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## Quantifying and elucidating the effect of CO<sub>2</sub> on the thermodynamics, kinetics and charge transport of AEMFCs†

Yiwei Zheng,<sup>a</sup> Travis J. Omasta,<sup>ib</sup> Xiong Peng,<sup>a</sup> Lianqin Wang,<sup>ib</sup>  
John R. Varcoe,<sup>ib</sup> Bryan S. Pivovar<sup>c</sup> and William E. Mustain<sup>ib</sup>\*<sup>a</sup>

It has been long-recognized that carbonation of anion exchange membrane fuel cells (AEMFCs) would be an important practical barrier for their implementation in applications that use ambient air containing atmospheric CO<sub>2</sub>. Most literature discussion around AEMFC carbonation has hypothesized: (1) that the effect of carbonation is limited to an increase in the Ohmic resistance because carbonate has lower mobility than hydroxide; and/or (2) that the so-called “self-purging” mechanism could effectively decarbonate the cell and eliminate CO<sub>2</sub>-related voltage losses during operation at a reasonable operating current density (>1 A cm<sup>-2</sup>). However, this study definitively shows that neither of these assertions are correct. This work, the first experimental examination of its kind, studies the dynamics of cell carbonation and its effect on AEMFC performance over a wide range of operating currents (0.2–2.0 A cm<sup>-2</sup>), operating temperatures (60–80 °C) and CO<sub>2</sub> concentrations in the reactant gases (5–3200 ppm). The resulting data provide for new fundamental relationships to be developed and for the root causes of increased polarization in the presence of CO<sub>2</sub> to be quantitatively probed and deconvoluted into Ohmic, Nernstian and charge transfer components, with the Nernstian and charge transfer components controlling the cell behavior under conditions of practical interest.

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### Broader context

Anion exchange membrane fuel cells (AEMFCs) have shown significant promise to provide clean, sustainable energy for grid and transportation applications – and at a lower theoretical cost than more established proton exchange membrane fuel cells (PEMFCs). Adding to the excitement around AEMFCs is the extremely high peak power that can now be obtained (>3 W cm<sup>-2</sup>) and continuously improving durability (1000+ h), which has made the future deployment of AEMFCs in real-world applications a serious consideration. For some applications (e.g. automotive), the most critical remaining practical issue with AEMFCs is understanding and mitigating the effects of atmospheric CO<sub>2</sub> (in the air supply) on cell behavior and performance. This study is the first comprehensive experimental investigation into the effects of CO<sub>2</sub> on operating AEMFCs. It is also the first study to be able to quantitatively determine the root causes for performance decline when CO<sub>2</sub> is added to the system, where cell behavior is directly linked to cell chemistry and reaction dynamics. In addition to the demonstrated technology, the lessons learned in this work can also provide transformational insights to other air breathing and/or AEM-based electrochemical systems such as metal–air batteries, regenerative fuel cells, electrochemical CO<sub>2</sub> capture, CO<sub>2</sub> reduction reactors and dialyzers.

## Introduction

For decades, the proton exchange membrane fuel cell (PEMFC) has dominated the research space for low temperature polymer electrolyte fuel cells. Though significant advances have been

made regarding the performance and stability of PEMFCs over the years, one of the factors that has limited its wide deployment is cost.<sup>1</sup> It has been broadly suggested in recent years that a change of electrolyte to a solid alkaline polymer electrolyte might be able to significantly reduce the cost of polymer-based fuel cell systems<sup>2</sup> because the alkaline environment would allow for the deployment of a broader range of noble metal free catalysts as well as less expensive materials to be used for other cell components such as the membrane and bipolar plates.

Early development of these so-called anion exchange membrane fuel cells (AEMFCs) was hindered by anion exchange membranes (AEMs) with very poor alkaline stability<sup>3</sup> and very

<sup>a</sup> Department of Chemical Engineering, University of South Carolina, Columbia, South Carolina 29208, USA. E-mail: [mustainw@mailbox.sc.edu](mailto:mustainw@mailbox.sc.edu)

<sup>b</sup> National Renewable Energy Laboratory, Golden, Colorado 80401, USA

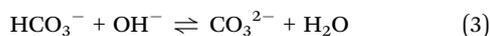
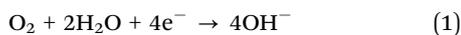
<sup>c</sup> Department of Chemistry, University of Surrey, Guildford, GU2 7XH, UK

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poor performance, with typical peak power densities well below  $0.5 \text{ W cm}^{-2}$ . The combination of low achievable power and limited durability<sup>4,5</sup> made AEMFCs uncompetitive with PEMFCs for years. However, over the past two years, a significant increase in the peak power density has been observed,<sup>5–9</sup> with state-of-the-art AEMFCs having the ability to achieve values over  $3 \text{ W cm}^{-2}$  operating on  $\text{H}_2/\text{O}_2$  gas feeds.<sup>10</sup> Also, the performance stability of AEMFCs has improved dramatically during this time, with multiple groups reporting 500+ hour stability at low degradation rates (5–10%).<sup>11–14</sup>

Now that AEMFC performance and stability has been enhanced to the point where their future deployment in real applications can be seriously contemplated, it is now an important time in AEMFC development to begin to answer some of the other lingering issues that have to date been mostly put aside in the literature. It can be argued that one of the most important of these issues is understanding and mitigating the effects of atmospheric  $\text{CO}_2$  on AEMFC performance. It is widely known that when  $\text{CO}_2$ -containing air is fed to the AEMFC cathode, the  $\text{OH}^-$  anions that are produced from the oxygen reduction reaction (ORR), eqn (1), react with  $\text{CO}_2$  to produce carbonate and/or bicarbonate anions, eqn (2) and (3).



As (bi)carbonate anions are produced, they are transported towards the anode by migration, resulting in a “carbonation” of the anion exchange membrane (AEM) as well as the ionomer in the electrodes (especially the anode). This carbonation results in a severe reduction in the operating cell voltage, with carbonate-related overpotentials as high as 400 mV.<sup>15</sup> Though theoretical studies have tried to shed some light on this phenomena,<sup>16,17</sup> unfortunately, there is a very small body of experimental work in the literature quantifying the impact of  $\text{CO}_2$  and determining the root causes behind the extensive performance drop for AEMFCs when  $\text{CO}_2$  is present.

Therefore, the purpose of this study is to establish a resolute understanding of the influence of  $\text{CO}_2$  on the performance of AEMFCs. Herein, the  $\text{CO}_2$  concentration in both the cathode and anode are parametrically changed over a wide range of conditions (current density and temperature) that represent reasonable ranges for their practical operation. Finally, this work explores the lower limits of  $\text{CO}_2$  exposure to determine whether or not there is a baseline  $\text{CO}_2$  tolerance in AEMFCs, which informs the field to what degree oxidant gas scrubbing might be needed.

## Experimental

### Electrode preparation

The electrodes in this work were prepared using a method that has been detailed in our previous publications.<sup>8,9</sup> Briefly, the anode and cathode catalysts were 60 wt% PtRu supported on

Vulcan XC-72R (Alfa Aesar HiSPEC 10000, 2 : 1 ratio of Pt : Ru by mass – Pt nominally 40 wt%, and Ru, nominally 20 wt%) and 40 wt% Pt supported on Vulcan XC-72R (Alfa Aesar HiSPEC 4000, Pt nominally 40 wt%), respectively. Electrode preparation was initiated by placing an ethylene tetrafluoroethylene (ETFE) benzyltrimethylammonium (BTMA) solid powder anion exchange ionomer (AEI) with an ion-exchange capacity (IEC) of  $1.24 \text{ mmol g}^{-1}$ <sup>18</sup> into a mortar and manually grinding it with a pestle for 10 min. The catalyst powder, additional Vulcan carbon (XC-72R, Cabot), and 1 mL of Millipore deionized (DI) water ( $18.2 \text{ M}\Omega \text{ cm}$  resistivity) were added to the mortar and ground for 10 min. The mass fraction of AEI in the catalyst layer was always 0.20 and the total mass fraction of carbon was maintained at 0.48 for both electrodes. Next, the catalyst-AEI slurry was transferred to a polypropylene vial. Isopropyl alcohol was added, and the mixture was sonicated (Fisher Scientific FS30H) for 60 min. The water in the ultrasonic bath was maintained below  $5 \text{ }^\circ\text{C}$  to avoid degrading the supported catalyst and the AEI and to maximize the electrochemically active area by avoiding agglomeration. The ink dispersions were sprayed onto Toray TGP-H-0600 gas diffusion layers with 5% PTFE wetproofing with an Iwata Eclipse HP-CS (feed gas was 15 psig Ultra High Purity  $\text{N}_2$ ) to create gas diffusion electrodes (GDEs). The target GDE catalyst loading was  $0.6 \pm 0.1 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ .

### Anion exchange membrane fuel cell (AEMFC) assembly and break-in procedure

Before cell assembly, the GDEs were soaked in 1 M aqueous KOH solutions (prepared from Fisher Chemical pellets/certified ACS and DI water) for 60 min, exchanging the solution twice during this time. At the same time, the AEM was also soaked in an identical solution. Two different AEMs were used in this work. The first was a  $50 \mu\text{m}$  thickness (fully swollen in water) ETFE–BTMA radiation-grafted AEM,<sup>19</sup> which was used for the  $\text{CO}_2$  dosing experiments at  $60 \text{ }^\circ\text{C}$ . The second AEM was a  $25 \mu\text{m}$  thickness (fully swollen in water) LDPE (low density polyethylene)–BTMA radiation-grafted AEM.<sup>7</sup> The LDPE–BTMA AEM is more chemically and mechanically stable at elevated temperatures than its ETFE–BTMA counterpart and was used when investigating the influence of elevated temperature on  $\text{CO}_2$ -related overpotential losses.

After soaking for 1 h, excess KOH was removed from the GDEs and AEMs before cell assembly. The GDEs and AEMs were pressed together in the cell to form the membrane electrode assembly (MEA) with no prior hot pressing. The MEAs were loaded into  $5 \text{ cm}^2$  Scribner hardware between two single pass serpentine graphite flow plates. An 850e Scribner Fuel Cell Test Station was used to control the gas stream dew points, cell temperature, gas flowrates and the operating current density.

Before  $\text{CO}_2$  measurements were made, all cells underwent a break in procedure. First, the cell was brought to its operating temperature under  $\text{N}_2$  flow on both sides of the cell at 100% relative humidity. Next, the feed gases were switched to ultra high purity  $\text{H}_2$  and  $\text{O}_2$  (Airgas) at the anode and cathode, respectively. Then, the cell was operated galvanostatically



stepwise from 0.7 V to 0.3 V (0.1 V steps, held for a minimum of 30 min at each step) as the reacting gas dew points were optimized per our standard procedure.<sup>8</sup> The optimized reacting gas dew points were very repeatable from cell-to-cell; the dew points were typically 52 °C at the anode and 54 °C at the cathode for an AEMFC operating at 60 °C. Following the optimization of the reacting gas dew points, the cells were operated galvanostatically at the current density of interest (0.2, 0.5, 1.0 or 2.0 A cm<sup>-2</sup>) and allowed to equilibrate for at least 30 min before CO<sub>2</sub> exposure was initiated. Multiple cells (no less than three) were constructed and tested for each measurement.

### AEMFC carbon dioxide measurements

Following the break-in procedure and 30 min equilibration, the cell current was maintained and CO<sub>2</sub> was parametrically added to the ultra high purity O<sub>2</sub> cathode stream. We chose to add CO<sub>2</sub> to O<sub>2</sub> instead of air in order to simplify observations and isolate the effects of CO<sub>2</sub> on performance, since air has additional O<sub>2</sub> mass transport impact (e.g. N<sub>2</sub> dilution) during cell operation, which is largely eliminated by utilizing O<sub>2</sub> as the reacting gas. The flowrate for O<sub>2</sub> and H<sub>2</sub> in all experiments was 1 L min<sup>-1</sup>. CO<sub>2</sub> cathode concentrations as low as 2 ppm and as high as 3200 ppm were tested. Typically, after CO<sub>2</sub> addition, the cell was operated for 30 min, which was much longer than the time required to reach quasi-steady-state operation (typically <5 min, though lower CO<sub>2</sub> concentrations took longer). After 30 min operation at constant current, CO<sub>2</sub> was removed from the gas stream and the cell was allowed to decarbonate for an initial 30 min. After this, the cell was further decarbonated through self-purging by one of two approaches: (i) the cell was allowed to operate at the same current density until the voltage reached its pre-CO<sub>2</sub> level and no CO<sub>2</sub> emission was measured at the anode (shown in Fig. S1 in the ESI†); or (ii) more typically, to reduce the time between CO<sub>2</sub> trials, the cell potential was pulsed down to 0.1 V for 1 min (Fig. S2 in the ESI†), after which no CO<sub>2</sub> emission was measured in the anode stream. When CO<sub>2</sub> was fed to the cathode, the concentration of CO<sub>2</sub> being emitted from the anode and cathode were both constantly monitored in real time using a PP Systems WMA-5 non-dispersive infrared CO<sub>2</sub> gas analyzer (a water trap was placed in-line before the WMA-5 in order to preserve the unit and its calibration).

A second set of experiments were done where CO<sub>2</sub> at concentrations between 2 and 400 ppm were added to the anode instead of the cathode. This was meant to simulate two possible scenarios: (i) CO<sub>2</sub> accumulation in the anode; and (ii) CO<sub>2</sub> exposure at the anode from the oxidation of carbonaceous fuels (through reforming or direct alcohol oxidation). When CO<sub>2</sub> was fed to the anode, the concentration of CO<sub>2</sub> being emitted from the anode and cathode was constantly monitored in real time using the WMA-5. The cathode data will not be shown since the CO<sub>2</sub> concentration there was always below the detection limit during operation (though a very small amount of CO<sub>2</sub> was observed in the cathode exhaust when the cell current was turned off due to diffusion across the AEM, which is shown).

The final set of experiments investigated the effects of temperature on CO<sub>2</sub>-related voltage losses. CO<sub>2</sub> was fed

separately to both the cathode and anode at 400 ppm. The cell setup and operation were identical to the previous description with one exception: the AEM used for these temperature studies was LDPE-BTMA (IEC = 2.5 mmol g<sup>-1</sup>), and not ETFE-BTMA (IEC = 2.05 ± 0.05 mmol g<sup>-1</sup>), because of its superior thermo-mechanical stability.

## Results and discussion

In a typical analysis of fuel cell performance, it is often assumed that the cell voltage ( $V_{\text{cell}}$ ) can be represented by eqn (4):

$$V_{\text{cell}} = V_{\text{OCV}} - i(R_{\Omega} + R_{\text{ct}} + R_{\text{mt}}) \quad (4)$$

where  $V_{\text{OCV}}$  is the open-circuit voltage,  $i$  is the cell current,  $R_{\Omega}$  is the ohmic resistance to ion transport,  $R_{\text{ct}}$  is the charge transfer resistance and  $R_{\text{mt}}$  is the mass transport resistance. In PEMFCs, it is typically assumed that  $R_{\text{ct}}$  is dominated by the oxygen reduction reaction (ORR), but this is likely a poor assumption in AEMFCs where the kinetics for the hydrogen oxidation reaction (HOR) are slower in alkaline *vs.* acid electrolyte and the HOR overpotential can be significant.<sup>20</sup> Therefore, discussion regarding charge transfer resistance should take into consideration both the ORR and HOR, which can be denoted as  $R_{\text{ctORR}}$  and  $R_{\text{ctHOR}}$ , respectively. PEMFCs also assume that  $R_{\text{mt}}$  is dominated by oxygen diffusion, which is likely to hold in AEMFCs as well (can be denoted as  $R_{\text{mtORR}}$ ), though this can often be neglected with high stoichiometry pure O<sub>2</sub> flows. However, the presence of CO<sub>2</sub> and carbonate anions complicates this type of analysis.

The electrochemical production of hydroxide anions in the presence of CO<sub>2</sub> and their subsequent equilibrium reactions were summarized in eqn (1)–(3). It should be noted here that OH<sup>-</sup>/CO<sub>3</sub><sup>2-</sup>/HCO<sub>3</sub><sup>-</sup> equilibrium constants exist such that OH<sup>-</sup> and HCO<sub>3</sub><sup>-</sup> can never exist together in large quantities. However, CO<sub>3</sub><sup>2-</sup> can exist in high concentrations with either OH<sup>-</sup> or HCO<sub>3</sub><sup>-</sup>. During cell operation at practical current densities, a significant amount of OH<sup>-</sup> is produced and CO<sub>2</sub> is purged from the cell. Therefore, the two ions that dominate under operating conditions are OH<sup>-</sup> and CO<sub>3</sub><sup>2-</sup>, which has been confirmed through theoretical modeling.<sup>16</sup> For this reason, the remainder of the discussion in this work will only consider the presence of “carbonate” as CO<sub>3</sub><sup>2-</sup>, although it is recognized that bicarbonate is often present in highly carbonated AEMs and AEMFCs before significant levels of electrochemical ORR have occurred at the cathode. It is also possible for there to be at least some bicarbonate accumulated in the anode if the degree of carbonation in the AEMFC is high.

After their formation at the cathode, the CO<sub>3</sub><sup>2-</sup> anions are transported through the AEM to the anode by migration, resulting in the “carbonation” of the AEM and the catalyst layer ionomers (Fig. 1). This carbonation reduces the AEM conductivity since CO<sub>3</sub><sup>2-</sup> has a lower intrinsic mobility than OH<sup>-</sup>,<sup>21–23</sup> which increases the area-specific resistance (ASR, estimated as the product of the measured high frequency resistance and the cell active area) relative to OH<sup>-</sup>-only operation ( $\Delta\text{ASR}$ ). However, this effect should not be overstated as it



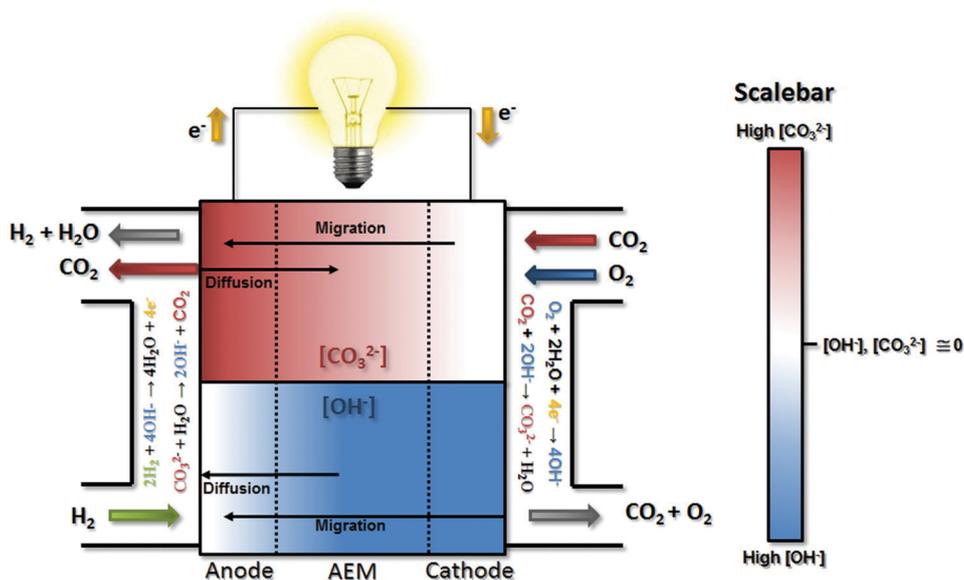


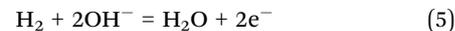
Fig. 1 Illustration of the carbonate and hydroxide transport and distribution in operating AEMFCs with  $\text{CO}_2$  present in the cathode reacting gas. The top section of the diagram isolates the  $\text{CO}_3^{2-}$  behavior in operating cells, with the color gradient representing the concentration gradient. The top section of the diagram shows the  $\text{OH}^-$  concentration gradient, as well as the directionality for hydroxide migration and diffusion.

is only able to account for a small fraction of the performance loss when  $\text{CO}_2$  is added to the cathode stream. Definitive experimental evidence will be presented below to support this. Less discussed, though thoughtfully pointed out and modeled by a few studies in the literature,<sup>16,24,25</sup> migration is not the only mass transport event that influences the location and distribution of  $\text{CO}_3^{2-}$ ; diffusion also plays a role. The interplay between migration and diffusion results in carbonate concentration profiles that impact performance in two primary ways beyond Ohmic considerations, one pH-based (Nernstian) and the other electrocatalytic.<sup>26</sup>

Nernstian performance loss in the presence of  $\text{CO}_2$  in operating AEMFCs is due to concentration gradients that develop across the cell. Under typical operating currents, net migration of ions across the AEM is very fast (on the order of 1 s at relevant current densities and AEM thicknesses). This ionic flux towards the anode leads to lower concentrations of  $\text{CO}_3^{2-}$  in the AEM and cathode compared to the anode (though the extent will depend on factors including membrane thickness, current density and the  $\text{CO}_2$  concentration in the cathode stream). The resulting  $\text{CO}_3^{2-}$  concentration gradient provides a driving force for back-diffusion of  $\text{CO}_3^{2-}$  anions from the anode towards the cathode – setting up a steady-state concentration gradient where there is significant carbonate accumulation within the anode,<sup>16,24,26</sup> although the absolute and variation of the carbonate level within the anode has yet to be determined directly. The presence of carbonate in the anode decreases the local pH, leading to an increase in the anode potential ( $\Delta V_{\text{Nernst}}$ ) according to the Nernst equation during operation, which has been theoretically estimated to be as high as 180–350 mV.<sup>16,27</sup>

Electrocatalytically-driven  $\text{CO}_2$ -related voltage losses arise from the reduced migrational supply and reduced local

concentration of reacting  $\text{OH}^-$  anions as  $\text{CO}_3^{2-}$  carries charge from the cathode to the anode and accumulates there. Previous work (and the data in Fig. S2 in the ESI† for a cell pulsing to 0.1 V) has shown evidence that at high anode overpotentials  $\text{CO}_2$  is quickly removed from operating AEMFCs – suggesting that carbonate may directly react with  $\text{H}_2$  at those overpotentials to produce water and  $\text{CO}_2$ , thereby significantly accelerating decarbonization (also supported by data on slide 17 in ref. 28). However, the long timescales needed to completely decarbonate AEMFCs at typical operating current and higher cell voltages (lower anode overpotentials), such as Fig. S1 in the ESI,† strongly suggests that such direct reaction does not appreciably occur at conditions of practical interest. Hence, it can be assumed in this work that essentially the entirety of the steady-state electrochemical current is generated through  $\text{OH}^-$ -based ORR and HOR reactions (eqn (1) and (5), respectively). Therefore, when  $\text{CO}_3^{2-}$  anions carry charge through the AEM, the balance of reacting  $\text{OH}^-$  that is no longer supplied by migration (due to  $\text{CO}_3^{2-}$  conduction) must be compensated for by diffusion, which is an intrinsically slower process.



Therefore,  $\text{CO}_3^{2-}$  in the anode effectively shuts off catalyst sites with high local  $\text{CO}_3^{2-}$  concentration due to reduced access to  $\text{OH}^-$  ions – increasing the effective current density on  $\text{OH}^-$  accessible anode catalysts. This means that although the presence of carbonate species does not negatively impact the intrinsic HOR electrocatalysis,<sup>29</sup> the high  $\text{CO}_3^{2-}$  concentration in the anode does cause an increase in the kinetic resistance, inducing polarization losses that lower the operating cell voltage (denoted as  $\Delta R_{\text{ctHOR}}$ ).



These new resistances lead to a more complex equation for the operating cell voltage, though one that is insightful for the analysis of AEMFCs that have been carbonated:

$$V_{\text{cell}} = V_{\text{OCV}} - i(R_{\Omega,\text{OH}} + R_{\text{ctORR}} + R_{\text{mtORR}} + R_{\text{ctHOR}}) - \Delta V_{\text{Nernst}} - i(\Delta\text{ASR} + \Delta R_{\text{ctHOR}}) \quad (6)$$

The assignment of all of the new kinetic overpotential to the anode is supported by experimental work by Matsui *et al.*<sup>30</sup> who found, using a three-electrode AEMFC configuration with a reversible hydrogen reference electrode, that the cathode overpotential was hardly changed by the presence of CO<sub>2</sub>, while the overpotential of the anode increased considerably.

The above-discussed behavior of carbonated AEMFCs is very similar to cation-contaminated PEMFCs,<sup>31–34</sup> though some critical differences do exist. Most importantly, in this case the “contaminant”, CO<sub>3</sub><sup>2-</sup>, is continuously created at the cathode, moved to the anode, and removed from the anode gas stream. Similar processes do not exist for cation-contaminated PEMFCs with the exception of the NH<sub>3</sub>/NH<sub>4</sub><sup>+</sup> couple.<sup>35</sup> For CO<sub>2</sub> containing AEMFCs, CO<sub>3</sub><sup>2-</sup> can be removed during operation by introducing a CO<sub>2</sub>-free oxidant, activating a “self-purging” mechanism, which has been discussed elsewhere.<sup>15</sup> For reasons discussed above, under normal operating conditions this self-purging is not a result of direct electrochemical reaction of carbonates, but rather thermodynamic equilibrium. Under pseudo steady-state conditions, the CO<sub>2</sub> uptake rates at the cathode equal the release rates at the anode and a static concentration polarization exists across the anode, AEM, and

cathode – based on balancing between migration and diffusion of OH<sup>-</sup> and CO<sub>3</sub><sup>2-</sup>, as illustrated in Fig. 1.

In order to minimize the effect of CO<sub>2</sub> and carbonation on operating AEMFCs, it is important for the field to better understand how CO<sub>2</sub> uptake, membrane carbonation, and CO<sub>2</sub> release occur. There are both transient and steady-state concerns with little experimental data to provide insight or validate existing models. The results presented here quantify the uptake and release rates of CO<sub>2</sub>, quantify the amount of CO<sub>2</sub> within the MEA under different steady-state conditions, and provide data as to the performance and resistance of AEMFCs under specific CO<sub>2</sub> conditions. This first of its kind data provides significant insight into the performance losses and ultimate potential of AEMFCs when exposed to CO<sub>2</sub>. This work provides direct evidence regarding the extent to which the CO<sub>2</sub> fed to the cathode becomes integrated into the AEMFC, directly correlates carbonation with AEMFC performance, and provides critical data needed to validate modeling efforts that try to quantify rates of CO<sub>2</sub> uptake and release, as well as the negative effects of CO<sub>2</sub> on performance.

### Dynamic observation of CO<sub>2</sub> uptake and transport in operating AEMFCs

To probe the uptake and release of CO<sub>2</sub> in AEMFCs, CO<sub>2</sub> (100, 200, 400, 800, 1600 and 3200 ppm) was added to the cathode of cells under open circuit conditions as well as cells operated at 0.2, 0.5, 1.0 and 2.0 A cm<sup>-2</sup>. For the entire data set, the concentration of CO<sub>2</sub> leaving both the anode and cathode was measured in real time. The results for 400 ppm CO<sub>2</sub> in O<sub>2</sub> are shown in Fig. 2a and b, and the results for all of the other

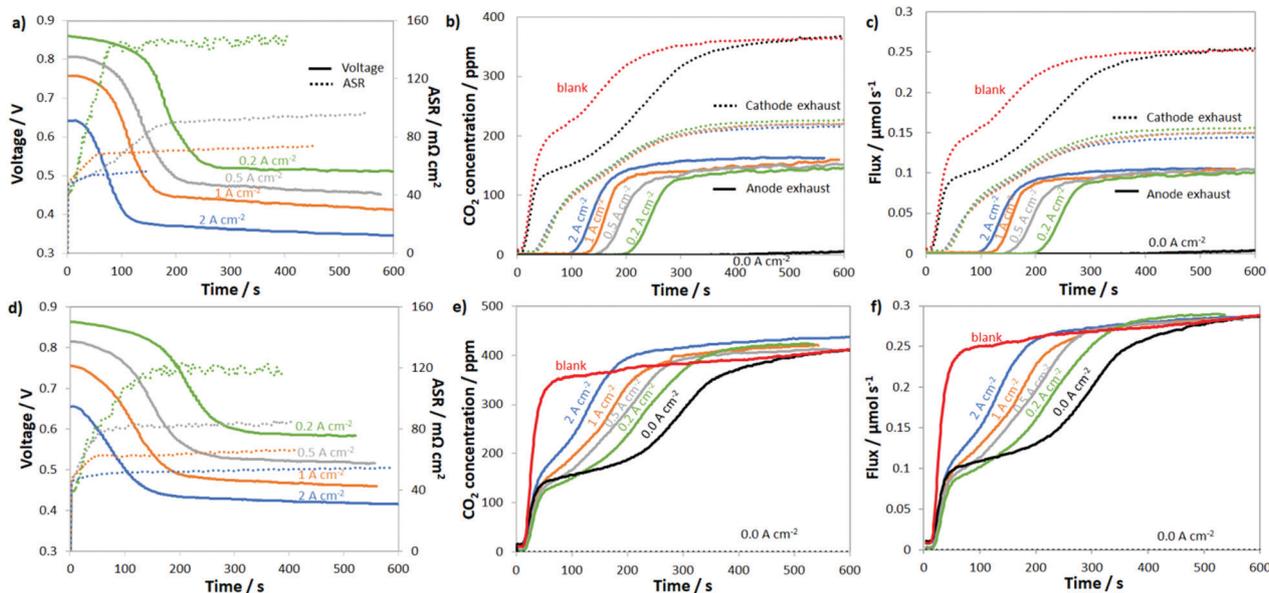


Fig. 2 Uptake of 400 ppm CO<sub>2</sub> fed to both the anode and cathode of H<sub>2</sub>/O<sub>2</sub> AEMFCs operating at 60 °C and discharging at 0.00 (load off), 0.20, 0.50, 1.0 and 2.0 A cm<sup>-2</sup> current densities. (a) Voltage decrease and ASR increase upon introduction of CO<sub>2</sub> into the cathode reacting gas; (b) CO<sub>2</sub> emission from the anode (solid lines) and cathode (dotted lines) when 400 ppm CO<sub>2</sub> was fed to the cathode; (c) CO<sub>2</sub> flux fed to the cell and released from the anode (solid lines) and cathode (dotted lines) when 400 ppm CO<sub>2</sub> was fed to the cathode; (d) voltage decrease and ASR increase upon introduction of CO<sub>2</sub> into the anode reacting gas; (e) CO<sub>2</sub> emission from the anode (solid lines) and cathode (dashed line) when 400 ppm CO<sub>2</sub> was fed to the anode; (f) CO<sub>2</sub> molar flux fed to the cell and released from the anode (solid lines) and cathode (dashed line) when 400 ppm CO<sub>2</sub> was fed to the anode. The AEM used was ETFE–BTMA (IEC = 2.05 mmol g<sup>-1</sup>).



CO<sub>2</sub> concentrations are shown in the ESI,<sup>†</sup> Fig. S3–S7. The first condition assessed was steady-state at the open-circuit voltage (OCV, labeled as 0.0 A cm<sup>-2</sup>), which allows the diffusional dynamics of ionomer and membrane carbonation to be observed since there is no current driving the movement of CO<sub>3</sub><sup>2-</sup> from the cathode to the anode. Though the OCV did not change, in agreement with the work by Inaba *et al.*,<sup>36</sup> it was clear during the experiment that the AEM and AEI were being converted to the carbonate form since the amount of CO<sub>2</sub> leaving the cathode was far below the 400 ppm feed, Fig. 2b, especially over the first 300 s.

After the CO<sub>2</sub> was added to the cathode at OCV, the concentration initially rose from zero to *ca.* 130 ppm as two things were occurring: absorption of CO<sub>2</sub> into the AEM and ionomer and the increase in the CO<sub>2</sub> partial pressure in the gas stream (the humidifier and cell lag in the CO<sub>2</sub> concentration is denoted as “blank” in Fig. 2b – determined in a cell containing a Teflon membrane, which does not uptake CO<sub>2</sub> and form CO<sub>3</sub><sup>2-</sup> anions). Comparing the “blank” and 0.0 A cm<sup>-2</sup> (black dotted line) plots in Fig. 2b, it was clear that there was rapid CO<sub>2</sub> uptake into the AEM because the concentration of CO<sub>2</sub> leaving the AEM-containing cell was always lower than the “blank”. By 600 s, the concentration of CO<sub>2</sub> in the cathode rose to the inlet concentration, suggesting that the AEM was extensively carbonated after 10 min, which is in good agreement with previous studies on AEM carbonation in the presence of gas-phase CO<sub>2</sub>.<sup>15,37,38</sup> Also from the difference in the response of the AEM and “blank”, it was possible to calculate that essentially all of the charge carrying groups in the AEM and AEI were carbonated during this time (and at steady-state contained a mixture of HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>, details in the ESI,<sup>†</sup> Fig. S8 and accompanying discussion).

When CO<sub>2</sub> was added to the cathode of a fully broken-in cell operating at a constant current density, the cell response was very different. In all cases (from 0.2 A cm<sup>-2</sup> to 2.0 A cm<sup>-2</sup>), after a brief time lag, the cell operating voltage precipitously declined, the ASR increased, and CO<sub>2</sub> was emitted at the anode; this is shown in Fig. 2a and b. What changed with current density were the magnitude and timing of these phenomena. At the highest current density that was tested, 2.0 A cm<sup>-2</sup>, it took approximately 31 s for CO<sub>2</sub> to be measured in the anode stream (from the time that the reacting gas CO<sub>2</sub> concentration increased). It took another 96 s after CO<sub>2</sub> was initially measured in the anode gas before a quasi-steady-state was achieved. When the current was halved to 1.0 A cm<sup>-2</sup>, the time for CO<sub>2</sub> break-through to the anode was approximately doubled (65 vs. 31 s), though the time to reach equilibration was very similar (90 vs. 96 s). This trend continued for 0.5 A cm<sup>-2</sup> and 0.2 A cm<sup>-2</sup>.

The CO<sub>2</sub> breakthrough time increasing with decreasing current density is intuitive as the rate of ion movement through the AEM is slower at lower current density. The timescale for CO<sub>2</sub> breakthrough was much longer than the amount of time it would take for an ion to travel between the cathode and anode. At current densities of 2.0 A cm<sup>-2</sup>, 1.0 A cm<sup>-2</sup>, 0.5 A cm<sup>-2</sup>, and 0.2 A cm<sup>-2</sup>, the average time for a net single-charged anion to

travel through the AEM is 410 ms, 820 ms, 1.6 s and 4.1 s, respectively (the ETFE–BTMA AEM had an IEC of 2.05 ± 0.05 mmol g<sup>-1</sup> with *ca.* 43 μmol of charge-carrying, covalently-bound positively-charged groups in the 5 cm<sup>2</sup> membrane active area). The fact that the breakthrough time for CO<sub>2</sub> was much longer than the average time it takes for an anion to move from the cathode to the anode directly supports the idea that CO<sub>2</sub> is not emitted as part of a direct electrochemical process during normal operation and needs time to reach a critical concentration in the anode that allows it to be released into the anode exhaust (through the equilibrium reactions of eqn (2) and (3)). This explains the lag in the CO<sub>2</sub> release as well as provides an explanation as to why breakthrough occurs earlier at higher currents since CO<sub>3</sub><sup>2-</sup> back-diffusion is less effective – resulting in critical anode concentrations being reached sooner. At steady-state, the rate of CO<sub>3</sub><sup>2-</sup> formation at the cathode will equal the rate of carbonate release (CO<sub>2</sub> emission) at the anode; the transient and steady-state fluxes for CO<sub>3</sub><sup>2-</sup> reaction and CO<sub>2</sub> emission at several current densities and CO<sub>2</sub> concentrations to the cathode are given in Fig. 2c.

From the transient flux data, the amount of carbonate in the system at steady-state, as well as the degree of carbonation, could be calculated (Table S1 and subsequent discussion in the ESI<sup>†</sup>). As expected, there was a greater amount of CO<sub>3</sub><sup>2-</sup> present in the system with higher concentrations of CO<sub>2</sub> in the cathode stream. It was also found that the total amount of CO<sub>3</sub><sup>2-</sup> in the system decreased with increasing current density. The change in the total number of CO<sub>3</sub><sup>2-</sup> anions in the system with current density and cathode CO<sub>2</sub> concentration clearly explains the trends in the ASR. However, one interesting observation was that a plot of the total carbonate in the system vs. the change in the ASR, Fig. 3, did not yield a single straight line for all conditions, but there were trends as a function of current density and CO<sub>2</sub> concentration. To understand this, it should be noted that the high frequency resistance measurement by

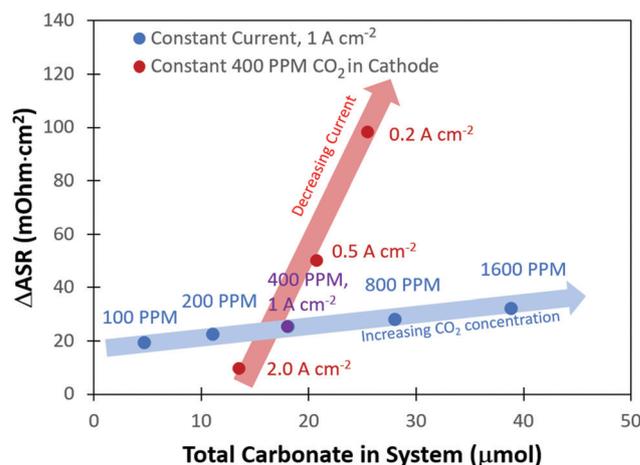


Fig. 3 ASR changes vs. quantity of carbonate in the cell as a function of current density and cathode CO<sub>2</sub> concentration. The fact that the relationship between the amount of carbonate and the change in the ASR does not fall on a single line suggests that more of the carbonates are in the anode electrode than the AEM with increasing current density.



the fuel cell test station is only measuring the two closest points separated by the ionomer; in other words, it is essentially a measurement of the membrane resistance. Therefore, the fact that the ASR is lower at a higher current density, even under conditions where the total amount of  $\text{CO}_3^{2-}$  in the cell is nearly identical to a lower current density, suggests that there is less carbonate in the AEM and more carbonate in the anode electrode as the current density is increased.

In summary, there were seven interesting observations when  $\text{CO}_2$  was fed to the AEMFC cathode: (1) the  $\text{CO}_2$  concentration leaving the cathode was only very modestly affected by the current density (Fig. 2b), at least at the high flowrates investigated in this work; (2) the decrease in the cell voltage (Fig. 2a) started to occur before  $\text{CO}_2$  was measured in the anode exhaust; (3) the ASR increased immediately when  $\text{CO}_2$  was added to the cell (Fig. 2a); (4) the steady-state ASR was realized before the steady-state voltage was achieved and  $\text{CO}_2$  was measured in the anode effluent (Fig. 2a and b); (5) the steady-state ASR increased with decreasing current density (Fig. 2a); (6) increasing current density decreased the amount of  $\text{CO}_3^{2-}$  present in the system at steady-state (Table S1, ESI<sup>†</sup>); and (7) even at the highest current density and lowest  $\text{CO}_2$  concentration (2.0 A  $\text{cm}^{-2}$  and 100 ppm, respectively) the  $\text{CO}_2$ -related overpotential was significant (167 mV), and the  $\text{CO}_2$ -related overpotential at 2.0 A  $\text{cm}^{-2}$  and pseudo-air conditions (400 ppm  $\text{CO}_2$ ) was even higher (259 mV). Combined, these observations suggest that: (i)  $\text{CO}_3^{2-}$  formation at the cathode is very rapid (likely in quasi-equilibrium, which will be discussed more later); (ii) initially  $\text{CO}_3^{2-}$  accumulates in the membrane and anode electrode and  $\text{CO}_2$  release is slow until a critical concentration is reached; and (iii) higher current densities increase the amount of  $\text{CO}_3^{2-}$  in the anode electrode.

To further study the dynamics of  $\text{CO}_2$  uptake and  $\text{CO}_3^{2-}$  formation in the AEMFC system, as well as to simulate  $\text{CO}_2$  that would build up in the anode or could be formed as an oxidative product of an alcohol fuel,  $\text{CO}_2$  was also directly fed to the anode. For comparison sake, the  $\text{CO}_2$  concentration in the anode  $\text{H}_2$  reacting gas was also 400 ppm. The results of these experiments are shown in Fig. 2d–f. The first thing that should be noted is that while current was flowing, no measurable  $\text{CO}_2$  was ever found leaving the cathode, which can be attributed to the high net anionic flux relative to typical diffusion rates. Simply,  $\text{CO}_3^{2-}$  cannot diffuse and accumulate to a critical concentration at the cathode faster than migration pushes it to the anode under the conditions tested. Therefore, Fig. 2e only shows the  $\text{CO}_2$  concentration of the anode effluent and Fig. 2f only shows the anode  $\text{CO}_2$  flux. Like the cathode, there was approximately a 45 s lag between the time that  $\text{CO}_2$  was turned on and its measurement (Fig. S3, ESI<sup>†</sup>). In this set of experiments, the dynamic  $\text{CO}_2$  concentration in the effluent (before steady-state) increased with increasing current density, suggesting lower  $\text{CO}_2$  uptake and  $\text{CO}_3^{2-}$  formation at higher currents. Also, the overall voltage decrease and ASR increase were both lower (but only slightly so) when  $\text{CO}_2$  was fed to the anode vs. the cathode, most likely because of reduced carbonation stemming from the direction of ion transport.

## Relationship between anode-evolved $\text{CO}_2$ and the $\text{CO}_2$ concentration in the cathode

At practical fuel cell current densities, the vast majority of the charge is carried by  $\text{OH}^-$ , not  $\text{CO}_3^{2-}$ , even at very high levels of carbonation. Therefore, a metric relating the amount of charge carried by  $\text{CO}_3^{2-}$  (measured by the flux of  $\text{CO}_2$  leaving the anode at steady state) at various current densities and  $\text{CO}_2$  levels in the cathode ( $e^-/\text{CO}_2$ ) would be useful – not only for fuel cells, but also for potential applications such as AEM-based electrochemical  $\text{CO}_2$  capture.<sup>39</sup> Relating this ratio to the partial pressure of  $\text{CO}_2$  in the cathode starts by defining the metric:

$$\log\left(\frac{e^-}{\text{CO}_2}\right) = \log\left(\frac{i}{i_c}\right) = \log i - \log i_c \quad (7)$$

where  $i$  is the total current and  $i_c$  is the component of the total charge carried by  $\text{CO}_3^{2-}$ . This is an acceptable definition because at steady-state, when the net accumulation of  $\text{CO}_2/\text{CO}_3^{2-}$  in the membrane is zero, the amount of  $\text{CO}_3^{2-}$  formed in the cathode and carried through the AEM by is balanced by current through the external circuit. An expression for  $i_c$  can be obtained by assuming Butler–Volmer-type kinetics (assuming that the ORR at the cathode, where the  $\text{CO}_3^{2-}$  is formed, is irreversible), and correcting the directionality of the current:

$$i_c = -i_0 \exp\left[\frac{-\alpha F}{RT}(E - E^{\circ'})\right] \quad (8)$$

where  $i_0$  is the exchange current density,  $\alpha$  is the effective transfer coefficient,  $F$  is Faraday's constant,  $R$  is the ideal gas constant,  $E$  is the electrode potential and  $E^{\circ'}$  is the formal potential. Rearranging:

$$\begin{aligned} E - E^{\circ'} &= \frac{RT}{\alpha F} \ln i_0 - \frac{RT}{\alpha F} \ln i_c \\ &= \frac{2.303RT}{\alpha F} \log i_0 - \frac{2.303RT}{\alpha F} \log i_c \end{aligned} \quad (9)$$

It has been noted in the literature,<sup>15</sup> and suggested by the data in Fig. 2, that carbonation during the ORR is very fast, and, therefore, it can be assumed that the  $\text{CO}_2$  in the cathode gas stream is always in quasi-equilibrium with the generated anions. This Nernstian process can be represented by the Nernst equation, combining the reactions in eqn (1) and (2), where the equilibrium potential is replaced by the actual electrode potential:

$$\begin{aligned} E - E^{\circ'} &= \frac{RT}{nF} \ln \frac{P_{\text{O}_2} P_{\text{H}_2\text{O}}^2 P_{\text{CO}_2}}{[\text{HCO}_3^-]^4} \\ &= \frac{2.303RT}{nF} \log \frac{P_{\text{O}_2} P_{\text{H}_2\text{O}}^2}{[\text{HCO}_3^-]^4} + \frac{2.303RT}{nF} \log P_{\text{CO}_2} \end{aligned} \quad (10)$$

where  $P_i$  is the partial pressure of each gas,  $[\text{HCO}_3^-]$  is the concentration of  $\text{HCO}_3^-$  in the AEM, and  $n$  is the number of electrons transferred in the ORR ( $n = 4$ ). It has been shown<sup>16</sup> and is generally accepted in the field (and assumed above) that the dominant anion in the operating AEMFC is  $\text{CO}_3^{2-}$ , not  $\text{HCO}_3^-$ . Therefore, it is important to express the Nernstian process relative to  $\text{CO}_3^{2-}$ , not  $\text{HCO}_3^-$ . Inserting the



equilibrium expression between the  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  (eqn (11)) into eqn (10):

$$[\text{HCO}_3^-] = \frac{[\text{CO}_3^{2-}]P_{\text{H}_2\text{O}}}{[\text{OH}^-]K_{\text{b}2}} \quad (11)$$

$$\begin{aligned} E - E^{\circ'} &= \frac{RT}{nF} \ln \frac{P_{\text{O}_2} P_{\text{CO}_2}^4 [\text{OH}^-]^4 K_{\text{b}2}^4}{P_{\text{H}_2\text{O}}^2 [\text{CO}_3^{2-}]^4} \\ &= \frac{2.303RT}{nF} \log \frac{P_{\text{O}_2} [\text{OH}^-]^4 K_{\text{b}2}^4}{P_{\text{H}_2\text{O}}^2 [\text{CO}_3^{2-}]^4} + \frac{2.303RT}{nF} \log P_{\text{CO}_2}^4 \end{aligned} \quad (12)$$

where  $[\text{CO}_3^{2-}]$  is the concentration of carbonate in the AEM and  $K_{\text{b}2}$  is the equilibrium constant for the reaction in eqn (3). Combining eqn (9) and (12),  $i_c$  can be found as a function of the partial pressure of  $\text{CO}_2$  in the cathode.

$$\log i_c = \log i_0 - \frac{\alpha}{n} \log \frac{P_{\text{O}_2} [\text{OH}^-]^4 K_{\text{b}2}^4}{P_{\text{H}_2\text{O}}^2 [\text{CO}_3^{2-}]^4} + \alpha \log P_{\text{CO}_2} \quad (13)$$

This result suggests that the  $\text{CO}_3^{2-}$  current should increase with the partial pressure of  $\text{CO}_2$  in the cathode, which is logical. The final step in the derivation, relating the number of electrons transferred to the  $\text{CO}_2$  partial pressure, combines eqn (7) and (13).

$$\begin{aligned} \log \left( \frac{e^-}{\text{CO}_2} \right) &= \left[ \alpha \log i - \log i_0 + \frac{\alpha}{n} \log \frac{P_{\text{O}_2} [\text{OH}^-]^4 K_{\text{b}2}^4}{P_{\text{H}_2\text{O}}^2 [\text{CO}_3^{2-}]^4} \right] \\ &\quad - \alpha \log P_{\text{CO}_2} \end{aligned} \quad (14)$$

Eqn (14) makes two predictions, both of which are confirmed experimentally in Fig. 4, which shows the results of steady-state

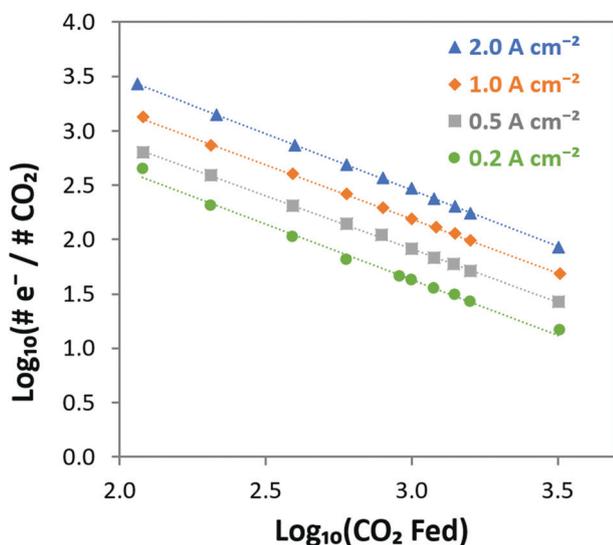


Fig. 4 Visualizing the steady-state transport of  $\text{CO}_2/\text{CO}_3^{2-}$  from the cathode to the anode in AEMFCs operating at 0.2, 0.5, 1 and 2  $\text{A cm}^{-2}$  at 60 °C over a wide range of  $\text{CO}_2$  concentrations. The linear relationship with a slope of  $-1$  verifies the relationship predicted in eqn (14) between the cathode  $\text{CO}_2$  feed concentration and the portion of the charge that is carried by  $\text{CO}_3^{2-}$ , showing that  $\text{CO}_2$  uptake and  $\text{CO}_3^{2-}$  incorporation is a Nernstian process and driven by the ORR.

measurements of  $\text{CO}_2$  emission at various current densities and concentrations. First, at any one current density (where everything in the brackets in eqn (14) is constant), there is a linear relationship between the  $\log e^-/\text{CO}_2$  and  $\log P_{\text{CO}_2}$  with a negative slope equal to the effective ORR transfer coefficient. The slope in Fig. 4 is approximately  $-1$ , which is consistent with measurements of the effective transfer coefficient for the ORR in operating fuel cells.<sup>40,41</sup> Second, this equation predicts that lines at other current densities should be parallel as long as the mechanism is unchanged, and that higher current densities will yield a lower portion of  $\text{CO}_3^{2-}$  carrying the charge (increasing  $\log e^-/\text{CO}_2$ ). In fact, Fig. 4 shows that charge is overwhelmingly carried by  $\text{OH}^-$  in these systems – even when the degree of carbonation at steady-state (Table S1 in the ESI†) is high. Only at very high  $\text{CO}_2$  concentrations (3200 ppm) and low operating current densities ( $0.2 \text{ A cm}^{-2}$ ) is the portion of the charge carried by the  $\text{CO}_3^{2-}$  ion significant (*ca.* 10%), though these are not realistic operating conditions for AEMFCs (whereas 400 ppm is). However, the fact that carbonate does carry charge through the system when  $\text{CO}_2$  is present has significant impacts on the operating voltage, which will be discussed later.

The results from Fig. 2, 4 and Table S1 (ESI†) show that the large overpotentials experienced by AEMFCs when  $\text{CO}_2$  is added to the inlet streams are caused by a relatively small overall  $\text{CO}_3^{2-}$  population. What is missing from the literature, and the discussion thus far, is a conclusive determination of which of the fundamental drivers (Ohmic, Nernstian or anode HOR kinetics) primarily control the carbonate-related losses. Such insight would be invaluable in understanding the behavior (and design) of ambient air-utilizing AEMFC systems.

#### Deconvolution of carbonate-related losses in operating AEMFCs

Though the previous two sections have established some basic parameters for the behavior of  $\text{CO}_3^{2-}$  in operating AEMFCs (*e.g.* it induces polarization losses, is formed in quasi-steady-state with the ORR and its concentration gradient changes with feed concentration and current density), what would be the most helpful from a design and operation perspective is a quantitative deconvolution of the polarization losses. Identifying which of the carbonate-related processes is performance-limiting would allow for solutions to be proposed and evaluated systematically.

The first step in quantifying the carbonate-related losses in operating AEMFCs was to track the performance decline for cells operating at steady-state at several current densities over a wide range of cathode  $\text{CO}_2$  concentrations. The response of a steady-state AEMFC operating at  $1 \text{ A cm}^{-2}$  to the introduction of 100, 200, 400, 800, 1600, and 3200 ppm  $\text{CO}_2$  to the cathode reacting gas is shown in Fig. 5a, and equivalent data for AEMFCs operating at 0.2, 0.5 and  $2.0 \text{ A cm}^{-2}$  are provided in Fig. S9a–c in the ESI.† Between each tested  $\text{CO}_2$  concentration, the cell was rapidly decarbonated as described in the Experimental section. The data shown in Fig. 5a and Fig. S9a–c (ESI†) show one hour of AEMFC behavior at each  $\text{CO}_2$  concentration – the first 30 min segment shows the carbonation event and the



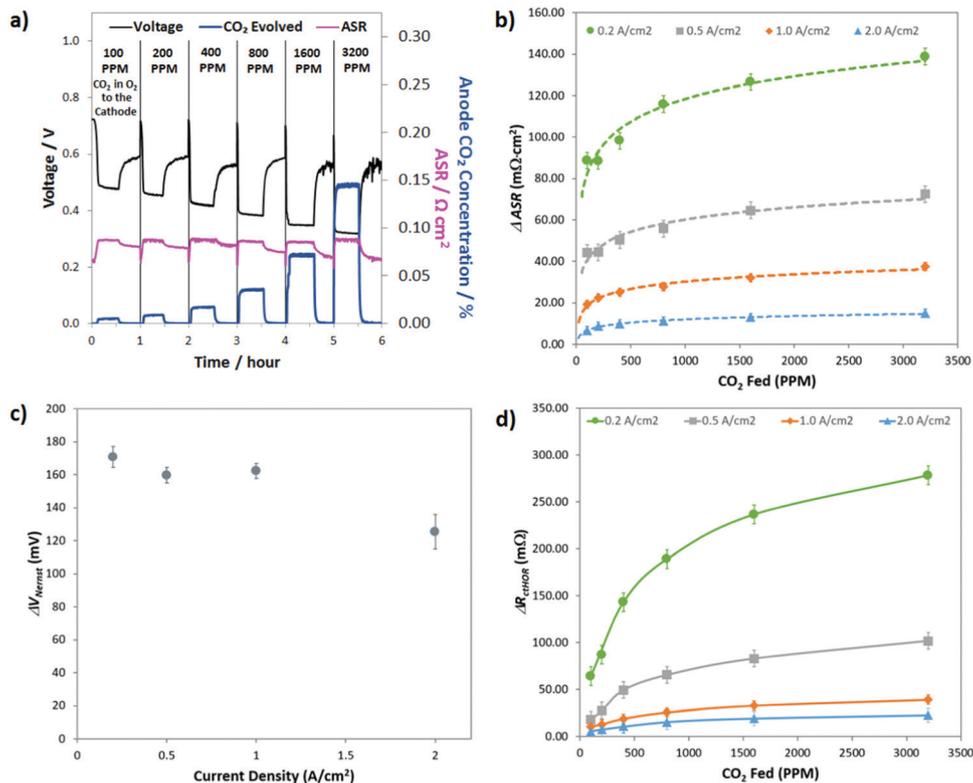


Fig. 5 (a) Response of an AEMFC operating at  $1.0 \text{ A cm}^{-2}$  to various concentrations of CO<sub>2</sub> in the cathode reacting gas; (b) summary of the change in the ASR at various current densities and CO<sub>2</sub> concentrations; (c) AEMFC Nernstian voltage loss as a function of current density; (d) increase in anode charge transfer resistance with increasing CO<sub>2</sub> concentration and decreasing current density. All cells were operated at  $60^\circ \text{C}$  with an ETFE–BTMA AEM (IEC =  $2.05 \pm 0.05 \text{ mmol g}^{-1}$ ).

re-establishment of a new steady-state. The second 30 min segment shows the initial response following CO<sub>2</sub> removal (where pure O<sub>2</sub> is again fed).

As discussed earlier, the introduction of CO<sub>2</sub> to operating AEMFCs initiates an interesting series of dynamic events that, in concert, lead to reduced steady-state performance through three mechanisms: increasing the Ohmic resistance ( $\Delta \text{ASR}$ ), increasing the anode charge transfer resistance ( $\Delta R_{\text{ctHOR}}$ ) and increasing the thermodynamic anode potential ( $\Delta V_{\text{Nernst}}$ ). The challenge here is to find a systematic way to use the CO<sub>2</sub> exposure and removal data in Fig. 5a (and Fig. S9 in the ESI†) to quantify the contribution of each of these resistances to the total CO<sub>2</sub>-related overpotential. The general approach to extracting these three losses from the data was consistent regardless of the experiment. A representative description for 400 ppm CO<sub>2</sub> at  $1.0 \text{ A cm}^{-2}$  is given here for illustrative purposes, and then the summary of all of the calculated parameters is shown in Fig. 5b–d.

Before adding any CO<sub>2</sub> to the AEMFC operating at  $1.0 \text{ A cm}^{-2}$ , steady-state performance was established. The steady-state operating voltage at this condition was 0.72 V. The operating voltage for this cell is given by eqn (4). What this means is that the CO<sub>2</sub>-free steady-state operating voltage already contains  $R_{\Omega, \text{OH}}$ ,  $R_{\text{ctORR}}$  and  $R_{\text{mtORR}}$ ; hence, the deviation of the operating voltage after adding CO<sub>2</sub> will only come from  $\Delta V_{\text{Nernst}}$ ,  $\Delta \text{ASR}$  and  $\Delta R_{\text{ctHOR}}$ , as shown in eqn (6). After adding 400 ppm CO<sub>2</sub> to the cell, the new

steady-state voltage that was reached was 0.44 V – meaning that the total CO<sub>2</sub>-related overpotential was *ca.* 280 mV. While the stoichiometries used in these experiments were high, leading to high CO<sub>2</sub> dosages, the observed performance losses (in combination with the total CO<sub>2</sub>-related overpotential of  $\sim 260 \text{ mV}$  for a cell operating at  $2.0 \text{ A cm}^{-2}$  with 400 ppm CO<sub>2</sub>) suggest that the “self-purging” mechanism has a relatively modest effect in decarbonating the cell, and reducing CO<sub>2</sub>-related voltage losses to an acceptable level during operation on direct ambient air will be a significant challenge, and may not be possible at all.

The first CO<sub>2</sub>-related loss that was calculated was  $\Delta \text{ASR}$ . The ASR as a function of time is shown in Fig. 5a, and under this operating condition,  $\Delta \text{ASR}$  was  $25 \text{ m}\Omega \text{ cm}^2$ . Assuming this  $\Delta \text{ASR}$  resulted in proportional Ohmic losses, at  $1 \text{ A cm}^{-2}$  this would result in an Ohmic loss of 25 mV. For completeness, we acknowledge that the measured ASR values do not yield the exact potential drop related to ion movement through the AEM due to the influence of diffusion.<sup>31,32</sup> However, the value measured here does give an accurate measure of average anion mobility and is presented here as an overestimation of the maximum Ohmic resistance that could be attributed to carbonation. Perhaps what is most important is that this observation clearly shows that the ASR change caused by the emergence and transport of CO<sub>3</sub><sup>2-</sup> through the AEM represents a very small portion of the overall CO<sub>2</sub>-related overpotential (<10%).



For the AEMFC operating at  $1.0 \text{ A cm}^{-2}$  with 400 ppm  $\text{CO}_2$  in the cathode, at minimum, 255 mV of the  $\text{CO}_2$ -related loss remains to be accounted for. The next stage of the deconvolution comes when  $\text{CO}_2$  is removed from the cathode stream. Experimentally, a rapid increase in the cell potential was observed, to *ca.* 0.54 V, though the potential never exactly levels off to reach a new steady-state. That is because the only way that a true steady-state can be reestablished is for all of the  $\text{CO}_3^{2-}$  to be removed, either by waiting for many hours (Fig. S1, ESI<sup>†</sup>), or by accelerated decarbonation at 0.1 V (Fig. S2, ESI<sup>†</sup>). However, it is important to consider what is happening phenomenologically in the AEMFC when the cathode gas is switched from  $\text{CO}_2$ -containing  $\text{O}_2$  to pure  $\text{O}_2$ . When  $\text{CO}_2$  is removed from the cathode, no new  $\text{CO}_3^{2-}$  anions are generated there and the concentration of  $\text{CO}_3^{2-}$  at that electrode drops towards zero. As  $\text{OH}^-$  is produced, the  $\text{CO}_3^{2-}$  that was in the cathode and the AEM is progressively pushed toward the anode by migration (recall that the migrational residence time through the AEM at this current is 820 ms). This suggests that there will be a brief transient period to establish a new quasi steady-state (on the order of  $\sim 10$  min according to Fig. 5a) after which essentially all of the migrational charge that is carried from the cathode to the anode is carried by  $\text{OH}^-$ . If this is the case, at the new quasi steady-state, no  $\text{OH}^-$  will need to be provided by diffusion in the anode for the HOR to occur. Therefore, the voltage increase during this 10 min establishment of the new quasi steady-state after  $\text{CO}_2$  is removed can be mostly attributed to the relaxation of the kinetic limitations described by  $\Delta R_{\text{ctHOR}}$  (though the new ASR acting on charge transport needs to be corrected for as well). At the condition above,  $1.0 \text{ A cm}^{-2}$  with 400 ppm  $\text{CO}_2$  fed to the cathode,  $\Delta R_{\text{ctHOR}}$  was calculated by eqn (15) and (16).

$$\begin{aligned} \Delta V_{\text{ctHOR}} \text{ (mV)} &= [0.544 \text{ V} - 0.443 \text{ V}] \times 1000 \\ &\quad - (1.0 \text{ A cm}^{-2})(83.5 \text{ m}\Omega \text{ cm}^2 - 75.3 \text{ m}\Omega \text{ cm}^2) \\ &= 93.7 \text{ mV} \end{aligned} \quad (15)$$

$$\Delta R_{\text{ctHOR}} \text{ (m}\Omega) = \frac{93.7 \text{ mV}}{(1.0 \text{ A cm}^{-2})(5 \text{ cm}^2)} = 18.7 \text{ m}\Omega \quad (16)$$

Because not all of the reacting catalyst in the anode can be assumed to be completely void of carbonation effects (because of the balance of carbonate migration and diffusion), the calculations made from eqn (15) and (16) are likely a lower limit for  $\Delta R_{\text{ctHOR}}$ , though the real value should be close since the rate of carbonate removal after the initial voltage increase is slow.

From here, the Nernst-related loss can be calculated for this case: 162 mV ( $281 \text{ mV} - 25 \text{ mV} - 94 \text{ mV} = 162 \text{ mV}$ ). Because the estimate for  $\Delta R_{\text{ctHOR}}$  is a lower bound, 162 mV is an upper bound for the for  $\Delta V_{\text{Nernst}}$ , though it should be close to the true value for the reasons discussed above. Interestingly, the Nernstian and charge-transport losses had a similar effect on the cell performance, and both were far more important in dictating the performance decline than the Ohmic loss.

Conducting the same analysis over the entire range of current densities and  $\text{CO}_2$  concentrations can yield values for the total  $\text{CO}_2$ -related overpotential,  $\Delta \text{ASR}$ ,  $\Delta R_{\text{ctHOR}}$ , and  $\Delta V_{\text{Nernst}}$  as well as the Ohmic voltage loss ( $\Delta V_{\text{Ohmic}}$ ) and the  $\text{CO}_2$ -related kinetic polarization ( $\Delta V_{\text{ctHOR}}$ ) at every condition. All of these values are given in Table S2 of the ESI.<sup>†</sup> Performing the data deconvolution over such a wide range of current densities and cathode  $\text{CO}_2$  concentrations yielded some very revealing trends and important insight into the behavior of carbonated AEMFCs. Not too surprisingly, the total  $\text{CO}_2$ -related overpotential was increased with decreasing current density and increasing  $\text{CO}_2$  concentration in the cathode (Table S2 in the ESI<sup>†</sup>). However, understanding why this happened requires digging into the trends in  $\Delta \text{ASR}$ ,  $\Delta R_{\text{ctHOR}}$ , and  $\Delta V_{\text{Nernst}}$  more extensively.

Fig. 5b presents the  $\Delta \text{ASR}$  values at all conditions. As the concentration of  $\text{CO}_2$  in the cathode reacting gas was decreased, there was less of a negative impact on the ASR. This makes sense from the transient and steady-state experimental results (Table S1, ESI<sup>†</sup>), which showed that the total amount of  $\text{CO}_3^{2-}$  in the AEMFC was lower at lower cathode  $\text{CO}_2$  concentration and increased current density. As discussed earlier, the overall trends in the ASR with current density and cathode  $\text{CO}_2$  concentration (Fig. 3) led to the conclusion that increasing the current density shifts the  $\text{CO}_3^{2-}$  concentration gradient toward the anode electrode. Hence, with increasing current density, relatively less and less  $\text{CO}_3^{2-}$  is present in the AEM (though the total  $\text{CO}_3^{2-}$  flux is higher, Fig. 2c), resulting in a lower ASR.

The fact that the concentration gradient shifts toward the anode with current density might lead to the assumption that  $\Delta V_{\text{Nernst}}$  (Fig. 5c) should also increase with current density. However, there are two counter points that require discussion. First, the total quantity of carbonate in the cell is decreasing with increasing current density, which alone might limit the achievable value for  $\Delta V_{\text{Nernst}}$ , particularly at high currents. Second, the anode potential is measured at the outermost portion of the anode at the gas diffusion layer, which is likely the point of the highest  $\text{CO}_3^{2-}$  concentration, as illustrated in Fig. 1, and it is possible for that one specific location to be close to saturation over a wide range of conditions. We observed that  $\Delta V_{\text{Nernst}}$  appeared to decrease with increasing current density, though the values at current densities  $\leq 1.0 \text{ A cm}^{-2}$  were very similar.

The assertion that the outermost portion of the anode can be close to saturation was supported by the magnitude of  $\Delta V_{\text{Nernst}}$  at the lower current densities,  $\sim 165 \text{ mV}$ . The effective alkalinity of an AEMFC cathode is between pH 13–14. It is also known that  $\text{CO}_3^{2-}$  is overwhelmingly the dominant carbonate-based charge carrier and this can only happen in water at pH values  $> 11$ . Therefore, the maximum pH shift that could be expected at the anode in an operating cell would be 3, resulting in a  $\Delta V_{\text{Nernst,max}}$  of *ca.* 180 mV. The only data point in Fig. 5c where  $\Delta V_{\text{Nernst}}$  is markedly lower is at very high current,  $2.0 \text{ A cm}^{-2}$ , where  $\Delta V_{\text{Nernst}}$  is  $\sim 125 \text{ mV}$ . This lower value can be explained by either the lower overall carbonate concentration in the cell and anode at higher currents, and/or the development of a mixed potential throughout the anode



because at high current density there is a significant number of  $\text{OH}^-$  ions being released throughout the anode as  $\text{CO}_2$  is evolved through the reverse of eqn (2) and (3), though the root cause for this behavior will likely need to be teased out through computational modeling. It is also noteworthy that  $\Delta V_{\text{Nernst}}$  was essentially unaffected by the cathode  $\text{CO}_2$  concentration, which gives additional support to the arguments above. One area where the higher carbonate concentration in the anode did have a major impact on the AEMFC behavior is  $\Delta R_{\text{ctHOR}}$ , Fig. 5d. At higher overall carbonate content (increased cathode  $\text{CO}_2$  concentration and/or lower current density)  $\Delta R_{\text{ctHOR}}$  was also higher, and the current density had a particularly profound influence on the effect of the cathode  $\text{CO}_2$  concentration. This observation yields important insight into the location of carbonate in electrodes, suggesting that higher current densities compress the volume occupied by carbonates to the outermost portion of the anode, which effectively allows more catalyst sites to have easy access to reacting  $\text{OH}^-$ .

### AEMFC response at low $\text{CO}_2$ concentrations

A practical interpretation of the experiments shown in Fig. 5 is that the polarization losses from AEMFC carbonation are significant at all current densities and near-ambient  $\text{CO}_2$  concentrations, and that AEMFCs will likely require pre-scrubbing of  $\text{CO}_2$  from the operating air. Additionally, the dynamics of  $\text{CO}_2$  uptake (fast) and release (slow) mean that even if  $\text{CO}_2$  could be quickly removed from the anode stream to avoid significant accumulation, losses would still be high. One sensible approach to reducing  $\text{CO}_2$ -related overpotential is to lower the cathode inlet concentration, which is particularly intriguing for stationary implementations of AEMFCs where the volume and weight of a  $\text{CO}_2$  scrubber is less of a concern than it is for mobile or transportation applications. Fig. 6a explores the response of an AEMFC operating at  $1 \text{ A cm}^{-2}$  with 5–50 ppm  $\text{CO}_2$  in the cathode reacting gas. Though the voltage loss was less than at higher concentrations, even down to 5–10 ppm  $\text{CO}_2$  in the cathode, the  $\text{CO}_2$ -related polarization was significant, approximately 140 mV.

Fig. 6b shows the response of an AEMFC operating at  $1 \text{ A cm}^{-2}$  with 5–50 ppm  $\text{CO}_2$  added to the anode  $\text{H}_2$  reacting gas.

The behavior of low-level  $\text{CO}_2$  in the anode is very similar to the cathode. At 10 ppm, the total  $\text{CO}_2$ -related voltage loss was 136 mV. For  $\text{CO}_2$  present in both the cathode and anode, Fig. 6 suggests that if there is a lower threshold below which an operating AEMFC is immune to carbonation, it is very low – below 5 ppm (although it should be noted that dosage is also important and decreasing flow rates could also have a beneficial impact).

### Influence of temperature on $\text{CO}_2$ -related polarization losses at 400 ppm

Fig. 6 shows that removing even a large portion of the  $\text{CO}_2$  in ambient air will not be sufficient to eliminate the  $\text{CO}_2$ -related losses in operating AEMFCs. In fact, we demonstrated that even at 5 ppm  $\text{CO}_2$  significant performance losses occurred. Therefore, it is important for researchers to identify some fundamental and operational properties of the system that can be manipulated to reduce the AEMFC sensitivity to  $\text{CO}_2$ . One pathway to reducing the amount of carbonate accumulated in the system is to increase the cell operating temperature. Increasing temperature could possibly impact cell carbonation because: (i)  $\text{CO}_2$  has lower solubility in water as the temperature is increased;<sup>42</sup> (ii) the kinetics for  $\text{CO}_2$  release (reverse of eqn (2) and (3)) at the anode will improve; (iii) the mass transport rate of evolved gaseous  $\text{CO}_2$  from the anode will increase; and (iv) the intrinsic kinetics for the ORR and HOR will improve.

Fig. 7 summarizes the response of AEMFCs with a LDPE-BTMA membrane operating at 0.2, 0.5, 1.0 and  $2.0 \text{ A cm}^{-2}$  and several temperatures (60, 65, 70, 75, and  $80 \text{ }^\circ\text{C}$ ) following the introduction of 400 ppm  $\text{CO}_2$  to the cathode or anode. Regardless of where the  $\text{CO}_2$  was introduced, increasing the temperature simultaneously decreased the total  $\text{CO}_2$  overpotential and the ASR (Fig. 7a and c). This experimental result is in stark contrast to recent modeling results that suggested increasing the cell temperature would not have a beneficial effect on AEMFC operation with  $\text{CO}_2$  in the feed gas.<sup>16</sup> Fig. 7b shows that as the temperature was increased, the concentration of  $\text{CO}_2$  being emitted from the anode side of the cell (when it is fed to the cathode) decreased. The most likely explanation for this trend, and coupled performance increase, is that less  $\text{CO}_2$

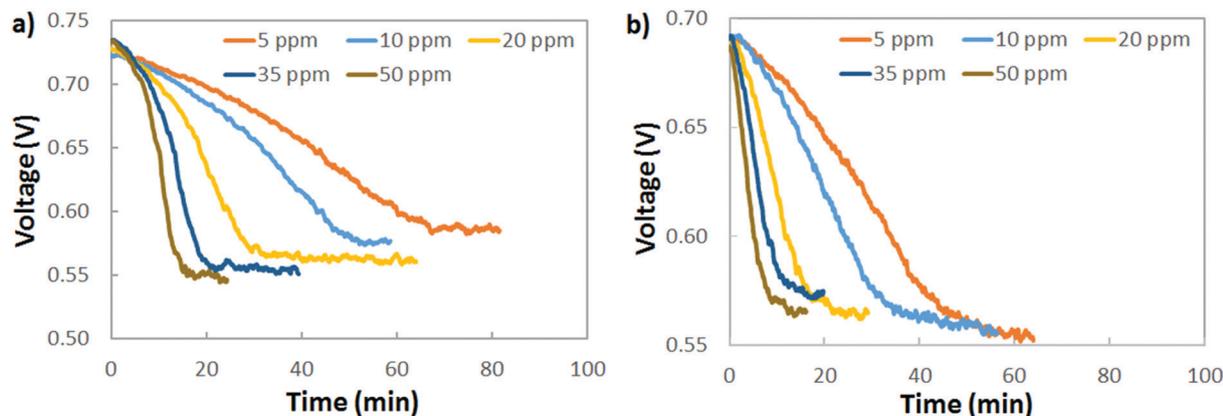


Fig. 6 Exploring the existence of a lower threshold concentration for  $\text{CO}_2$  present in the (a) cathode and (b) anode compartments. The AEMFCs were operated at a current density of  $1.0 \text{ A cm}^{-2}$  at  $60 \text{ }^\circ\text{C}$  with an ETFE-BTMA AEM.



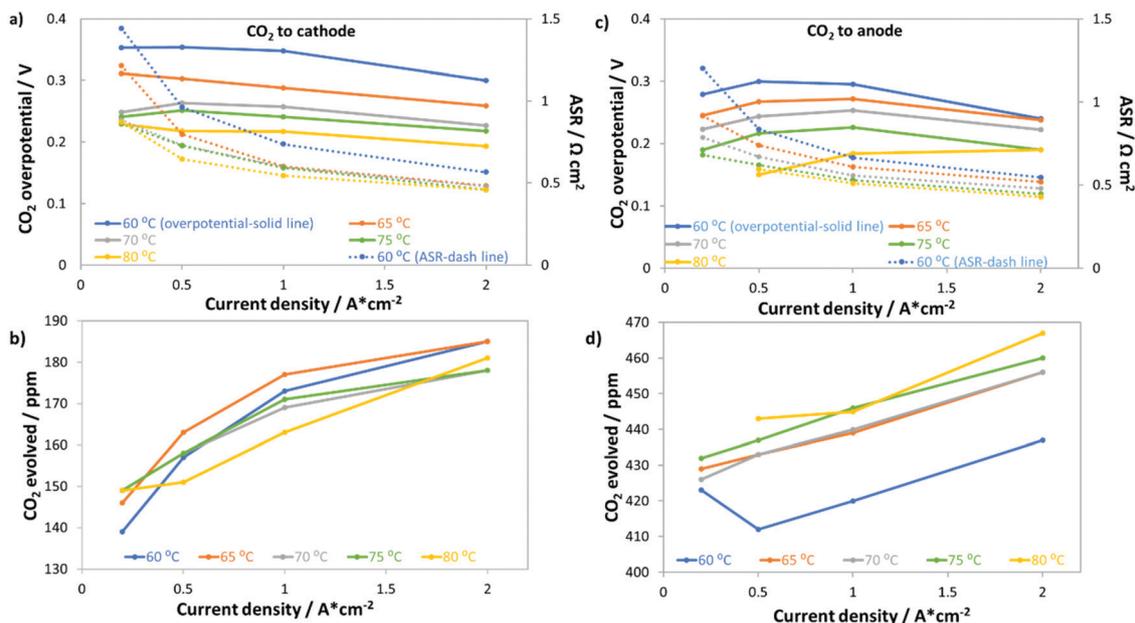


Fig. 7 Impact of temperature on the total CO<sub>2</sub>-related overpotential, ASR and anode CO<sub>2</sub> exhaust with 400 ppm CO<sub>2</sub> fed to the cathode at multiple current densities. Total CO<sub>2</sub> overpotential (solid lines) and ASR (dashed lines) when CO<sub>2</sub> was fed to the (a) cathode and (c) anode. CO<sub>2</sub> concentration in the anode effluent when CO<sub>2</sub> was fed to the (b) cathode and (d) anode. An LDPE–BTMA AEM (IEC = 2.5 mmol g<sup>-1</sup>) was used in these experiments.

was taken up into the system. Fig. 7d shows that when CO<sub>2</sub> was fed to the anode, increasing the temperature resulted in lower CO<sub>2</sub> uptake at that electrode as well, which is shown by the increasing concentration of CO<sub>2</sub> in the anode effluent. It should also be noted in Fig. 7b and d that the values trend upward with increasing current density due to the consumption of the fuel and oxidant gases. Positively, the improved performance at elevated temperatures suggests that increasing temperature is indeed one possible mechanism to improve the CO<sub>2</sub> tolerance of operating AEMFCs; however, the CO<sub>2</sub>-related overpotential is still too high for many practical applications. A combination of lower CO<sub>2</sub> concentration, more modest air stoichiometry, and elevated temperature can further reduce the total CO<sub>2</sub> overpotential. For instance, we observed that an AEMFC operating at 1 A cm<sup>-2</sup> and 80 °C with 10 ppm CO<sub>2</sub> fed to the cathode (the same LDPE–BTMA membrane) had a total CO<sub>2</sub> overpotential of only 90 mV.

Deconvoluted data for AEMFCs operating at different temperatures but at a constant current of 1 A cm<sup>-2</sup> and constant cathode CO<sub>2</sub> concentration of 400 ppm (showing the  $\Delta$ ASR,  $\Delta V_{\text{Nernst}}$  and  $\Delta R_{\text{c(HOR)}}$ ) can be found in Table S3 in the ESI†. As expected, the ASR generally decreased with increasing temperature due to the lower quantity of carbonates that were taken up into the membrane. However, the ASR value only varied slightly with increasing temperature, which meant that a similar portion of CO<sub>3</sub><sup>2-</sup> anions were carrying the charge through the AEM (supported by the results of accelerated decarbonation experiments at 0.1 V, Table S4 in the ESI†), which led  $\Delta R_{\text{c(HOR)}}$  to be fairly constant with temperature as well. Therefore, the primary impact of an overall reduced number of CO<sub>3</sub><sup>2-</sup> anions in the AEM was that the carbonate accumulation in the anode (and hence the concentration

gradient across the cell) was less severe with increased temperature. As a result,  $\Delta V_{\text{Nernst}}$  was the most dependent on temperature, decreasing by nearly 50% from 60–80 °C.

It is possible that even higher temperatures (>90 °C) may help. Though no AEMs are currently readily available with stability above 80 °C in highly alkaline media that also have acceptable conductivity and water transport properties,<sup>3</sup> there is promising work ongoing in this area. Recent reports by Yan and coworkers<sup>3,43</sup> have shown that it is possible to create AEMs that are conductive and stable to at least 95 °C. Another important consideration for AEM and AEMFC researchers is that the membrane chemistry (both backbone and headgroup) and morphology are likely to influence the uptake, transport and release of CO<sub>2</sub>. What this really points to is that improving the CO<sub>2</sub> tolerance of AEMFCs will likely require a combination of approaches to achieve success, at least some of which are not known today and will be particularly challenging for dynamic operation.

## Conclusions

Even in highly performing AEMFCs, the addition of CO<sub>2</sub> has a severe negative impact, where the cell operating voltage is generally decreased by 200–400 mV depending on the reaction conditions. Lower CO<sub>2</sub> concentration in the reacting gas, higher current density and higher operating temperature all reduce the voltage penalty, but none have been shown to be able to sufficiently minimize the CO<sub>2</sub> impact. One of the primary reasons for this is that decarbonation of the cell does not occur through direct electrochemical reaction. This means that decarbonation during operation by the so-called “self-purging”



mechanism is slow, taking several hours even after only transient exposure to CO<sub>2</sub>. Hence, “self-purging” cannot be relied upon to decarbonate AEMFCs efficiently.

The dominating loss in operating AEMFCs in the presence of CO<sub>2</sub> is not due to an increase in the Ohmic resistance from electrolyte carbonation. The dominating mechanism for voltage loss is accumulation of carbonate anions in the anode, which results in two performance-robbing mechanisms: (1) a Nernstian thermodynamic shift in the anode potential from a decrease in the anode pH with carbonates; and (2) an increase in charge transfer resistance due to a lack of availability of reacting OH<sup>-</sup> anions. The CO<sub>2</sub> concentration in the cathode and the current density are both determining factors for the quantity of CO<sub>3</sub><sup>2-</sup> in the system, and the current density appears to play a primary role in dictating the CO<sub>3</sub><sup>2-</sup> location and distribution. The HOR charge transfer resistance increases markedly with both increased CO<sub>2</sub> concentration and lower current density. Increasing the cell operating temperature appears to have almost no effect on the charge transfer resistance, but a significant effect on the Nernstian loss, meaning that the total CO<sub>2</sub>-related overpotential can be reduced by increasing the temperature – or better yet, through a combination of higher current density, lower CO<sub>2</sub> concentration and higher operating temperature.

These new insights can help both modeling groups and experimental researchers to better understand operating AEMFCs, as well as allow them to pose and assess new solutions.

## Conflicts of interest

There are no conflicts to declare.

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