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## Towards membrane-electrode assembly systems for CO<sub>2</sub> reduction: a modeling study†

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Membrane-electrode assemblies (MEAs) are an attractive cell design for the electrochemical reduction of CO<sub>2</sub> because they exhibit low ohmic loss and high energy efficiency. We describe here the development and application of a multiphysics model to investigate the fundamental limitations of two MEA designs: one with gaseous feeds at both the anode and cathode (full-MEA), and the other with an aqueous anode feed (KHCO<sub>3</sub> or KOH exchange solution) and a gaseous cathode feed (exchange-MEA). The total current density for the three cases follows the order: KOH-MEA > KHCO<sub>3</sub>-MEA > full-MEA. This trend is established by examining the distribution of the applied voltage. We show that the main charge-carrying species are carbonate anions for an MEA that uses an anion-exchange membrane (AEM). The amount of CO<sub>2</sub> consumed but not converted to CO decreases with increasing current densities above 100 mA cm<sup>-2</sup> for a full-MEA, but converges to 50% for exchange-MEAs. The full-MEA becomes limited by ohmic resistance as the membrane dehydrates with increasing cell temperature, and eventually becomes limited due to water mass transport. The exchange-MEAs can maintain membrane hydration and the local ion concentration at the anode, but are limited by salt precipitation at the cathode, as well as a higher tendency to flood. Finally, we explore the effects of temperature and discuss the possibility of increasing water supply to the full-MEA to improve its performance at elevated temperatures. The MEA model and the understanding of MEA performance for the electrochemical reduction of CO<sub>2</sub> presented in this study should help guide the design of next-generation CO<sub>2</sub> reduction cells.

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### Broader context

CO<sub>2</sub> electrolyzers powered by solar energy, either directly or indirectly, have become increasingly attractive as solar prices decline and atmospheric CO<sub>2</sub> levels rise. The product formed by CO<sub>2</sub> reduction can be used as fuel or as precursors to fuel or chemical industry, thereby enabling the storage of intermittent solar radiation in chemical bonds. For CO<sub>2</sub> electrolyzers to be commercially viable, high current densities must be achieved with good selectivity at relatively low power inputs. The design and optimization of such devices require understanding the underlying physics, which includes transport phenomena, electrochemistry, heat transfer, and reaction kinetics. The work presented here describes a numerical model that accounts for the aforementioned physical phenomena occurring in membrane electrode assemblies (MEAs). The model reveals intrinsic tradeoffs and limitations of MEAs for the electrochemical reduction of CO<sub>2</sub>, and establishes design and operating criteria for such systems. The model also confirms that ohmic losses in MEAs are low because charge transport through a liquid electrolyte is eliminated.

## Introduction

Electrochemical reduction of CO<sub>2</sub> allows conversion of this greenhouse gas to value-added products under mild conditions. This process also provides a way to store excess electrical energy and tackle intermittency issues associated with

renewable energy sources (*e.g.*, wind and solar).<sup>1,2</sup> For the electrochemical reduction of CO<sub>2</sub> to be commercially viable, it is necessary to carry out CO<sub>2</sub> reduction (CO<sub>2</sub>R) at current densities >100 mA cm<sup>-2</sup>, while minimizing the power input (or cell voltage).<sup>3</sup> Such current densities require higher local concentrations of CO<sub>2</sub>, which have been achieved predominantly with gas-diffusion electrodes (GDEs), architectures that allow for new avenues of exploration and efficiency.<sup>4</sup> GDEs overcome the significant mass-transfer resistances associated with CO<sub>2</sub>R carried out in aqueous electrolytes—a consequence of the large mass-transfer boundary layer near the planar electrodes.<sup>5–13</sup>

Minimizing cell ohmic overpotential requires increasing the conductivity of the electrolyte, and decreasing the distance

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between the anode and cathode. Membrane-electrode-assemblies (MEAs) satisfy these two requirements by removing the aqueous electrolyte compartments between the electrodes and utilizing an ion-conducting polymer (ionomer) as both the separator and electrolyte. Membranes used in electrochemical systems are typically on the order of 10 to 100  $\mu\text{m}$  thick, with conductivities ranging from 10 to 200  $\text{mS cm}^{-1}$ .<sup>14</sup>

There have been numerous reports demonstrating the feasibility of MEA-like cells attaining  $\text{CO}_2\text{R}$  current densities upwards of 100  $\text{mA cm}^{-2}$ , an order of magnitude higher than can be achieved using typical aqueous architectures.<sup>5–11,15</sup> Various configurations and materials have been presented, with much debate as to which design is the most effective for scale-up and commercialization, as reviewed<sup>13</sup> and discussed<sup>4</sup> recently. Cook *et al.* first illustrated the electrochemical reduction of  $\text{CO}_2$  to hydrocarbons in an MEA design, showing an approximately 0.5 V reduction in the cell potential at 10  $\text{mA cm}^{-2}$  when removing the anolyte compartment.<sup>16</sup> Hori *et al.* found that an anion-exchange membrane (AEM) is more suitable for  $\text{CO}_2\text{R}$  than a cation-exchange membrane (CEM), as the CEM not only prevents transport of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  anions, but also allows high proton concentrations that promote the competing hydrogen evolution reaction (HER).<sup>17</sup> In agreement with Hori *et al.*, Delacourt *et al.* noted the importance of minimizing proton concentration near the cathode to suppress HER. However, these authors did not observe  $\text{CO}_2\text{R}$  products over Ag using a CEM, but obtained an 80%  $\text{CO}_2\text{R}$  faradaic efficiency (FE) after adding a  $\text{KHCO}_3$  buffer layer between the cathode and CEM. They found a FE of only 3% for  $\text{CO}_2\text{R}$  with an AEM but did not fully explain why the efficiency was so low.<sup>18</sup> It is notable that Salvatore *et al.* also explored adding a buffer layer between the cathode and membrane to improve the  $\text{CO}_2\text{R}$  current efficiency for an MEA-like cell (aqueous anode feed and gaseous cathode feed, with no anolyte or catholyte compartments). These authors found that the buffer layer provided better hydration, since adding a water layer in place of the buffer layer also achieved a higher  $\text{CO}_2\text{R}$  FE than could be reached in the absence of such a layer.<sup>19</sup> While it is tempting to draw general conclusions from the above studies, it is important to note that each one was performed using cell designs that differed from each other. Hori *et al.* retained the aqueous anolyte compartment but removed the aqueous catholyte compartment,<sup>17</sup> Narayanan, Li, and Salvatore removed the aqueous electrolyte compartments and used an aqueous feed instead,<sup>19–21</sup> and Delacourt, Kriescher, and Wang utilized pure gaseous feeds with no aqueous electrolyte.<sup>18,22,23</sup> Without a quantitative understanding of the limitations of each design, it is difficult to compare the results reported in different studies and to draw general conclusions from them. To date, there has been limited analysis of an MEA performing  $\text{CO}_2\text{R}$  in the absence of aqueous electrolyte compartments at low temperature (as opposed to solid-oxide electrolyzers<sup>24,25</sup>). Delacourt *et al.* simulated an electrochemical cell with a cation exchange membrane and a catholyte (no anolyte), and briefly mentioned replacing the catholyte with an anion-exchange membrane to obtain a higher current density. They concluded that a fully solid-state MEA could enhance performance of a

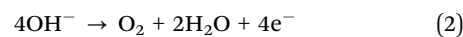
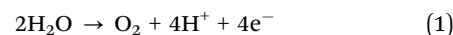
$\text{CO}_2$  electrolyzer, but did not go into details to describe MEA operation and limitations.

In this paper, we present a modeling framework that describes mass transport, electrochemical and homogenous reaction kinetics, and thermal effects for an AEM-MEA cell with pure gaseous feeds (full-MEA), and with a gaseous cathode feed but an aqueous anode feed (exchange-MEA). Our model differs from that for an alkaline fuel-cell/electrolyzer in two main aspects. First, there are competing electrochemical reactions occurring at the cathode (HER and  $\text{CO}_2\text{R}$ ) and second, the  $\text{CO}_2$  concentration is much higher in the  $\text{CO}_2\text{R}$  system (compared to a maximum of 400 ppm for fuel cell systems), which means that the homogeneous acid/base bicarbonate reactions are significant and must be accounted for, especially in an alkaline environment. We use our model to examine the performance of an MEA system for the  $\text{CO}_2$  reduction over an Ag catalyst, which primarily produces CO and  $\text{H}_2$ . Based on our simulations, we discuss the advantages and limitations of different MEA cell designs for performing  $\text{CO}_2\text{R}$ , and examine potential methods for improving water management in the membrane and the overall cell efficiency. Finally, the presented model, methodology, and subsequent analysis provides a framework for investigating these and related electrochemical energy-conversion processes that involve complex and multiple reaction and transport processes.

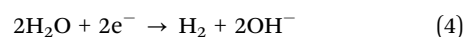
### Model development

This section aims to discuss the modeling approach, governing equations, and assumptions to give the reader a primer and methodology for tackling complex multiphysics problems common for electrochemical energy-devices. The discussion includes justifications, governing equation formulation, and determination of key parameter values. The MEA model comprises a 50  $\mu\text{m}$  anion-exchange membrane (AEM), a 5  $\mu\text{m}$  Ag cathode catalyst layer (CL), and a 100  $\mu\text{m}$  cathode diffusion medium (DM), as shown in Fig. 1. The anode, an  $\text{IrO}_2$  mesh pressed against the membrane, is treated as an interface.  $\text{N}_2$  with 100% relative humidity (RH) is fed to the anode chamber for the full-MEA, and an aqueous solution is fed for the exchange-MEA; humidified  $\text{CO}_2$  (100% RH) is fed to the cathode chamber for both MEA configurations.

At the anode, the oxygen evolution reaction (OER) occurs *via* both acidic and alkaline processes,



HER and  $\text{CO}_2\text{R}$  reaction occur at the cathode. Similar to the OER, both acidic and alkaline HER can occur,



For a Ag cathode, CO has been shown to be the predominant  $\text{CO}_2\text{R}$  product formed, therefore, CO evolution reaction (COER) is equivalent to  $\text{CO}_2\text{R}$  reaction for our system.<sup>10,26,27</sup> Shen *et al.* have observed a less prominent pH-dependence of the COER compared to the HER at low pH, suggesting that  $\text{H}_2\text{O}$  serves

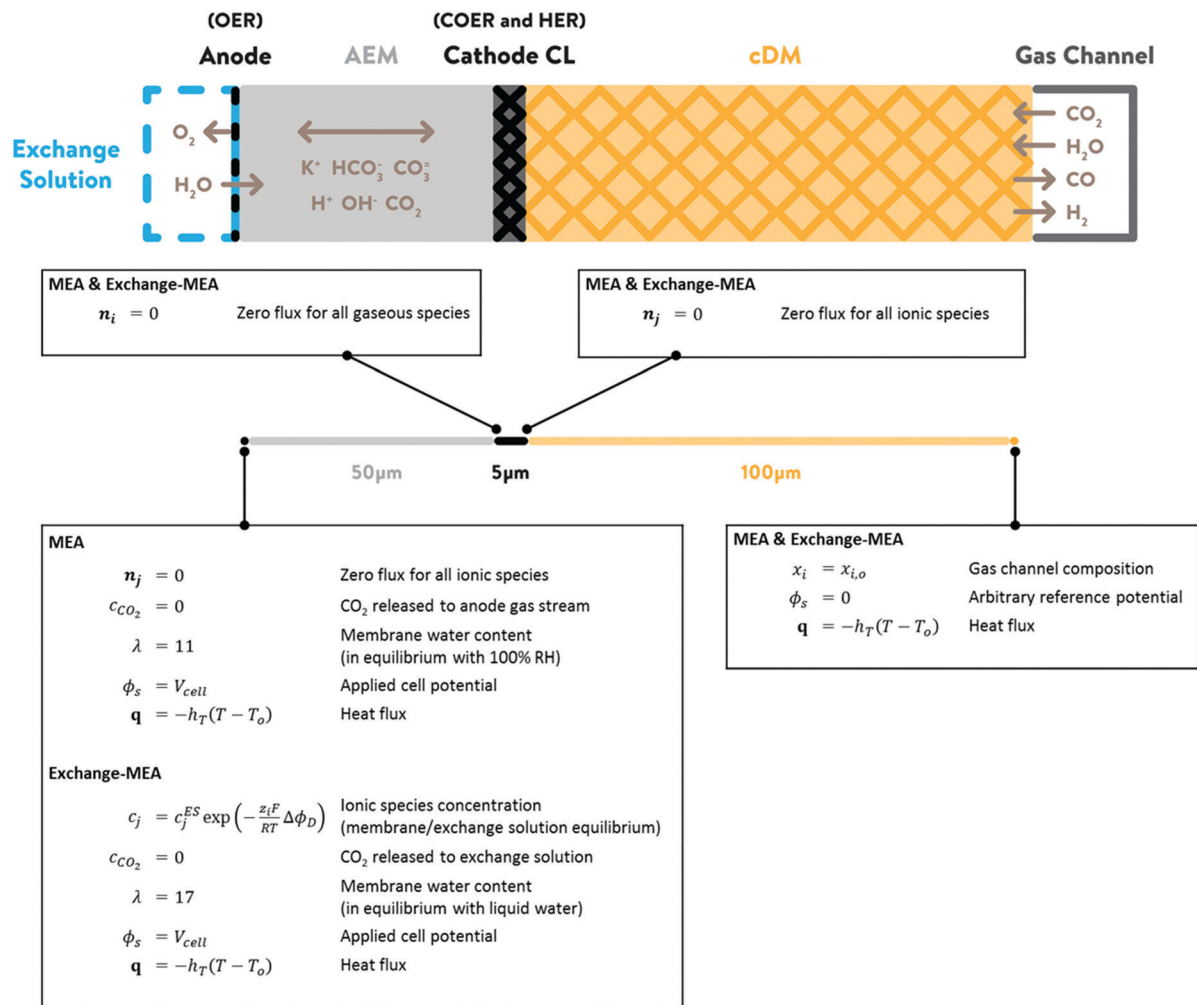


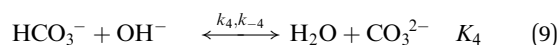
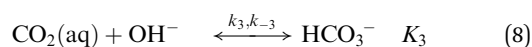
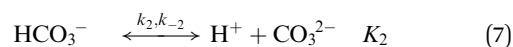
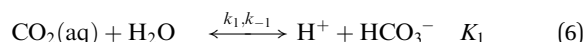
Fig. 1 Schematic of modeling framework and boundary conditions.

as the proton source for the reaction.<sup>28</sup> For this reason, the alkaline reaction is used for COER,



The ionomer membrane electrolyte has a fixed positive charge concentration,  $c_M$ , determined by the product of its ion-exchange capacity, IEC, and its density,  $\rho_M$ . We use properties of a Tokuyama A201 membrane, listed in Table 1. The water content,  $\lambda$ , describes the extent of hydration of the membrane, and is defined as the number of water molecules per cationic group in the membrane. For simplicity, we use the water-uptake isotherm measured by Peng *et al.* for a  $\text{HCO}_3^-$  AEM at 25 °C, and ignore its dependence on the anion type and temperature.<sup>29</sup> Water-uptake isotherms reported for several Tokuyama A201 membranes show a weak dependence on temperature.<sup>29–31</sup> Results of temperature-dependent membrane isotherms are discussed in the ESI.† Additionally, the membrane is determined to be primarily in the  $\text{HCO}_3^-/\text{CO}_3^{2-}$  form (discussed later), making the  $\text{HCO}_3^-$  form of the isotherm a reasonable approximation. The water-uptake isotherm also describes the relationship between water concentration and water activity in the membrane.

Homogeneous reactions, including bicarbonate buffer and water-dissociation reactions, occur in the ionomer and aqueous phases,



Here,  $K_n$  denotes the equilibrium constant for reaction  $n$ , calculated from van't Hoff equation using the change of entropy,  $\Delta S_n$ , and the heat of reaction,  $\Delta H_n$ , listed in Table 1

$$K_n = \exp\left(\frac{\Delta S_n}{R}\right) \exp\left(-\frac{\Delta H_n}{RT}\right) \quad (11)$$

The kinetics of these reactions are described using the rate coefficients measured by Shultz *et al.* rounded to the nearest

Table 1 List of parameters

Parameter	Value	Unit	Ref.
<b>Membrane</b>			
$L_M$	$5 \times 10^{-5}$	M	
IEC	1.7	mmol g <sup>-1</sup>	29
$\rho_M$	1.2	g ml <sup>-1</sup>	29
<b>DM</b>			
$L_{DM}$	$10^{-4}$	M	
$\varepsilon_{DM}$	0.8		
$r_{p,DM}$	$7.33 \times 10^{-7}$	M	38
$\sigma_{DM}$	220	S m <sup>-1</sup>	39
$\kappa_{sat,DM}^0$	$1.72 \times 10^{-11}$	m <sup>2</sup>	40
$k_{T,DM}$	0.015	W m <sup>-1</sup> K <sup>-1</sup>	41
<b>CL</b>			
$L_{CL}$	$5 \times 10^{-6}$	M	
$\varepsilon_{CL}$	0.5		
$r_{p,CL}$	$25 \times 10^{-7}$	M	38
$a_v$	$10^7$	m <sup>-1</sup>	42
$\sigma_{CL}$	100	S m <sup>-1</sup>	39
$\kappa_{sat,CL}^0$	$8 \times 10^{-16}$	m <sup>2</sup>	40
$k_{T,CL}$	0.003	W m <sup>-1</sup> K <sup>-1</sup>	41
<b>Gas species properties</b>			
$\nu_{p,H_2}$	7.07		43
$\nu_{p,H_2O}$	12.7		43
$\nu_{p,CO}$	18.9		43
$\nu_{p,CO_2}$	26.9		43
$P_{vap}$	$10^{8.07 - \frac{1730.63}{T[K] - 39.724}}$	mmHg	44
$H_{CO_2}$	$34 \exp\left(2400\left(\frac{1}{T[K]} - \frac{1}{298}\right)\right)$	mM atm <sup>-1</sup>	44
<b>Aqueous species properties</b>			
$D_{K^+}$	$1.96 \times 10^{-5} \exp\left(-2300\left(\frac{1}{T[K]} + \frac{1}{298}\right)\right)$	cm <sup>2</sup> s <sup>-1</sup>	45
$D_{H^+}$	$4.49 \times 10^{-5} \exp\left(-1430\left(\frac{1}{T[K]} + \frac{1}{273}\right)\right)$	cm <sup>2</sup> s <sup>-1</sup>	46
$D_{OH^-}$	$2.89 \times 10^{-5} \exp\left(-1750\left(\frac{1}{T[K]} + \frac{1}{273}\right)\right)$	cm <sup>2</sup> s <sup>-1</sup>	46
$D_{HCO_3^-}$	$7.016 \times 10^{-5} \left(\frac{T[K]}{204.03} - 1\right)^{2.3942}$	cm <sup>2</sup> s <sup>-1</sup>	47
$D_{CO_3^-}$	$5.447 \times 10^{-5} \left(\frac{T[K]}{210.26} - 1\right)^{2.1919}$	cm <sup>2</sup> s <sup>-1</sup>	47
$D_{CO_2}$	$2.17 \times 10^{-5} \exp\left(-2345\left(\frac{1}{T[K]} + \frac{1}{303}\right)\right)$	cm <sup>2</sup> s <sup>-1</sup>	44
$D_w$	$9 \times 10^{-17} \exp(5.9a_w)$	cm <sup>2</sup> s <sup>-1</sup>	29
<b>Homogeneous reactions</b>			
$S_1$	-96.31	J mol <sup>-1</sup> K <sup>-1</sup>	44
$S_2$	-148.1	J mol <sup>-1</sup> K <sup>-1</sup>	44
$S_w$	-80.66	J mol <sup>-1</sup> K <sup>-1</sup>	44
$H_1$	7.64	kJ mol <sup>-1</sup>	44
$H_2$	14.85	kJ mol <sup>-1</sup>	44
$H_w$	55.84	kJ mol <sup>-1</sup>	44
$k_1$	$10^{-2}$	s <sup>-1</sup>	32
$k_2$	$10^2$	s <sup>-1</sup>	32
$k_3$	$10^3$	L mol <sup>-1</sup> s <sup>-1</sup>	32
$k_4$	$10^9$	L mol <sup>-1</sup> s <sup>-1</sup>	32
$k_w$	$10^{-3}$	mol L <sup>-1</sup> s <sup>-1</sup>	32
<b>Charge transfer reactions</b>			
$\Pi_{OER}$	$240 \frac{T[K]}{298}$	mV	41
$\Pi_{HER}$	$13 \frac{T[K]}{298}$	mV	Approximated

Table 1 (continued)

Parameter	Value	Unit	Ref.
$\Pi_{\text{COER}}$	$40 \frac{T [\text{K}]}{298}$	mV	Approximated
Others			
$h_{\text{T,liquid}}$	$10^4$	$\text{W m}^{-2} \text{K}^{-1}$	Assumed
$h_{\text{T,gas}}$	$10^3$	$\text{W m}^{-2} \text{K}^{-1}$	Assumed

order of magnitude.<sup>32</sup> Results by Divekar *et al.* suggest that these rate coefficients, as well as equilibrium constants, likely differ in an ionomer compared to those for an aqueous solution;<sup>33</sup> however, to the best of our knowledge, the magnitudes of these differences have not been established, and are likely to vary with membrane hydration, counterion identity, *etc.*<sup>34,35</sup> Such investigation is beyond the scope of the current efforts. The effects of varying the rate of reaction for eqn (8) are discussed in the ESI† (Fig. S2).

The CL and DM are both porous structures. The solid fraction of the CL is composed of Ag nanoparticles in an ionomer binder, and the DM is a hydrophobic carbon-fiber structure. We assume that the thickness of the anionic ionomer coating the Ag nanoparticles within the CL is 10 nm, which is sufficient to provide an ionic pathway for anions between the catalyst nanoparticles and the membrane.<sup>36</sup> The DM is assumed to remain liquid free, which is reasonable considering its hydrophobic nature and existence of a temperature gradient discussed later.

The MEA model is built upon framework of the GDE model we reported previously.<sup>37</sup> The governing equations and a list of parameters are summarized in Tables 2–4. The model describes five main physical phenomena: transport of neutral and ionic species (including diffusion, migration, and convection), fluid flow through a porous medium, current and (over)potential distribution, chemical (homogeneous) and electrochemical (heterogeneous) reactions, and heat transfer. The model applies conservation of mass, momentum, charge, and energy to solve for the following state variables: mole fractions of gaseous species  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ , and  $\text{H}_2$  in the cathode GDE, concentrations of dissolved  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in the membrane and ionomer, concentrations of ionic species  $\text{K}^+$ ,  $\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$  in the membrane and ionomer, gas-phase velocity in the cathode GDE, potentials of the solid-phase electrode and ionic-phase electrolyte, and temperature of the MEA. Fig. 1 provides an overview of the boundary conditions imposed. Below, we discuss in further detail relevant equations used to obtain effective parameter values, the source terms in each phase, and the boundary conditions for the three cases studied in this paper: full-MEA, 0.5 M  $\text{KHCO}_3$  exchange-MEA, and 0.5 M  $\text{KOH}$  exchange-MEA.

### Electrolyte/ionomer membrane equilibrium

The fixed background charge of an ionomer membrane leads to an electric potential difference at the membrane ( $\phi_1^{\text{M}}$ )/exchange

Table 2 Governing equations (see nomenclature for symbol definitions)

Solid phase variable: $\phi_s$	
$\nabla \cdot \mathbf{i}_s = -\nabla \cdot \mathbf{i}_l = -a_v \sum_k \mathbf{i}_k$	(12)
$\mathbf{i}_s = -\sigma_s^{\text{eff}} \nabla \phi_s$	(13)
Aqueous phase variables: $\omega_j, j = \text{CO}_2(\text{l}), \text{K}^+, \text{H}^+, \text{OH}^-, \text{HCO}_3^-, \text{CO}_3^{2-}, \text{H}_2\text{O}; \phi_l$	
$\nabla \cdot \mathbf{n}_j = R_{\text{CT},j} + R_{\text{B},j} + R_{\text{PT},j}$	(14)
$\mathbf{n}_{j \neq \text{H}_2\text{O}} = -D_j^{\text{eff}} \rho_l \nabla \omega_j + \frac{z_j F}{RT} D_j^{\text{eff}} \rho_l \omega_j \nabla \phi_l$	(15)
$\mathbf{n}_w = -D_w \rho_l \nabla \omega_w + \sum_j \frac{\xi_j \mathbf{n}_j}{M_j}$	(16)
$\sum_j \frac{z_j \omega_j}{M_j} = 0$	(17)
Gas phase variables: $\omega_i, i = \text{CO}_2(\text{g}), \text{CO}, \text{H}_2, \text{H}_2\text{O}; p_G$	
$\nabla \cdot \mathbf{n}_i = R_{\text{CT},i} + R_{\text{B},i} + R_{\text{PT},i}$	(18)
$\mathbf{n}_i = \mathbf{j}_i + \rho_i \mathbf{u}_g$	(19)
$\mathbf{j}_i = -\rho_g D_i^{\text{eff}} \nabla \omega_i - \rho_g D_i^{\text{eff}} \omega_i \frac{\nabla M_n}{M_n}$	(20)
$\mathbf{u}_g = -\frac{k_m^{\text{eff}}}{\mu_g} \nabla p_G$	(21)
$\sum_i \omega_i = 1$	(22)
Energy variable: $T$	
$\nabla \cdot \mathbf{q} = Q_{\text{CT}} + Q_{\text{B}} + Q_{\text{J}}$	(23)
$\mathbf{q} = -k_{\text{T},m} \nabla T$	(24)

Table 3 Model parameter equations (see nomenclature for symbol definitions)

$D_j^{\text{eff}} = \epsilon_L^q \frac{D_{i,w}}{x_w (1 + \zeta_i)}$	(25)
$D_i^{\text{eff}} = \frac{\epsilon_m}{\tau_m} D_i = \epsilon_m^{3/2} \left( \frac{1}{D_i^{\text{SM}}} + \frac{1}{D_i^{\text{K}}} \right)^{-1}$	(26)
$D_i^{\text{SM}} = \frac{1 - \omega_i}{\sum_{n \neq i} \frac{y_n}{D_n}}$	(27)
$D_i^{\text{K}} = \frac{2r_{p,m}}{3} \sqrt{\frac{8RT}{\pi M_i}}$	(28)
$D_{iq} [\text{cm}^2 \text{s}^{-1}] = \frac{10^{-3} T [\text{K}]^{1.75} (M_i [\text{g mol}^{-1}]^{-1} + M_q [\text{g mol}^{-1}]^{-1})^{0.5}}{p [\text{atm}] (v_{p,i}^{0.33} + v_{p,q}^{0.33})^2}$	(29)

solution ( $\phi_1^{\text{E}}$ ) interface, the Donnan potential:  $\Delta \phi_{\text{D}} = \phi_1^{\text{M}} - \phi_1^{\text{E}}$ . At equilibrium, the electrochemical potential of each species in the two phases must be equal, resulting in the following



**Table 4** Source terms (see nomenclature for symbol definitions)

	$R_{CT,i} = -M_i \sum_k \frac{s_{i,k} a_v \dot{\mathbf{i}}_k}{n_k F}$	(30)	
	$R_{B,j} = M_j \sum_n s_{j,n} \left( k_n \prod_{s_{j,n} < 0} c_j^{-s_{j,n}} - \frac{k_n}{K_n} \prod_{s_{j,n} > 0} c_j^{s_{j,n}} \right)$	(31)	
	$R_{PT,j} = -R_{PT,i} = a_v M_j \frac{D_j^{\text{eff}}}{\delta_{\text{TF}}} (c_j^g - c_j)$	(32)	
Species	$R_{CT}$	$R_B$	$R_{PT}$
CO <sub>2</sub> (g)	—	—	Gas/ionomer
H <sub>2</sub> O(g)	—	—	Gas/ionomer
CO(g)	COER	—	—
H <sub>2</sub> (g)	HER	—	—
CO <sub>2</sub> (l)	COER	Eqn (6) and (8)	Gas/ionomer
H <sub>2</sub> O(l)	OER, HER, COER	Eqn (6), (9) and (10)	Gas/ionomer
K <sup>+</sup>	—	—	—
H <sup>+</sup>	OER, HER	Eqn (6), (7) and (10)	—
OH <sup>-</sup>	OER, HER, COER	Eqn (8)–(10)	—
HCO <sub>3</sub> <sup>-</sup>	—	Eqn (6)–(9)	—
CO <sub>3</sub> <sup>=</sup>	—	Eqn (7) and (9)	—

relationship between species concentration in the membrane,  $c_i^M$ , and in the exchange solution,  $c_i^E$ ,

$$c_i^M = c_i^E \exp\left(-\frac{z_i F}{RT} \Delta\phi_D\right) \quad (33)$$

The Donnan potential can then be determined by enforcing electroneutrality in the membrane, taking into consideration the background charge.  $\Delta\phi_D$  is positive for an AEM, due to its fixed positive background charge. This creates an extra energy barrier for cations to enter the membrane ( $z_i > 0$ , so the exponential term is less than unity), but does not necessarily completely exclude cations from the membrane. For simplicity, species concentration and the ionic potential in the membrane will be denoted as  $c_i$  and  $\phi_i$ , respectively, for the remainder of the paper.

### Electron transport and charge transfer reactions

The solid-phase electronic potential,  $\phi_s$ , is described by charge conservation, eqn (12), and Ohm's law, eqn (13). Charge-transfer reactions occur at the electrode/electrolyte interface, and can be described by the Tafel equation for overpotentials greater than 0.2 V (with less than 0.01% error compared to Butler–Volmer equation),<sup>48</sup>

$$\dot{\mathbf{i}}_k = -i_{o,k} \left( \frac{c_j}{c_j^{\text{ref}}} \right)^{\gamma_k} \exp\left(-\frac{\alpha_{c,k} F}{RT} \eta_k\right) \quad (34)$$

Here,  $\gamma_k$  is the reaction order with respect to some reactant,  $\alpha_{c,k}$  is the cathodic transfer coefficient, and  $\eta_k$  is the overpotential for reaction  $k$ . The exchange current density,  $i_{o,k}$ , depends on the pre-exponential factor,  $A_k$ , and the apparent activation energy,  $E_{a,k}$ , according to the Arrhenius equation,

$$i_{o,k} = A_k \exp\left(-\frac{E_{a,k}}{RT}\right) \quad (35)$$

Studies have shown that the activation energy for the HER is pH-dependent, with a slope of approximately 1 (kJ mol<sup>-1</sup>)/pH.<sup>49–55</sup> For the OER, we also assumed a linear dependence of  $E_a$  on pH and obtained a slope of, coincidentally, 1 (kJ mol<sup>-1</sup>)/pH from a fit to the experimental data reported by Kuo *et al.*<sup>56</sup> Designing electrocatalysts that lower the energy barrier for CO<sub>2</sub>R products and improve CO<sub>2</sub>R activity is an area of active research; the effects of  $i_{o,\text{COER}}$  on MEA performance are described in the ESI.† We note that such rate expressions are used empirically to capture the pH-dependence observed in experiments. The pre-exponential factors were fit to the exchange current densities reported in the references listed in Table 5; all kinetic parameters, including the standard electrode potential relative to the standard hydrogen electrode (SHE) of reaction  $k$ ,  $U_k^0$ , are summarized in Table 5.

Charge-transfer reactions contribute to source terms,  $R_{CT,i}$ , as listed in eqn (30); they apply to aqueous species CO<sub>2</sub>, OH<sup>-</sup>, and H<sup>+</sup>, and for gaseous species CO and H<sub>2</sub>. The electronic potential is set to  $\phi_s = 0$  at the cathode boundary, and varied from 2 to 4 V (cell voltage) at the anode boundary.

### Ionic and neutral species transport and acid/base reactions in the ionomer

Mass conservation, eqn (14), and the Nernst–Planck equation, eqn (15), govern the transport of ionic and neutral species and the electrolyte potential profile,  $\phi_i$ , in the ionomer. Commonly, Stefan–Maxwell diffusion is used to capture species/species interaction that become significant under non-dilute conditions. However, using the Stefan–Maxwell approach would introduce 28 additional degrees of freedom, and require that composition-dependent diffusion coefficients be determined (frictional interactions between six species, water, and membrane). Since this would considerably increase the uncertainty and the complexity of our numerical model, we resort to using Nernst–Planck equation for our system even though we are not necessarily under dilute conditions. For water, electro-osmosis replaces

**Table 5** Kinetic parameters for charge transfer reactions

	$U_k^0$ (V)	$A_k$ (mA cm <sup>-2</sup> )	$E_a$ (kJ mol <sup>-1</sup> )	$\alpha_{a/c}$	$\left(\frac{c_i}{c_i^{\text{ref}}}\right)^{\gamma_i}$	Ref.
Anode						
OER acid	1.23	$9.40 \times 10^{-7}$	11 + 1 × pH	1.5	—	56–58
OER base		$1.23 \times 10^{-4}$			[OH <sup>-</sup> ]/(1 M)	
Cathode						
HER acid	0	$2.77 \times 10^{19}$	83 + 1 × pH	0.44	[H <sup>+</sup> ]/(1 M)	49–55
HER base		$8.84 \times 10^6$			—	
COER	-0.11	$7.25 \times 10^8$	100	1	[(CO <sub>2</sub> )/(1 M)] <sup>1.5</sup>	26, 27 and 59

migration, represented by the second term on the right side of eqn (16), and thus some of the coupling between frictional forces is maintained. The electro-osmotic coefficients for water carried by ionic species  $i$  ( $\xi_i$ ) have not been well characterized for AEMs in the presence of CO<sub>2</sub>. Therefore, we adopt a value of one for the electro-osmotic coefficients, consistent with what is commonly used for a vapor-equilibrated CEM and close to the experimentally measured  $0.61 \pm 0.12$  for a vapor-equilibrated, OH<sup>-</sup> form of the Tokuyama A201 membrane.<sup>60,61</sup> The electro-osmotic coefficient tends to be higher for a liquid-equilibrated membrane, and has been reported to range from 2 to 7 for a KOH-equilibrated AEM.<sup>30,62</sup> We note that our model proved not to be strongly dependent on the value of the electro-osmotic coefficient (see Fig. S3, ESI†), so a value of one was used for all scenarios.

The effective diffusion coefficient for species other than H<sub>2</sub>O in the membrane,  $D_{j,M}^{\text{eff}}$ , is calculated using eqn (25) in Table 3 following Grew *et al.*<sup>63,64</sup> The water mole fraction,  $x_w$ , and water volume fraction in the ionomer,  $\varepsilon_L$ , are defined as

$$x_w = \frac{\lambda}{1 + \lambda} \quad (36)$$

and

$$\varepsilon_L = \frac{\lambda V_w}{\lambda V_w + V_M} \quad (37)$$

respectively, where  $V_M = 1/(\text{IEC} \cdot \rho_M)$  and  $V_w$  are the molar volume of the membrane and water, respectively.  $\zeta_i$  describes the ratio of species-water and species-membrane interaction and is approximated from kinetic theory to be<sup>65</sup>

$$\zeta_i = \frac{1}{\lambda} \left( \frac{V_M}{V_w} \right)^{2/3} \left( \frac{M_{i,M}}{M_{i,w}} \right)^{1/2} \quad (38)$$

where  $M_{i,M} = \left( \frac{1}{M_i} + \frac{1}{M_M} \right)^{-1}$  is the reduced molar mass. Water diffusivity in the membrane,  $D_{w,M}$ , is a function of ionomer water activity,  $a_w$ , as measured by Peng *et al.*, and fit to the expression listed in Table 1.<sup>29</sup> Finally, source terms due to homogeneous bulk reactions,  $R_{B,j}$ , eqn (31) in Table 4, are calculated using apparent rate coefficients (Table 1), which were approximated based on values reported by Schulz *et al.* rounded to the nearest order of magnitude.<sup>32</sup> Water activity instead of water concentration is used for homogeneous reactions involving water to ensure that equilibrium can be established at the electrolyte/ionomer membrane interface.  $R_{B,j}$  applies to aqueous species involved in reactions listed in eqn (6)–(10). Other source terms for aqueous species include charge-transfer reactions, eqn (30), discussed in the previous section, and phase-transfer reactions, eqn (32), discussed in the following section.

The flux for all species is set to zero at the CL/DM boundary at the cathode. At the anode boundary, CO<sub>2</sub> and H<sub>2</sub>O are taken to be in equilibrium with the anode feed gas (inert gas N<sub>2</sub> with 100% RH). The flux for all ionic species is set to zero for the full-MEA case, and for the exchange-MEA cases, all species are taken to be in equilibrium with the exchange solution, which is assumed to be at constant concentration. The anode boundary

condition assumes fresh exchange solution being circulated at a high flowrate in the anode channel.

### Gas-phase species transport

Concentration profiles for gaseous species are determined within the CL and DM domains. The Stefan–Maxwell equation, eqn (20) and Darcy's law, eqn (21) are used to describe the diffusion and convection terms, respectively. The effective diffusivity is an average of the Stefan–Maxwell diffusivity,  $D_i^{\text{SM}}$ , and Knudsen diffusivity,  $D_i^K$  (assuming both forms of diffusion occur in parallel) and is corrected for the porosity,  $\varepsilon_m$ , and the tortuosity,  $\tau_m$ , of medium  $m$  using Bruggeman's relationship, eqn (26)–(28). The binary gas-phase diffusion coefficients are calculated using the equation derived by Fuller *et al.*, eqn (29), where  $\nu_{p,i}$  is the diffusion volume of species  $i$ , listed in Table 1.<sup>43</sup>

The source terms for gaseous species occur in the CL domain. They include the charge transfer reactions producing H<sub>2</sub> and CO, eqn (30), and the adsorption/desorption of CO<sub>2</sub> and H<sub>2</sub>O into/out of the ionomer,  $R_{\text{PT},i}$ , eqn (32). The volumetric rate of gas dissolution into the ionomer phase is estimated using Fick's law, where  $c_i^g$  is the concentration of species  $i$  in equilibrium with its gas-phase concentration. For H<sub>2</sub>O,  $c_w^g = c_M \lambda^g$ , where  $\lambda^g$  corresponds to the water content in equilibrium with water activity  $a_w = p_{\text{G},w}/p_{\text{vap}}$ , obtained using the isotherm reported by Peng *et al.*<sup>29</sup> for CO<sub>2</sub>,  $c_{\text{CO}_2}^g = H_{\text{CO}_2} p_{\text{G},\text{CO}_2}$  where  $H_{\text{CO}_2}$  is the temperature-dependent Henry's constant for CO<sub>2</sub>, listed in Table 1. It should be noted that the ionomer and salinity effects of the water vapor pressure are not accounted for, since these are estimated to be small. H<sub>2</sub> and CO are neglected in the ionomer phase based on their limited solubility in water, an order of magnitude lower than CO<sub>2</sub>.<sup>44</sup> The fluxes of all gaseous species are set to zero at the membrane/CL boundary, and their mass fractions set to the cathode feed gas composition at the GDL/gas channel boundary.

### Energy transport

There are three sources of heat generation in the system: heat generated from charge-transfer reactions at the two electrodes,  $Q_{\text{CT}}$ , the heat of reaction from homogeneous bulk bicarbonate buffer reactions,  $Q_B$ , and Joule heating,  $Q_J$ .  $Q_{\text{CT}}$  consists of both irreversible losses and reversible heat generation,<sup>48</sup>

$$Q_{\text{CT}} = \sum_k (i_k \eta_k + i_k \Pi_k) \quad (39)$$

where  $\Pi_k$  is the Peltier coefficient for reaction  $k$ , listed in Table 1.  $\Pi_{\text{COER}}$  was approximated from the change in entropy for the overall reaction  $2\text{CO}_2 \leftrightarrow 2\text{CO} + \text{O}_2$ .<sup>41,48</sup>

$$\frac{\Pi_{\text{COER}}}{T} = \frac{\Delta S}{nF} - \frac{\Pi_{\text{OER}}}{T} \quad (40)$$

The term  $Q_B$  results from the change in enthalpy,  $\Delta H_n$ , for homogeneous reactions listed in eqn (6)–(10),

$$Q_B = \sum_n \Delta H_n \left( k_n \prod_{s_{j,n} < 0} c_j^{-s_{j,n}} - \frac{k_n}{K_n} \prod_{s_{j,n} > 0} c_j^{s_{j,n}} \right) \quad (41)$$



Finally, Joule heating due to electrical resistance is determined by,

$$Q_J = \frac{i_s^2}{\sigma_m} \quad (42a)$$

or

$$Q_J = \frac{i_l^2}{\kappa_1} \quad (42b)$$

for the solid and ionomer phase, respectively. The ionomer-phase conductivity is derived from the Nernst-Planck equation,<sup>48</sup>

$$\kappa_1 = \frac{F^2}{RT} \sum_j z_j^2 c_j D_j^{\text{eff}} \quad (43)$$

A Robin boundary condition is set at the two boundaries using a heat transfer coefficient,  $h_T$ , to describe the heat flux, driven by the difference between the cell temperature at that boundary and room temperature,  $T_0$ .

$$q_T = -h_T(T - T_0) \quad (44)$$

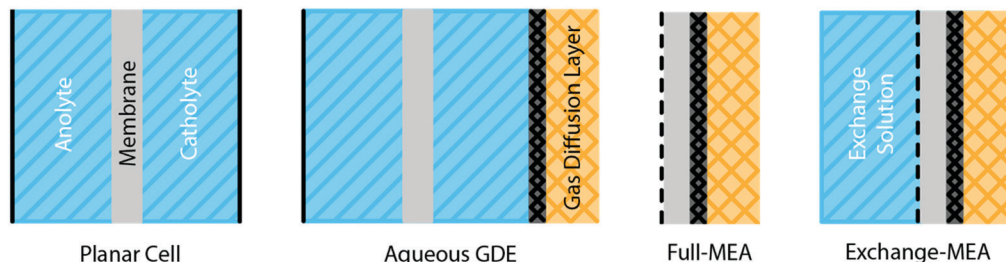
## Numerical method

The governing equations are solved using the MUMPS general solver in COMSOL Multiphysics 5.3a with a relative tolerance of 0.001. The modelling domain has a maximum element size of 0.01  $\mu\text{m}$ . Element sizes were decreased to 0.001  $\mu\text{m}$  near the boundaries to capture sharp concentration gradients. The base-case model has been provided in the ESI.†

## Results and discussion

### Dependence of the ohmic drop on cell configuration

An order-of-magnitude improvement in the  $\text{CO}_2\text{R}$  current density occurs in moving from a planar cathode to a GDE cathode configuration due to the increased active surface area and decreased mass-transfer resistances associated with the latter configuration.<sup>37</sup> Simply substituting the planar cathode with a GDE cathode (aqueous GDE cell shown in Fig. 2) results in an order-of-magnitude increase in the ohmic drop when the total current density is increased from 10 to 100  $\text{mA cm}^{-2}$ , rendering such cell designs impractical for industrial application. By



Potential distribution	Planar (10 $\text{mA cm}^{-2}$ )	Aqueous GDE (100 $\text{mA cm}^{-2}$ )	Full-MEA & Exchange-MEA (100 $\text{mA cm}^{-2}$ )
Thermodynamic potential under normal conditions (V) (OER + COER)	1.34		
Cathode overpotential (V)	1.1 <sup>59</sup>	0.7 <sup>37</sup>	0.7 <sup>37</sup>
Anode overpotential (V)	0.3*	0.4*	0.4*
Electrolyte ohmic potential (V) (0.5 M $\text{KHCO}_3$ , 6 $\text{S m}^{-1}$ )	0.2**	2**	0
Membrane ohmic potential (V) (50 $\mu\text{m}$ , 0.5 $\text{S m}^{-1}$ )	0.01	0.1	0.1
Total cell potential (V)	<b>2.95</b>	<b>4.54</b>	<b>2.54</b>

\*assuming OER on planar  $\text{IrO}_2$ , approximated from Butler-Volmer equation fitted to experimental data<sup>66</sup>

\*\*assuming 1 cm distance between anode and cathode

Fig. 2 Graphical illustration for various cell designs and a breakdown of the applied voltage. There is a 44% reduction in applied voltage for MEA compared to the aqueous GDE cell at the same total current density.

comparison, both the full-MEA and exchange-MEA eliminate the large ohmic drop by removing the electrolyte compartments and significantly decreasing the anode–cathode distance, allowing the cell to maintain the  $100 \text{ mA cm}^{-2}$  current density with a 44% reduction in the applied cell voltage. The values in Fig. 2 are first-order approximations and do not include effects such as concentration polarization, temperature changes, membrane dehydration, *etc.*; additional details on the approximation method are included in the ESI.† A mesh-like structure or GDE is required for the anode in the full-MEA and exchange-MEA designs where OER occurs to prevent layer delamination caused by the evolution of oxygen bubbles.

While the full-MEA and exchange-MEA minimize the ohmic loss across the cell, reactant and product crossover becomes a concern due to the small distance between the two electrodes. For an Ag cathode, almost no liquid product is produced and the CO solubility is low, limiting the CO crossover current density to approximately  $1 \text{ mA cm}^{-2}$  at room temperature (estimated using Fick's law and the solubility and diffusivity of CO in water). It should be noted though that the aqueous GDE cells can serve diagnostic purposes due to their isolation of a single electrode and easier implementations of a reference electrode for interrogation possibilities.<sup>13</sup> The GDE type designs though are efficiency and performance cells due to the reasons above.

#### Applied voltage breakdown and precipitation issues for a full-MEA and exchange-MEAs

Fig. 3 shows the (a) total current density (TCD) and (b) CO FE for the three cases considered: full-MEA, 0.5 M  $\text{KHCO}_3$  exchange-MEA, and 0.5 M KOH exchange-MEA. The exchange-MEA's produce a higher TCD and CO FE than the full-MEA at the same applied cell potential, with the KOH exchange-MEA achieving the highest performance. The variance in CO FE for the three cases can be explained by the cathode pH: the alkalinity at the cathode increases in the order MEA <  $\text{KHCO}_3$  exchange-MEA < KOH exchange-MEA because of the exchange solution, as well as the higher TCD producing  $\text{OH}^-$  at a higher rate at the cathode.

To understand the trend observed for the TCD, we plot the applied voltage breakdown (AVB) for the three cases (Fig. 3c, e and f). The applied voltage is comprised of the thermodynamic potential, the kinetic overpotential, and the transport overpotential (Nernstian plus ohmic components). The thermodynamic potential depends on the species concentrations near the two electrodes at the open circuit. Assuming that all gaseous species are at normal conditions, the thermodynamic potential,  $\eta_{\text{th}}$ , for a cell performing OER at the anode and COER at the cathode can be calculated as

$$\eta_{\text{th}} = (U_{\text{OER}}^{\circ} - U_{\text{COER}}^{\circ}) + \frac{RT}{F} \ln \left( \frac{c_{\text{OH}^-}^{\text{C}}}{c_{\text{OH}^-}^{\text{A}}} \right) \quad (45)$$

where  $c_{\text{OH}^-}^{\text{C}}$  and  $c_{\text{OH}^-}^{\text{A}}$  refers to the  $\text{OH}^-$  concentration at the cathode and anode, respectively. The Nernstian overpotential is

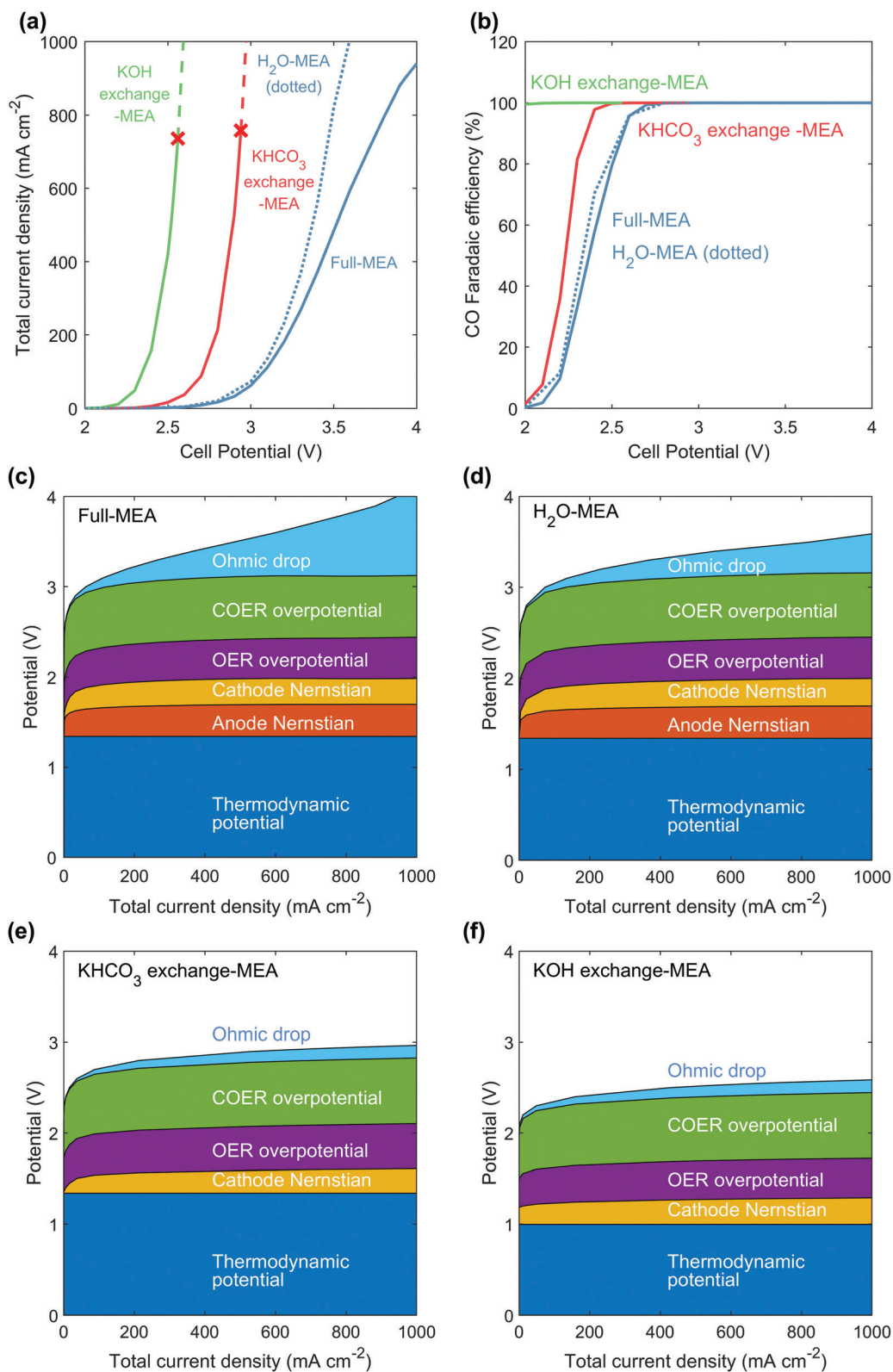
defined as the potential developed due to the change in  $\text{OH}^-$  concentration at the electrode relative to that at open circuit,

$$\eta_{\text{N}} = \pm \frac{RT}{F} \ln \left( \frac{c_{\text{OH}^-}}{c_{\text{OH}^-}^{\circ}} \right) \quad (46)$$

The sign on the right side is negative for the anode and positive for the cathode. Therefore, a higher  $\text{OH}^-$  concentration at the anode during operation would result in a negative (more favorable) Nernstian overpotential, while a higher  $\text{OH}^-$  concentration at the cathode leads to a positive (less favorable) Nernstian overpotential. The applied voltage is broken down for OER and COER, since CO is the product of interest, and the CO FE reaches almost 100% for all cases above a cell potential of 2.5 V. The voltage contributions to the OER and HER can be calculated analogously.

Comparing the AVB for the three cases, it is clear that the exchange-MEAs substantially minimize two overpotential sources observed in the full-MEA case: the anode Nernstian potential and the ohmic drop. The anode Nernstian potential is eliminated in the exchange-MEAs because the local environment at the anode is maintained by the circulating exchange solution. In contrast, sharp concentration gradients develop in the full-MEA and increase with increasing TCD, as shown in Fig. 4a. The exchange solution also improves membrane hydration, and, consequently, its conductivity, thereby decreasing the ohmic drop across the cell. For a full-MEA, the membrane water content decreases with increasing current density (Fig. 5a) because the water concentration in the gas channel is limited to its vapor pressure and water is transported and consumed in the reactions. Furthermore, as the temperature of the cell increases (Fig. 5d), the gas-phase RH decreases (Fig. 5b) even though the partial pressure of water increases (Fig. 5c), causing water in the CL ionomer to evaporate. Finally, the KOH exchange solution reduces the thermodynamic potential of the system due to the  $\text{OH}^-$  concentration gradient that develops: the anode remains at the concentration of the circulating KOH solution, while the  $\text{OH}^-$  concentration is lower near the cathode as the  $\text{CO}_2$  feed at the cathode gas channel neutralizes the  $\text{OH}^-$  (Fig. 4b). The concentration profile where the anode  $\text{OH}^-$  concentration is higher than that at the cathode is opposite to the one established for the full-MEA and  $\text{KHCO}_3$  exchange-MEA, resulting in a lower thermodynamic potential, or a negative (more favorable) Nernstian potential. A higher  $\text{OH}^-$  concentration at the anode compared to the cathode makes the second term on the right side of eqn (45) negative, thereby decreasing the thermodynamic overpotential for the KOH exchange-MEA (Fig. 3f).

The main limitation for the exchange-MEAs is the precipitation of  $\text{K}_2\text{CO}_3$  at the cathode. Driven by both the chemical and electric potential gradients,  $\text{K}^+$  exchanges with  $\text{H}^+$  produced at the anode and moves to the cathode. Eventually, at  $\sim 750 \text{ mA cm}^{-2}$ , the concentration of  $\text{K}_2\text{CO}_3$  exceeds its solubility limit and it precipitates at the cathode (indicated by the red crosses in Fig. 3a). Therefore, batch operation with salt removal is required to operate exchange-MEAs at current densities above that where precipitation can occur. It is possible to offset this precipitation limit by



**Fig. 3** (a) The total current density and (b) the CO faradaic efficiency (FE) for the four cases considered and their applied voltage breakdown (AVB), (c) full-MEA, (d) H<sub>2</sub>O-MEA, (e) KHCO<sub>3</sub> exchange-MEA, and (f) KOH exchange-MEA. Dashed line in (a) represent current densities at which salt precipitations and batch operation is required. Cathode feed composition is 97 mol% CO<sub>2</sub> and 3 mol% H<sub>2</sub>O.

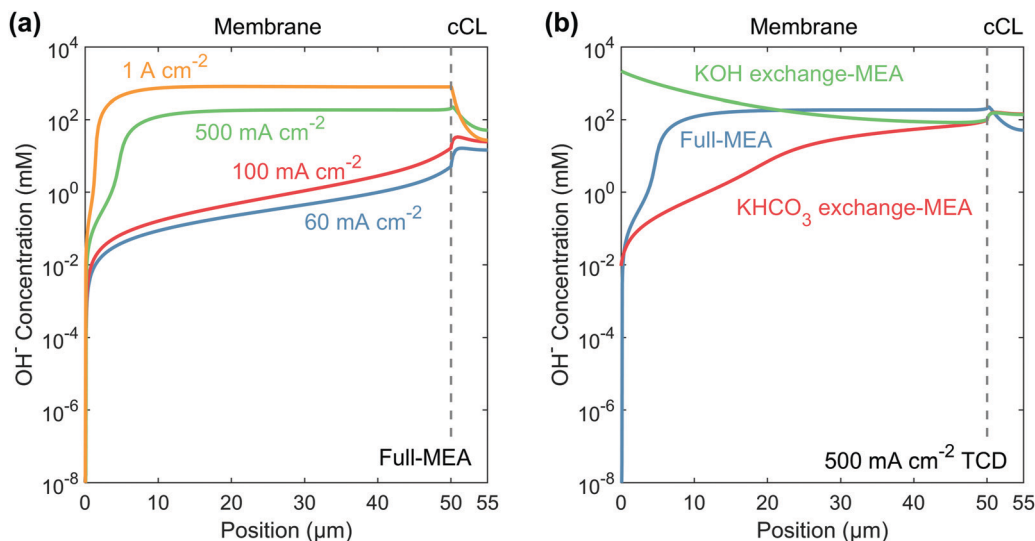


Fig. 4 Hydroxide concentration across (a) a full-MEA at 60, 100, 500 and 1000 mA cm<sup>-2</sup>; and (b) at 500 mA cm<sup>-2</sup> comparing full-MEA, KHCO<sub>3</sub> exchange-MEA, and KOH exchange-MEA. The hydroxide concentration across the full-MEA increases with increasing current density, creating significant concentration (Nernstian) overpotentials. In the case of KOH exchange-MEA, the hydroxide concentration is reversed due to the bicarbonate buffer reactions at the cathode side, resulting in a negative Nernstian overpotential.

feeding liquid water to the anode in order to provide better hydration. A H<sub>2</sub>O-MEA improves the total current density (but not the CO FE) of the full-MEA due to better membrane hydration, but does not provide the same advantageous as an exchange-MEA with dissolved salt (Fig. 3d) because of its inability to exchange ions. Thus, exchange-MEAs exhibit low voltage for a given current density but the full-MEA allows achievement of higher current densities without consideration of additional engineering controls.

#### Ion transport and the charge-carrying species in a full-MEA

At equilibrium, an OH<sup>-</sup> form AEM exposed to CO<sub>2</sub> will convert to HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> form due to bicarbonate buffer reactions (6)–(9). The ratio of HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> depends on the partial pressure of CO<sub>2</sub> in contact with the membrane and has been measured experimentally for an AEM exposed to 400 ppm CO<sub>2</sub>.<sup>33,67</sup> Fig. 6 shows the distribution of anion fraction ( $|z_i c_i|/c_M$ ) across the MEA for low, medium, and high current densities. As the current density increases, the membrane gradually converts to the CO<sub>3</sub><sup>2-</sup> form, and eventually to the OH<sup>-</sup> form starting from the cathode side. This occurs because OH<sup>-</sup> is produced by the COER and HER (see eqn (4) and (5)) at the cathode. OH<sup>-</sup> reacts with the HCO<sub>3</sub><sup>-</sup> initially in the membrane to form CO<sub>3</sub><sup>2-</sup>; OH<sup>-</sup> also reacts with dissolved CO<sub>2</sub> to form HCO<sub>3</sub><sup>-</sup> and eventually CO<sub>3</sub><sup>2-</sup>. The CO<sub>3</sub><sup>2-</sup> then transports from the cathode to the anode, driven by its concentration gradient (diffusion), and the potential gradient (migration). At the anode, bicarbonate buffer reactions drive the conversion of CO<sub>3</sub><sup>2-</sup> to HCO<sub>3</sub><sup>-</sup> and eventually back to CO<sub>2</sub>, which is released into the anode gas channel. As the current density increases, the rate of OH<sup>-</sup> production at the cathode also rises, eventually exceeding the homogeneous reaction

rates, resulting in accumulation of OH<sup>-</sup> at 500 mA cm<sup>-2</sup> and 1 A cm<sup>-2</sup>, as shown in Fig. 6c and d.

Regarding the transport and distribution of species across the MEA: (1) CO<sub>3</sub><sup>2-</sup> is the main charge carrying species for a full-MEA with an AEM performing CO<sub>2</sub>R, consistent with experimental observations reported by Liu *et al.*<sup>68</sup> The HCO<sub>3</sub><sup>-</sup> diffusion flux from anode to cathode is larger than its migration flux from cathode to anode, which means HCO<sub>3</sub><sup>-</sup> is moving against the flow of current. OH<sup>-</sup> begins to accumulate at high current densities and the membrane will eventually return to the OH<sup>-</sup> form as the charge-transfer rate exceeds the homogeneous reaction rates. (2) A portion of the CO<sub>2</sub> fed at the cathode is transported as CO<sub>3</sub><sup>2-</sup> and eventually released as CO<sub>2</sub> at the anode for a full-MEA. CO<sub>2</sub> in the anode gas outlet has also been observed by Liu *et al.* and Pătru *et al.*<sup>68,69</sup> For KHCO<sub>3</sub> exchange-MEA and KOH exchange-MEA, CO<sub>2</sub> can be flushed out as HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> by the exchange solution. While helpful in terms of performance, this becomes a source of inefficiency for the system as discussed below.

#### CO<sub>2</sub> utilization efficiency and observed limitations

The CO<sub>2</sub> losses need to be defined and quantified as a function of operating conditions because a portion of the CO<sub>2</sub> is consumed homogeneously at the cathode, transported to and released at the anode (*i.e.*, electrochemically pumped in a similar fashion as that observed in AEM fuel cells<sup>70</sup>), as expected from reactions (6)–(10) and the transport equations in Table 2. Using the gaseous species fluxes obtained from the model and assuming a 50 sccm CO<sub>2</sub> feed at 100% RH (97 mol% CO<sub>2</sub>), the CO<sub>2</sub> consumption (the percentage of CO<sub>2</sub> feed that is consumed either electrochemically or by homogeneous reactions) and the CO<sub>2</sub> conversion (the percentage of CO<sub>2</sub> feed



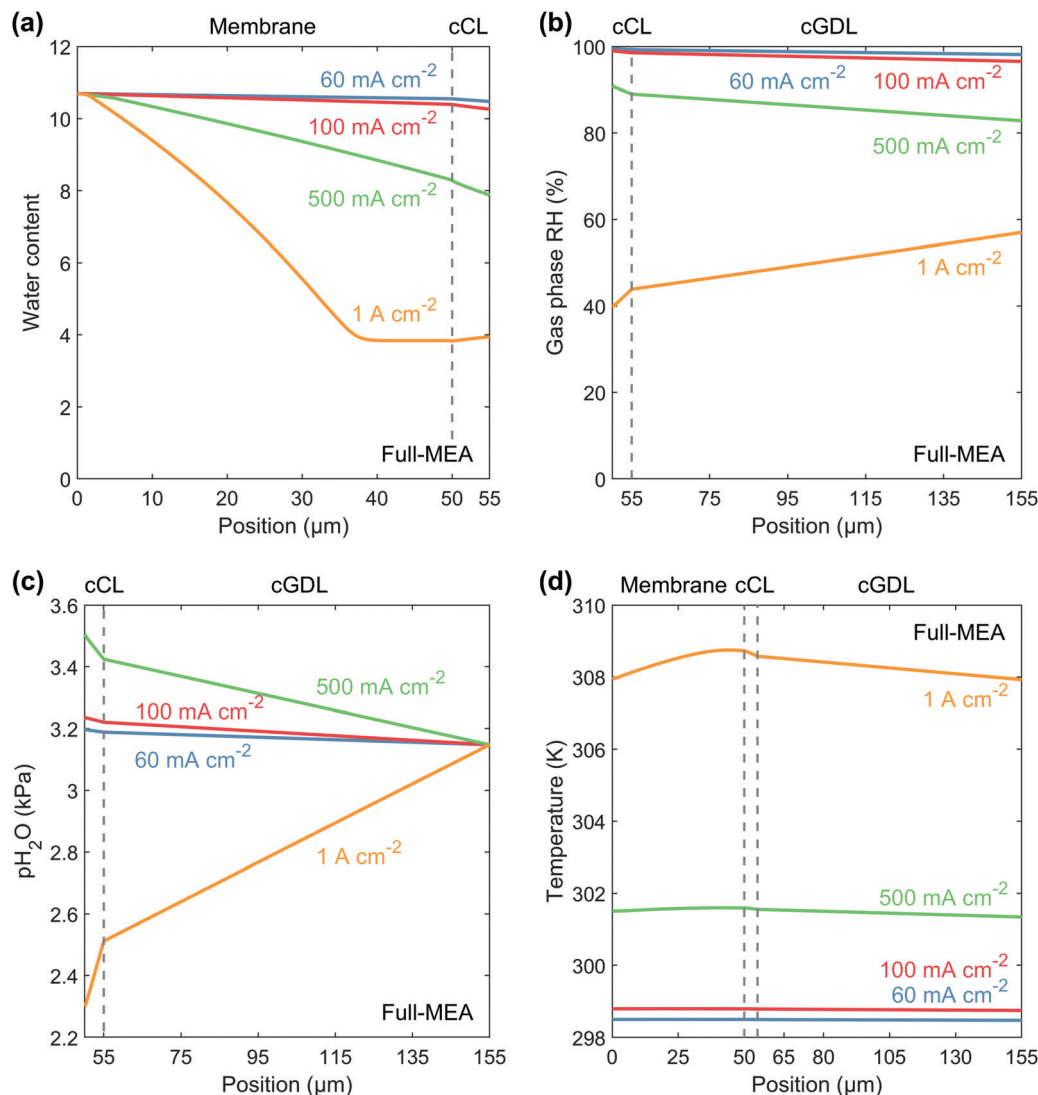


Fig. 5 (a) Water content in the membrane, (b) gas phase RH, (c) water partial pressure in the gas phase, and (d) the temperature for a full-MEA at 60, 100, 500, and 1000 mA cm<sup>-2</sup>. The gas phase RH decreases with increasing current density because of the increase in vapor pressure as the cell heats up. Cathode feed composition is 97 mol% CO<sub>2</sub> and 3 mol% H<sub>2</sub>O (water vapor pressure at 25 °C).

that is converted to CO) as a function of the TCD (Fig. 7a) is derived. More specifically,

CO<sub>2</sub> consumption

$$= \frac{\text{Molar flowrate of CO}_2 \text{ into the DM from the gas channel}}{\text{Inlet molar flowrate into the cell}}$$

and

CO<sub>2</sub> conversion

$$= \frac{\text{CO partial current density converted to molar flowrate}}{\text{Inlet molar flowrate into the cell}}$$

The CO<sub>2</sub> conversion for the three cases deviates slightly from each other at low TCD due to differences in the CO FE (not visible in figure), and eventually converges as CO FE approaches 100% for all three cases. At 100% CO FE, the CO<sub>2</sub> conversion scales linearly with the TCD (which is equal to the

partial CO current density), as expected. CO<sub>2</sub> consumption is higher for the KOH exchange-MEA case at low TCD because CO<sub>2</sub> constantly reacts with the OH<sup>-</sup> from the exchange solution, resulting in a lower CO<sub>2</sub> utilization efficiency (defined as the ratio of CO<sub>2</sub> conversion to consumption), shown in Fig. 7b. For the full-MEA and KHCO<sub>3</sub> exchange-MEA, since the membrane is in the HCO<sub>3</sub><sup>-</sup> form (and does not consume CO<sub>2</sub> as the OH<sup>-</sup> does) for TCD close to zero, the utilization efficiency starts at a higher value than that for a KOH exchange-MEA, and decreases with increasing TCD as more OH<sup>-</sup> is produced. As the TCD increases, the OH<sup>-</sup> concentration in the CL becomes comparable for a KHCO<sub>3</sub> exchange-MEA and a KOH exchange-MEA, but remains slightly lower for a full-MEA (Fig. 4b). The lower OH<sup>-</sup> concentration in the full-MEA CL means less CO<sub>2</sub> consumption by homogeneous reactions, as shown in Fig. 7a, as well as a higher CO<sub>2</sub> utilization efficiency (Fig. 7b). The utilization efficiency for KHCO<sub>3</sub> exchange-MEA

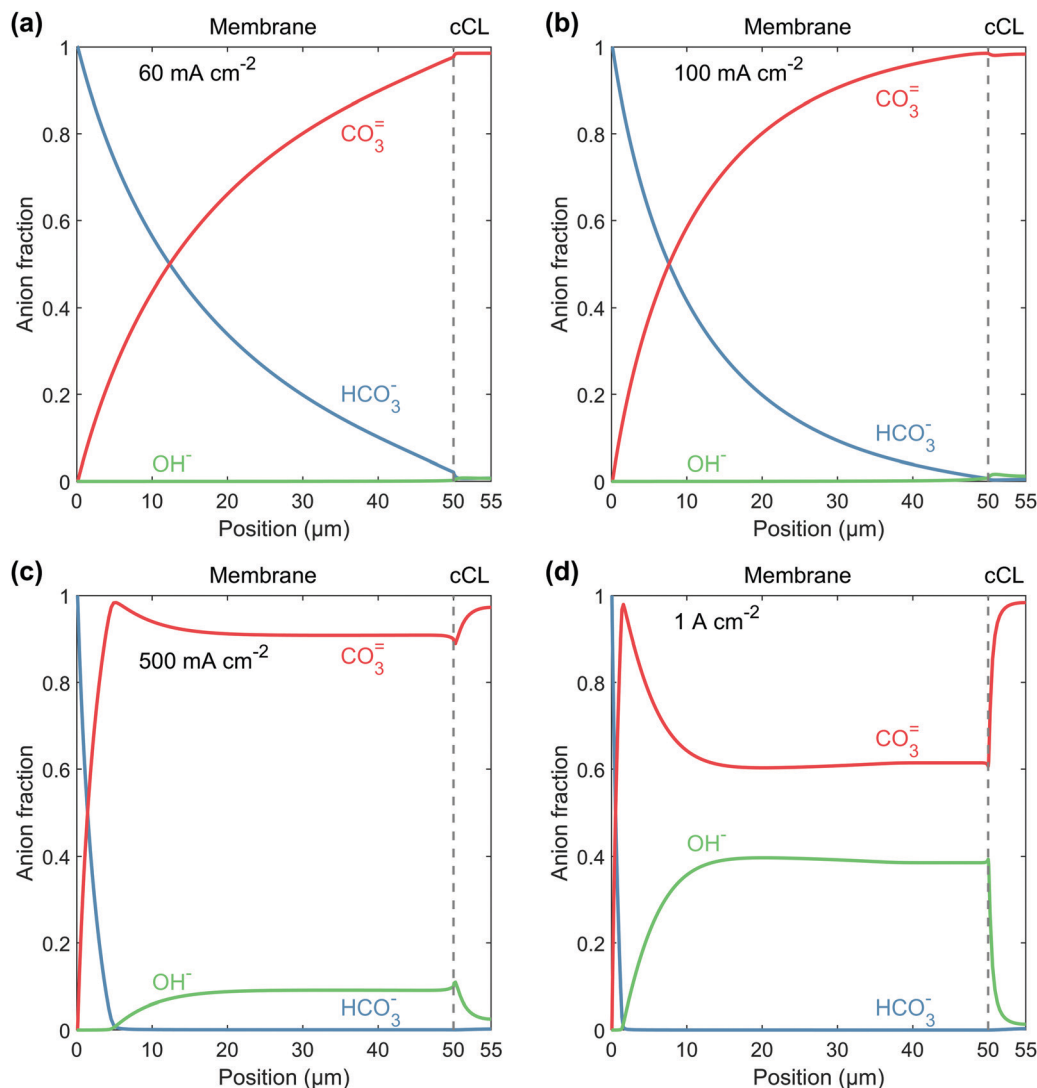


Fig. 6 Anion distribution in the membrane and cathode CL across a full-MEA cell at (a)  $60 \text{ mA cm}^{-2}$ , (b)  $100 \text{ mA cm}^{-2}$ , (c)  $500 \text{ mA cm}^{-2}$ , and (d)  $1 \text{ A cm}^{-2}$ .  $\text{CO}_2$  is converted to  $\text{CO}_3^{2-}$  at the cathode by the  $\text{OH}^-$  produced from COER, transported as  $\text{CO}_3^{2-}$  to the anode, and released by the  $\text{H}^+$  produced from OER. Cathode feed composition is 97 mol%  $\text{CO}_2$  and 3 mol%  $\text{H}_2\text{O}$ .

and KOH exchange-MEA converges to 50% for TCD  $> 500 \text{ mA cm}^{-2}$ , a result that can be explained by considering the stoichiometry of the electrochemical and homogeneous reactions, listed in Fig. 7c. The reaction stoichiometry also suggests a 1:2  $\text{O}_2$  to  $\text{CO}_2$  ratio at the anode gas outlet, consistent with measurements by Liu *et al.*<sup>68</sup> To increase the utilization efficiency for exchange-MEAs, the consumption of  $\text{CO}_2$  by  $\text{OH}^-$  needs to be reduced, which could be achieved by a lower rate coefficient for the homogeneous reaction of  $\text{CO}_2$  and  $\text{OH}^-$  (Fig. S2, ESI<sup>†</sup>). However, this would also result in a more rapid pH change near the cathode, and a larger Nernstian overpotential. Understanding such tradeoffs is crucial to fine-tuning the cell design and maximizing efficiency.

In the model, the gas-channel composition is assumed to remain constant at the feed composition, which is valid only under conditions of low feed consumption (*e.g.*, high feed flowrate). Note that  $\text{CO}_2$  concentration varies in the CL, and

its profile is plotted in Fig. S1 (ESI<sup>†</sup>). In practice, however,  $\text{CO}_2$  consumption can be as high 30% for a feed flowrate of 50 scfm and  $1 \text{ A cm}^{-2}$ , as shown above. This means that the gas composition in the cathode gas channel will vary based on the rate of consumption of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , and the rate of production of CO and  $\text{H}_2$ . Assuming that the gas channel is well-mixed, we estimate its composition from a simple mass balance:

$$y_{\text{GC},i} = \frac{N_{\text{F},i} - N_{\text{R},i}}{N_{\text{F}} - N_{\text{R}}} \quad (47)$$

where  $y_{\text{GC},i}$  is the mol fraction of gaseous species  $i$  in the gas channel;  $N_{\text{F}}$  and  $N_{\text{R}}$  are the total molar flowrate of the feed gas going into and out of the gas chamber into the GDL, respectively;  $N_{\text{F},i}$  and  $N_{\text{R},i}$  are the molar flowrate of species  $i$  in the feed gas going into and out of the gas chamber, respectively. Fig. 8 shows the resulting gas chamber composition for the full-MEA



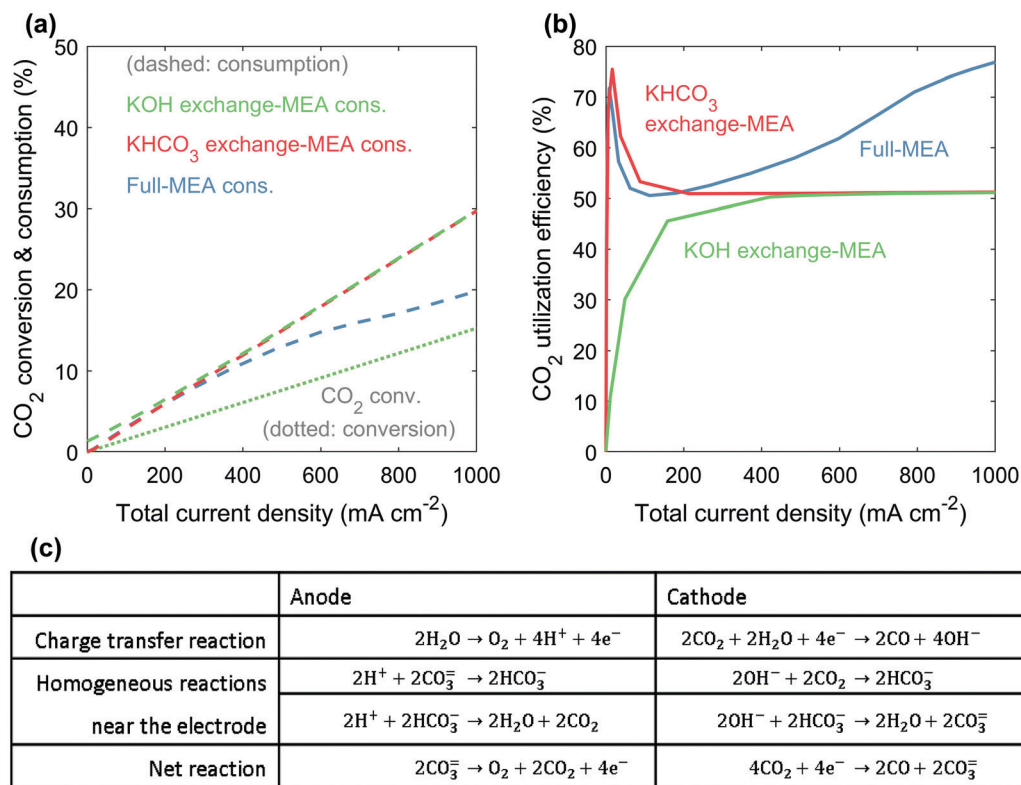


Fig. 7 (a) CO<sub>2</sub> consumption (dotted) and conversion (dashed) calculated for a 50 sccm CO<sub>2</sub> feed at 100% RH (97 mol% CO<sub>2</sub>, 3 mol% H<sub>2</sub>O), room temperature. (b) CO<sub>2</sub> utilization efficiency defined as the fraction of CO<sub>2</sub> consumed that converts to CO. (c) Stoichiometric balance of the electrochemical and homogenous reactions across the cell showing only half of the CO<sub>2</sub> consumed is converted to CO.

(Fig. 8a) and the KOH exchange-MEA (Fig. 8b). At zero TCD, the gas composition in the cathode gas channel for the full-MEA is close to its feed composition since there are minimal reactions and crossover occurring. For the KOH exchange-MEA case, however, the CO<sub>2</sub> mole fraction is much lower than that in

the feed (0.97) because CO<sub>2</sub> will be consumed by OH<sup>-</sup> anions in the CL ionomer; the H<sub>2</sub>O mole fraction is higher due to diffusion of H<sub>2</sub>O from the anode chamber. The CO mole fraction increases steadily and the H<sub>2</sub> mole fraction is close to zero, as expected from the partial current densities. However,

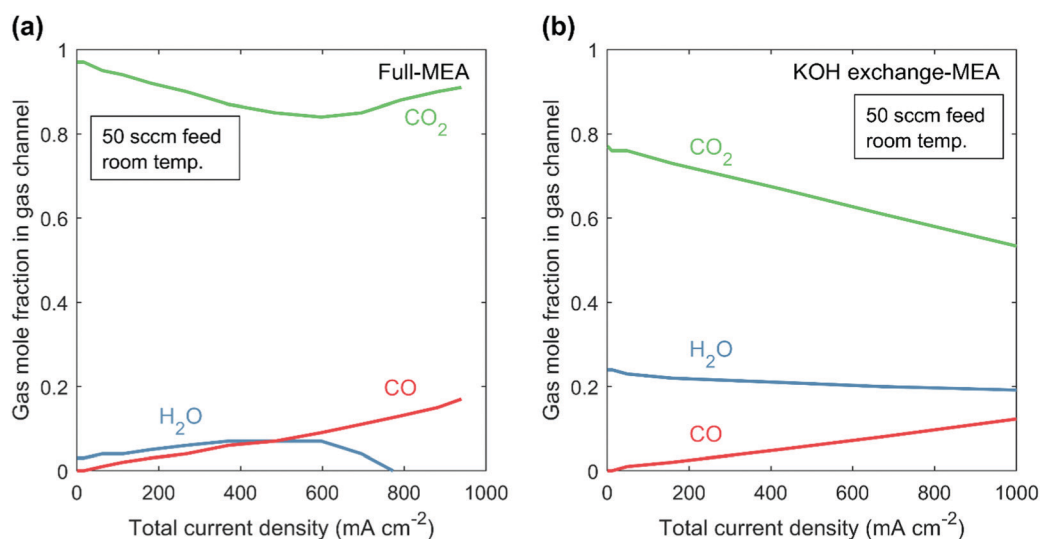


Fig. 8 Gas mol fraction in the cathode gas channel calculated assuming 50 sccm CO<sub>2</sub> feed with 100% RH (97 mol% CO<sub>2</sub>, 3 mol% H<sub>2</sub>O) at room temperature for (a) full-MEA and (b) KOH exchange-MEA. The vapor pressure at 298 K is 0.03 atm. Full-MEA becomes water-limited at approximately 750 mA cm<sup>-2</sup>, and KOH-MEA is likely to be flooded.

two issues become apparent regarding water management. For the full-MEA, the  $\text{H}_2\text{O}$  mole fraction first increases slightly due to the temperature increase in the CL, as discussed in Fig. 5, and then drops to zero at approximately  $750 \text{ mA cm}^{-2}$ , indicating that the full-MEA becomes limited by the supply of water before it is limited by the supply of  $\text{CO}_2$ . On the other hand, the partial pressure for  $\text{H}_2\text{O}$  in the gas channel of the KOH exchange-MEA is significantly above its vapor pressure at ambient temperature ( $\sim 0.03 \text{ atm}$ ), suggesting that flooding is likely to occur at the cathode GDE as water diffuses from the anode. Flooding in the cathode GDE will increase  $\text{CO}_2$  mass-transport resistances significantly and decrease catalyst utilization.<sup>37</sup> Fig. 8 suggests a need for a higher-dimensional, integrated multiphase model to capture changes in the gas-channel composition, as well as additional physics to capture water condensation and

multiphase flow in the GDE; studies of these effects are currently in progress.

#### Water management: temperature and membrane-thickness effects

To address issues concerning full-MEA dehydration and exchange-MEA flooding, we studied the effects of increasing the operating temperature and changing membrane thickness. In terms of the operating temperature, the water vapor pressure is  $\sim 0.46 \text{ atm}$  at  $80^\circ\text{C}$ , compared to  $\sim 0.03 \text{ atm}$  at  $25^\circ\text{C}$ . Thus, operating at  $80^\circ\text{C}$ , a higher TCD can be achieved with more rapid kinetics (see eqn (35)), but the CO FE decreases below a cell potential of 3 V due to the lower solubility of  $\text{CO}_2$  at elevated temperatures (Fig. 9a and b). The gas-channel composition shown in Fig. 9c also indicates that a current density of  $1 \text{ A cm}^{-2}$  lies below the  $\text{CO}_2$ - or  $\text{H}_2\text{O}$ -limited current densities

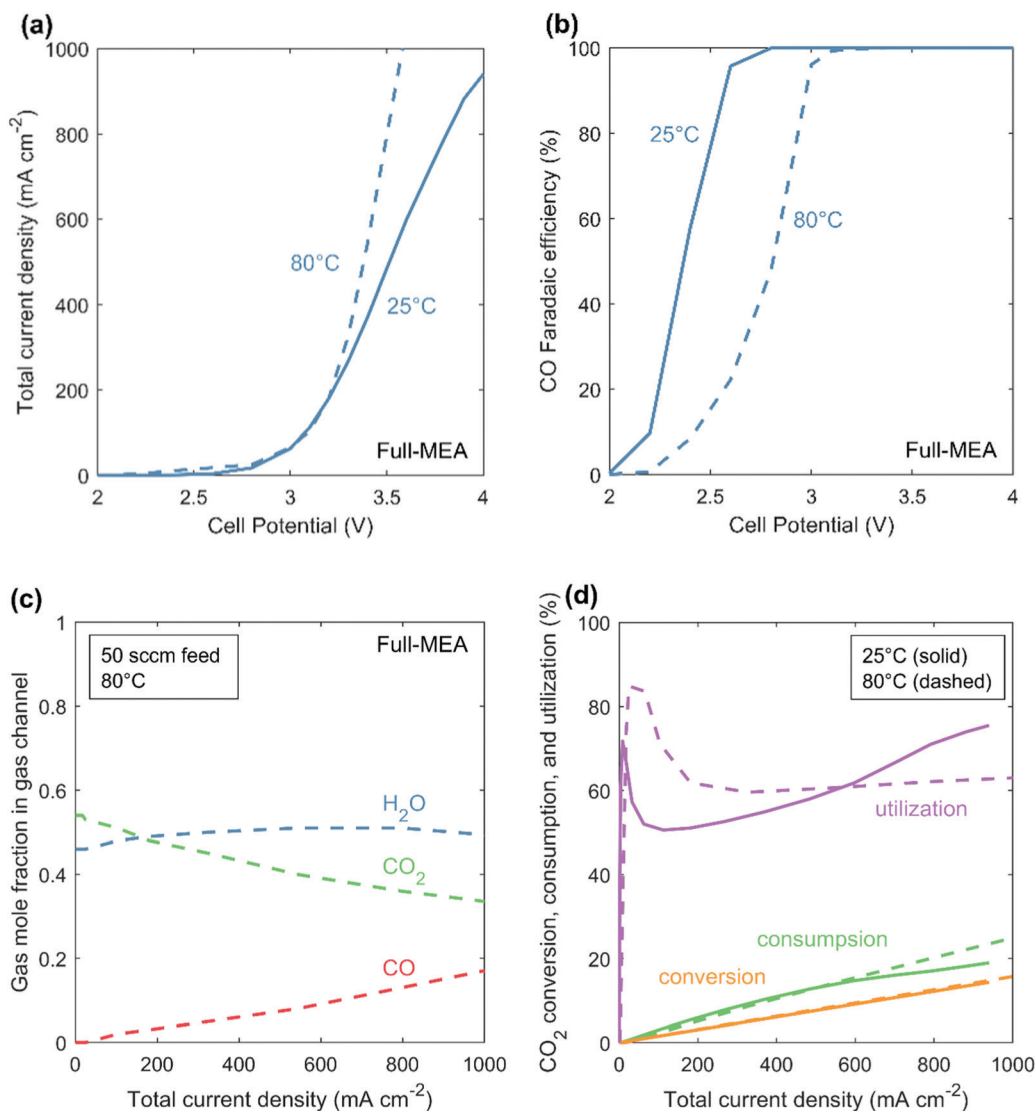


Fig. 9 (a) Total current density, (b) CO faradaic efficiency, (c) gas channel composition, and (d)  $\text{CO}_2$  utilization analysis for a full-MEA at  $80^\circ\text{C}$  with  $\text{CO}_2$  feed at 100% RH (54 mol%  $\text{CO}_2$ , 46 mol%  $\text{H}_2\text{O}$ ). Operating the cell at higher temperature increases the exchange current density, as well as water feed to the system. However,  $\text{CO}_2$  solubility is compromised, resulting in lower CO faradaic efficiencies.

for a full-MEA. It should be noted that to obtain the same molar flowrate of CO<sub>2</sub> at 80 °C as at 25 °C for a feed flowrate of 50 sccm, the feed flowrate needs to be raised to 105 sccm in order to compensate for the higher vapor pressure of water. However, Fig. 9c shows that the full-MEA can operate up to 1 A cm<sup>-2</sup> even at a third of the CO<sub>2</sub> molar flowrate provided at 80 °C. This observation reinforces our finding that the cell is operating in a low CO<sub>2</sub> utilization regime up to 1 A cm<sup>-2</sup> at 50 sccm feed (Fig. 7).

The operating temperature can also affect CO<sub>2</sub> utilization, as it changes the reactions rates of electrochemical reactions and homogeneous reactions, as well as the equilibrium constants of the bicarbonate and water reactions. Since limited data is available for the buffer reaction rate constants in an ionomer, we show results assuming the same forward rate constants at 80 °C as at 25 °C for reactions (6)–(10). The equilibrium constant will vary based on eqn (11), as well as the reverse rate constant ( $k_{-n} = k_n/K_n$ ). As shown in Fig. 9d, better CO<sub>2</sub> utilization can be achieved at higher temperatures when operating below approximately 600 mA cm<sup>-2</sup> TCD, but the reverse is true when operating at higher TCDs. This effect is a consequence of increased diffusivity of ionic and neutral species, the shifted equilibria for reactions (6)–(10), and the relative rates of the homogeneous consumption of CO<sub>2</sub> and its electrochemical conversion at 80 °C. We note that the results shown here are based on the assumed temperature dependence of the various rate constants, which will vary based on the ionomer used. These results demonstrate the importance of studying homogeneous reaction rates of the bicarbonate buffer system in different ionomer environments under various temperatures; manipulation of the bicarbonate buffer reaction rates is a potential route to increase CO<sub>2</sub> utilization of CO<sub>2</sub>R systems.

Finally, as noted, one can also decrease the membrane thickness to help alleviate the dehydration issue in full-MEAs (although perhaps not the flooding issue in exchange-MEAs). Fig. 10 shows the effects of membrane thickness on the

full-MEA performance. As expected, the TCD increases with a thinner membrane, with the difference becoming more significant with higher cell potentials due to both enhanced water transport as well as less ohmic losses, thereby reinforcing the finding that the full-MEA is ohmic-limited. Unlike changing temperature, the CO FE is not strongly impacted. Of course, decreasing the membrane thickness will result in increased crossover and worse CO<sub>2</sub> utilization. This is another tradeoff to consider, and is more prominent when producing aqueous products that have high solubility in the membrane.

## Summary

A multiphysics model describing the effects of species transport, heat transfer, and the kinetics of all electrode and electrolyte reactions occurring in an MEA was developed and used to explore the electrochemical reduction of CO<sub>2</sub> to CO over Ag. As the current density rises above 100 mA cm<sup>-2</sup>, MEAs become advantageous relative to planar cells containing an aqueous electrolyte or an aqueous GDL cell because they minimize the ohmic drop across the cell. Full-MEAs with gaseous feeds to both the anode and cathode gas channels can achieve a current density of 100 mA cm<sup>-2</sup>, with approximately 40% reduction in the cell potential compared to an aqueous GDE cell, a consequence of their lower ohmic potential drop. However, such cells suffer from concentration polarization and membrane dehydration. Circulating an exchange solution through the anode channel enables an exchange-MEA to better maintain the local environment at the anode, and hydrate the membrane. With a KOH-exchange-solution feed, a reverse OH<sup>-</sup> concentration gradient develops across the cell, lowering the thermodynamic potential that needs to be overcome. The alkaline environment created by KOH also suppresses the HER. For exchange-MEAs, cation transport

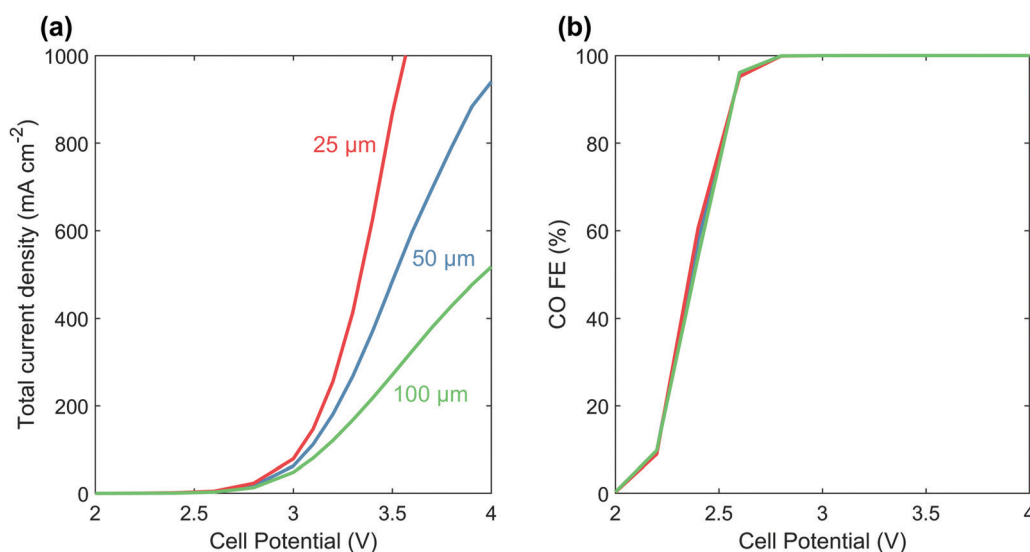


Fig. 10 (a) Total current density, (b) CO faradaic efficiency for the full-MEA case simulated with a 25 μm membrane (red), 50 μm membrane (base case, blue), and 100 μm membrane (green).

down the potential gradient limits the current density due to precipitation of the salt used in the exchange solution. It should also be noted that flooding is likely to occur in the cathode GDE of an exchange-MEA, as water diffuses from anode to cathode. High-temperature operation of a full-MEA allows introduction of more water vapor into the system, thereby overcoming the water limitations observed at room temperature; this also improves the charge transfer kinetics, although the reduction in CO<sub>2</sub> solubility and the changes in the homogeneous reaction rates and reaction equilibria can affect the CO<sub>2</sub> FE and the CO<sub>2</sub> utilization efficiency of the cell. It is also possible to minimize flooding in an exchange-MEA by increasing the temperature at the cathode GDE in order to evaporate condensed water.

## List of symbols

### Roman

$a_v$	Specific surface area, m <sup>-1</sup>
$a_i$	Activity of species $i$
$A_k$	Pre-exponential factor for reaction $k$ , mA cm <sup>-2</sup>
$c_i$	Concentration of species $i$ , mol m <sup>-3</sup>
$D_i$	Diffusivity of species $i$ , m <sup>2</sup> s <sup>-1</sup>
$E_{a,k}$	Activation energy for reaction $k$ , kJ mol <sup>-1</sup>
$F$	Faraday's constant, C mol <sup>-1</sup>
$H_i$	Henry's constant of species $i$ , M atm <sup>-1</sup>
$\Delta H_n$	Change of enthalpy for reaction $n$ , kJ mol <sup>-1</sup>
$i_k$	Current density for reaction $k$ , mA cm <sup>-2</sup>
$i_l$	Electrolyte current density, mA cm <sup>-2</sup>
$i_{o,k}$	Exchange current density of reaction $k$ , mA cm <sup>-2</sup>
$i_s$	Electrode current density, mA cm <sup>-2</sup>
IEC	Ion-exchange capacity, mmol g <sup>-1</sup>
$j_i$	Diffusive mass flux of species $i$ , g m <sup>-2</sup> s <sup>-1</sup>
$k_n$	Rate constant for homogeneous reaction $n$ , s <sup>-1</sup> or L mol <sup>-1</sup> s <sup>-1</sup>
$k_{T,m}$	Heat transfer coefficient of medium $m$ , W m <sup>-1</sup> K <sup>-1</sup>
$K_n$	Equilibrium constant for reaction $n$
$M_i$	Molar mass of species $i$ , g mol <sup>-1</sup>
$M_n$	Average molar mass of gaseous mixture, g mol <sup>-1</sup>
$n_i$	Mass flux of species $i$ , g m <sup>-2</sup> s <sup>-1</sup>
$n_k$	Number of electrons transferred in reaction $k$
$p_\alpha$	Total pressure in phase $\alpha$ , atm
$p_{\text{vap}}$	Vapor pressure, atm
$q$	Heat flux, J m <sup>-2</sup>
$q_l$	Electrolyte flow rate, ml min <sup>-1</sup>
$r_{p,m}$	Pore radius in medium $m$ ,
$R$	Gas constant, J mol <sup>-1</sup> K <sup>-1</sup>
$R_{\beta,i}$	Volumetric rate of reaction of species $i$ from bulk reaction $\beta$ , g m <sup>-3</sup> s <sup>-1</sup>
$s_{i,k}$	Stoichiometric coefficient of species $i$ in reaction $k$
$\Delta S_n$	Change of entropy for reaction $n$ , J mol <sup>-1</sup> K <sup>-1</sup>
$T$	Temperature, K
$u_\beta$	Mass-averaged fluid velocity of fluid $\beta$ , m s <sup>-1</sup>
$u_i$	Mobility of species $i$ , s mol kg <sup>-1</sup>

$U_k^0$	Reference potential of reaction $k$ , V
$v_{p,i}$	Diffusion volume of species $i$
$V_i$	Molar volume of species $i$ , ml mol <sup>-1</sup>
$x_j$	Mole fraction of aqueous species $j$
$y_i$	Mole fraction of gaseous species $i$
$z_i$	Charge of species $i$

### Greek

$\alpha_k$	Transfer coefficient of reaction $k$
$\gamma_k$	Reaction order of reaction $k$
$\delta_{\text{TF}}$	Electrolyte thin film thickness
$\varepsilon_m$	Porosity of medium $m$
$\zeta_i$	Species-water to species-membrane interaction ratio
$\eta_k$	Surface overpotential of reaction $k$ , V
$\kappa_m$	Permeability of medium $m$ , m <sup>2</sup>
$\lambda$	Water content
$\mu_\beta$	Viscosity of fluid $\beta$ , Pa s
$\xi$	Electro-osmotic coefficient
$\rho_i$	Mass density of species $i$ , g cm <sup>-3</sup>
$\sigma_m$	Electronic conductivity in medium $m$ , S m <sup>-1</sup>
$\tau_m$	Tortuosity of medium $m$
$\phi_\alpha$	Electric potential of phase $\alpha$ , V
$\omega_i$	Mass fraction of species $i$
$\Pi_k$	Peltier coefficient of reaction $k$ , V

### Subscript

B	Bulk
CT	Charge transfer
$g$	Gaseous mixture
$i$	Gaseous species
$j$	Aqueous species
$k$	Reaction
l	Liquid phase
$n$	Homogeneous reaction number
p	Pore
PT	Phase transfer
s	Solid
TF	Electrolyte thin film
w	Water

### Superscript

o	Intrinsic value or standard state
ref	Reference
eff	Effective
E	Electrolyte
K	Knudsen
$m$	Mass-averaged
M	Membrane

### Acronyms

AEM	Anion-exchange membrane
CL	Catalyst layer
CO <sub>2</sub> R	CO <sub>2</sub> reduction
COER	CO evolution reaction
CT	Charge transfer

DM	Diffusion medium
HER	H <sub>2</sub> evolution reaction
MEA	Membrane-electrode assembly
OER	Oxygen evolution reaction
RH	Relative humidity

## Conflicts of interest

There are no conflicts to declare.

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