transport of CO₂ (aq) from catholyte to anolyte in alkaline pH.

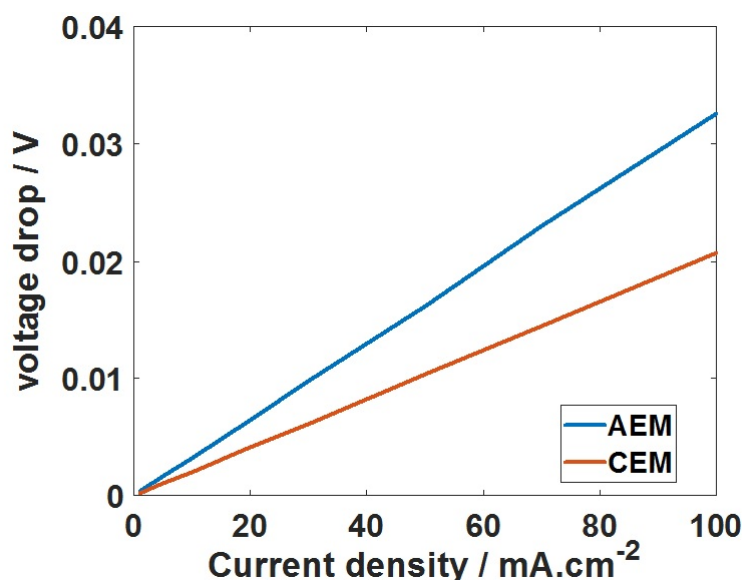


Figure 8. The potential drop across the CEM and AEM, respectively, at the current density up to 100 mA·cm^{−2}. The potential ($\phi = 0$) on the anolyte side of the membrane for CEM and catholyte side of the membrane for AEM is fixed to zero.

For the BPM, we consider that H⁺ and OH[−] ions are the main charge carriers. However, at low current density (<10 mA·cm²), the salt ions are the main charge carrier. Since the current density considered here is above the limiting current of salt ions, the total current is carried only by H⁺ and OH[−] ions. Though it is possible to use several electrolyte combinations for BPM operation, only the pH 7–14 and pH 7–7 system is the most suitable and widely used combination for the CO₂RR and OER reactions. The flux of water ions generated at the interfacial region depends on the water dissociation rate constant, which in turn depends on the pK_b of the weak base and the electric field strength. Figure 9a shows the value of the dissociation rate constant calculated for different pK_b. At pK_b 7, the dissociation rate constants for the protonation and deprotonation of a weak base are equal. The electric field enhanced rate constant for the electric field intensity ranges from 1 × 10⁸ V·m^{−1} to 1 × 10⁹ V·m^{−1}, which is calculated based on a second Wien effect (Figure 9b). The enhancement of the rate constant value depends on the relative permittivity of the electrolyte, in this case water. To support the high current density, the value of the dielectric constant, ϵ_r , should be lower than 30. Therefore, both the catalytic and electric field effect is needed to calculate the effective water dissociation rate constant.

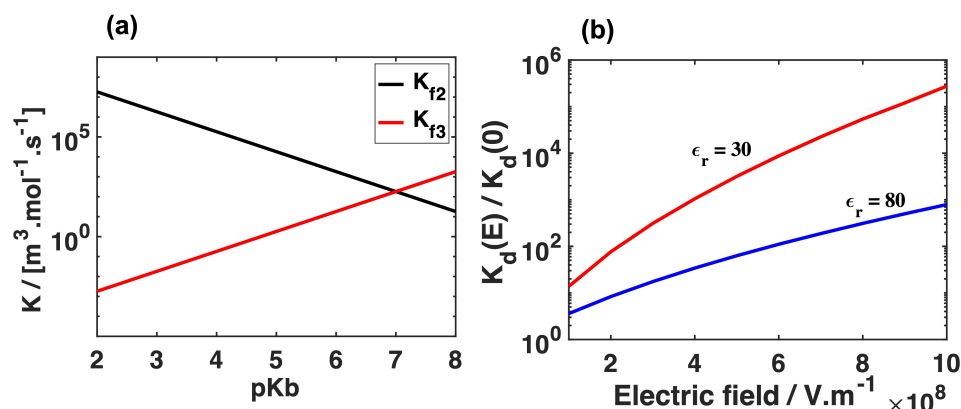


Figure 9. (a) pK_b dependent rate constant for protonation and deprotonation of a weak base group at the BPM interface. At $pK_a = 7$, the protonation and deprotonation rate constant is equal. The K_{f2} and K_{f3} indicate the forward rate constant of protonation and deprotonation reaction of the neutral base; (b) the electric field influenced rate constant at different dielectric constants of water.

The concentration changes within the CEM and AEM layer, and the corresponding membrane/electrolyte interface for the pH 7–7 and pH 7–14 is shown in Figure 10a,b. Since the H^+ ions and OH^- ions are migrated through the CEM and AEM layers, respectively, the pH gradient is formed in the DBL at either side of the BPM. For the current density of $50 \text{ mA} \cdot \text{cm}^{-2}$, there is a difference of 6 pH units between membrane and the catholyte bulk (Figure 10b), which corresponds to 350 mV loss (Equation (32)). At the same time, there is a small pH difference, approximately 0.2 pH unit at the anolyte side of the membrane. This small pH difference is due to high alkaline pH of the anolyte. If the 0.5 M KHCO_3 with the pH value of 7 is used as the anolyte, there will be a loss of additional 350 mV as a result of a 6 pH unit difference on the anolyte side of the membrane as well. Therefore, it is evident that use of alkaline anolyte is beneficial for the low polarization losses across the BPM. The concentration changes that appeared on the right side of the CEM layer is attributed to the flux of the H^+ ion that moved out of the membrane to support the required current density. Another important observation from Figure 10 is that the concentration polarization in AEM is higher compared to CEM. These differences in the concentration polarization are attributed to the lower mobility of hydroxide ions. Similar results were reported by Weber et al. [73].

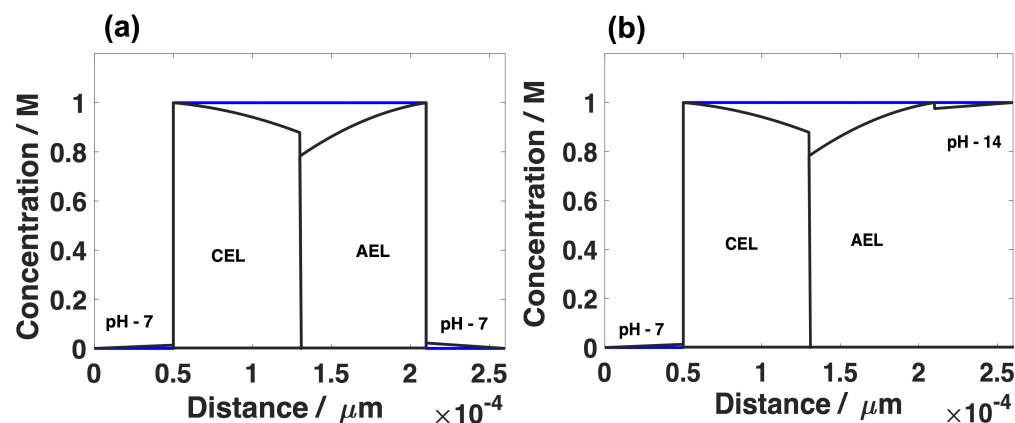


Figure 10. The concentration changes of H^+ and OH^- ions within the CEM and AEM layer for pH 7–7 (a) and pH 7–14 (b). The concentration profile is obtained at the applied current density of $50 \text{ mA} \cdot \text{cm}^{-2}$. The blue lines indicate the concentration at $t = 0$.

The polarization curve generated for the electrochemical reduction of CO_2 is shown in Figure 11. The E_T value of approximately 2.5 V is obtained from the onset potential of the

polarization curve shown in Figure 11. The onset potential is a combination of equilibrium potential (1.03 V), activation overpotential of cathode and anode, and also the membrane activation voltage (0.8 V) (Equation (30)). This is the minimum voltage required to start the reaction. The current density shown in Figure 11 is the total current density obtained from the Butler–Volmer equation by combining the partial current density of formate/formic acid, CO and H₂ formation. It can be clearly observed that the current density obtained from the model is in close agreement with the experimental value. To conclude, our investigation of mass transport limitations predicted crucial parameters needed for the scale-up process. Importantly, mass transport limitations at the electrode surface reveal that CO₂ solubility limitations can be overcome by operating at high pressure. A nearly seven-fold increase in current density was observed at 40 bar compared with the atmospheric pressure. The monopolar membrane model predicted a minimum electrolyte concentration of 0.1 M to operate the electrolyzer without membrane transport limitations. However, BPM allows the operation of low electrolyte salt concentrations because, at a high current density, the contribution of salt ions is negligible. The water ions (H⁺ and OH[−]) produced at the BPM interface will dominate the ion transport. Though BPM allows two different electrolytes with different pHs at the cathode and anode compartment, the value of the electrolyte pH is crucial. The BPM model showed that neutral or slightly acidic catholyte and alkaline anolyte are required to reduce the potential drop across the membrane. It results in lower cell voltage and enhanced Faradaic efficiency. With this versatile capability, the bipolar membrane will contribute tremendously to large-scale CO₂ electrolyzer operations in the near future. However, higher activation potential to initiate the water dissociation reactions pushes up the operating voltage of the electrolyzer. Therefore, better catalysts need to be developed to lower the water activation potential and future research on the BPM will move towards this direction.

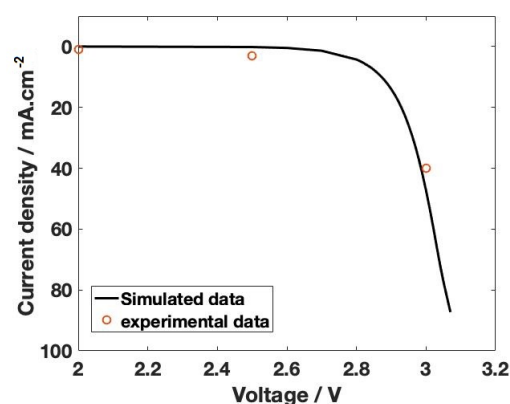


Figure 11. The polarization curve of CO₂ electrolyzer at 5 bar. The curve is generated by combining equilibrium potential (E_{equ}) and activation overpotential of respective electrode reactions (cathode and anode) and the membrane. The value for E_{equ} is assumed from the onset voltage of the polarization curve obtained from experimental data. The mass transport resistance of CO₂ is included in calculating the total current density, which is the sum of partial current density of formate/formic acid, CO and H₂. The ohmic loss is not included in the polarization curve, and it can be added as a series resistance to calculate the current density. The black bold line is the simulated polarization curve, and the hollow circles are experimental data points.

4. Conclusions

In this work, we developed a model to understand the transport limitations in the electrochemical conversion of CO₂ to formic acid. In particular, the mass transport of CO₂ to the electrode surface and ion transport through the membrane is modelled. The electrochemical reduction of CO₂ at the cathode and the oxygen evolution reaction at the anode are described by a 1D diffusion–reaction model. In the bulk catholyte, dissolution of CO₂ and the effect of pH at different electrolyte concentration are analysed. The effect of mass transport limitation on the partial current density of formate/formic acid formation

are significant. The maximum attainable current density is increasing with CO₂ pressure due to the high concentration of CO₂. The membrane model reveals important information about which type of electrolyte should be used, and it clarifies the role of pH on the polarization loss in CO₂ electrolyzers. The model predicted that, for electrolyte concentration below 0.1 M, the system is limited by the transport of the ions through the membrane. The high electrolyte salt concentration will eliminate the influence of transport limitation through the membrane. Another finding of this work is that polarization loss across the bipolar membrane depends on the pH of the electrolyte and the polarization losses due to membrane, which increases with decreasing anolyte pH.

Author Contributions: Conceptualization, M.R. and T.J.H.V.; methodology, S.C., M.R. and T.J.H.V.; investigation, S.C., M.R. and T.J.H.V.; writing—original draft preparation, S.C.; writing—review and editing, S.C., M.R. and T.J.H.V.; supervision, M.R. and T.J.H.V. All authors have read and agreed to the published version of the manuscript.

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Institutional Review Board Statement: Not applicable.

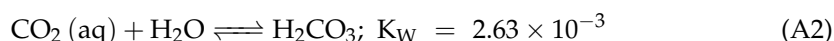
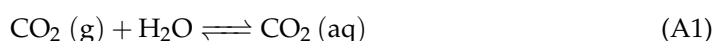
Informed Consent Statement: Not applicable.

Data Availability Statement: Available from the authors upon reasonable request.

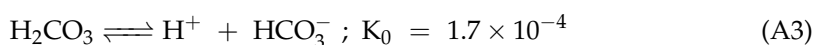
Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

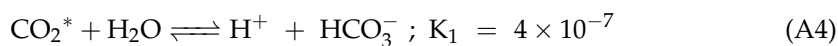
The cathode side of the cell contains three parts which include CO₂ dissolution reaction in the bulk electrolyte, transport of the species to the electrode surface through the diffusion layer and electrochemical reactions at the electrode surface. When gaseous CO₂ (g) is dissolved in water, it undergoes a series of chemical reactions and produces several reactive species. The dissolved CO₂ (aq) reacts with water to form carbonic acid (H₂CO₃)



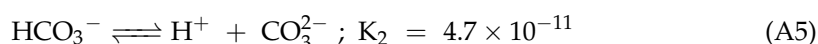
The carbonic acid is a diprotic acid which further undergoes two subsequent acid dissociation reactions and produces HCO₃[−] and CO₃^{2−} ions:



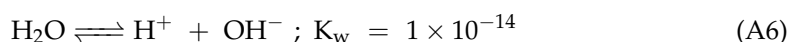
The concentration of H₂CO₃ is very low compared with the concentration of CO₂. Therefore, it is assumed to be in equilibrium with HCO₃[−] at all times and represented as CO₂^{*}:



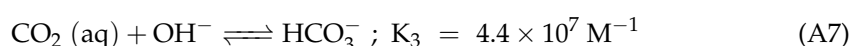
The HCO₃[−] ion further undergoes an acid dissociation reaction which produces carbonate ions with the following reaction:



In addition to the CO₂ dissolution reaction, water dissociation also occurs in the electrolyte:



At higher pH (pH > 7), CO₂ (aq) directly reacts with OH[−] and forms HCO₃[−]:



The concentration of HCO_3^- and CO_3^{2-} can be calculated from

$$[\text{HCO}_3^-] = K_1 \times \frac{[\text{CO}_2^*]}{[\text{H}^+]} \quad (\text{A8})$$

$$[\text{CO}_3^{2-}] = K_2 \times \frac{[\text{HCO}_3^-]}{[\text{H}^+]} \quad (\text{A9})$$

The mass balance and charge balance in the electrolyte are described as follows:

$$C_{\text{Total}} = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

$$[\text{K}^+] + [\text{H}^+] = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{OH}^-]$$

The distribution of reactive species at equilibrium in the bulk electrolyte can be calculated by substituting Equations (A8) and (A9) in the carbon and charge balance. The species present in the bulk electrolyte are also considered to be present in the diffusion layer. These species will react with hydroxide ions generated during the electrochemical reactions.

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