Quantifying and Elucidating the effect of CO2 on the Thermodynamics, Kinetics and Charge Transport of AEMFCs

Yiwei Zheng

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Quantifying and Elucidating the effect of CO$_2$ on the Thermodynamics, Kinetics and Charge Transport of AEMFCs

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Abstract

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$^{-2}$) 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$_2$ (in the air supply) on cell behavior and performance.

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$_2$-related voltage losses during operation at a reasonable operating current density (> 1 A cm$^{-2}$). However, this study definitively shows that neither of these assertions are correct. This study is the first comprehensive experimental investigation into the effects of CO$_2$ on operating AEMFCs. It is also the first study to be able to quantitatively determine the root causes for performance decline when CO$_2$ is added to the system, where cell behavior is directly linked to cell chemistry and reaction dynamics. 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⁻²), operating temperatures (60 – 80°C), and CO₂ concentrations (5 – 3200 ppm) in the reactant gases. I have also investigated the influence of reactant gas flowrates (0.2 – 1 L/min) and dew points (50 – 57°C at 60°C cell temperature) on cell carbonation. The resulting data provides for new fundamental relationships to be developed and for the root causes of increased polarization in the presence of CO₂ 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. 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 CO₂ capture, CO₂ separator and concentrator, CO₂ reduction reactors and dialyzers.
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List of symbols

\( i_0 \)  Exchange current density
\( \alpha \)  Effective transfer coefficient
\( F \)  Faraday’s constant
\( R \)  Ideal gas constant
\( E \)  Electrode potential
\( E' \)  Formal potential
\( i \)  Total current
\( i_c \)  Component of the total charge carried by \( \text{CO}_3^{2-} \)
\( P_i \)  Partial pressure of each gas
\( \varepsilon \)  Average charge per \( \text{CO}_2 \)
\( n \)  Number of electrons transferred in the ORR
\( K_{b2} \)  Equilibrium constant
List of abbreviations

AEI……………………………………………...…...…………..Anion Exchange Ionomer
AEM ...........................................................Anion Exchange Membrane
AEMFC........................................Anion Exchange Membrane Fuel Cell
AFC............................................................Alkaline Fuel Cell
ASR...........................................................Area-Specific Resistance
DOC...............................................................................Degree of Carbonation
ETFE-BTMA.................................Ethylene Tetrafluoroethylene-Benzyltrimethylammonium
GDE.................................................................Gas Diffusion Electrode
HOR.................................................................Hydrogen Oxidation Reaction
LDPE............................................................Low Density Polyethylene
MEA.................................................................Membrane Electrode Assembly
OCV.............................................................Open-Circuit Voltage
ORR..............................................................Oxygen Reduction Reaction
PEM........................................................... Proton Exchange Membrane
PEMFC................................................ Proton Exchange Membrane Fuel Cell
RH................................................................. Relative Humidity
Chapter 1

Introduction

Proton-exchange membrane fuel cells (PEMFCs) shown as Figure 1.1a are considered to be a promising technology for clean and efficient power generation in the twenty-first century. The proton exchange membrane (PEM) is the key component in this fuel cell system. The PEM in the PEMFC is a Teflon-like film that is used to conduct protons between two porous electrodes. The researchers have aimed to prepare PEMs with high proton conductivity, low electronic conductivity, low fuel permeability, low electroosmotic drag coefficient, good chemical/thermal stability, good mechanical properties and low cost. The operating temperature of PEMFCs are typically around 90 °C. The low operating temperature makes the technology competitive in transportation and commercial applications.¹

Nafion, which is a typical PEM, has a structure of a copolymer that consists of a Teflon backbone, which gives the backbone a hydrophobic character, and sulfonic acid groups (HSO₃⁻) grafted into backbone, which give the head groups a hydrophilic character. These two tend to phase separate and the hydrophilic domains provide the ability for the membrane to be ionically conductive and uptake the water needed to hydrate the polymer.
Figure 1.1 Operating principles for (a) acidic fuel cell (PEMFC) and (b) alkaline fuel cell (AEMFC) showing reactions, as well as ion and water movement. ²
For decades, the PEMFC has dominated the research space for low temperature polymer electrolyte fuel cells. The advantages of the PEMFC are its higher power density and quick start up for automotive vehicles. Though significant advances have been made regarding the performance and stability of PEMFCs over the years, the major drawbacks of the PEMFC are its lower operating efficiency (40–45%) and use of high cost platinum catalyst. Figure 1.2 shows that experts believed that high Pt group metal loading as the most significant barrier to reducing cost. Research and development funding was recommended to allocate to “catalysts and electrodes,” followed in decreasing amount by “fuel cell performance and durability”.

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 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.

Therefore, alkaline fuel cells (AFCs) have some advantages over more commonly researched PEMFC. AFCs operate between 200 °C – 240 °C in order to improve the ionic conductivity of the electrolyte as well as the electrode kinetics. This fast kinetics and high electrical efficiency allows the use of a lower quantity of a noble metal catalyst or non-noble metal electro-catalysts like nickel, silver, etc.

Most importantly, the liquid KOH electrolyte used in the AFC is much cheaper than the polymer electrolyte commonly used in PEMFC, which needs appropriate hydration level for good performance and proper functioning. That is to say, water management is not a major issue for AFC as liquid electrolyte was used, thus allowing simple design and
Figure 1.2. Experts’ rankings of barriers to reducing automotive PEMFC system cost. The number of experts who selected each barrier is indicated (darker cells indicate more experts). The barriers shown were selected from a list.\textsuperscript{4}
fabrication. Therefore, considering the cost and the simplicity of operation, AFCs are advantageous over other types of fuel cell and promising on the commercialization of fuel cells. AFC Energy is a producer of alkaline fuel cells which developed a scalable AFC system located in Surrey, UK.

AFCs operating with H₂/air have better prospects for developing the lowest cost devices than PEMFCs. Unfortunately, AFCs have a significant fundamental problem: the aqueous KOH electrolyte reacts with CO₂ from ambient air to form carbonates,⁷⁻⁹ which lowers the performance and stability of the fuel cell because of large metal carbonate crystals, such as K₂CO₃, precipitate in the electrodes as well as by decreasing the concentration of OH⁻ in the electrolyte. The latter decreases the number of hydroxyl ions available for reaction at the anode, leading to sluggish anode kinetics. Additionally, CO₂ poisoning modifies the composition of the electrolyte and thus reduces its ionic conductivity, increasing the Ohmic polarization and leading to lower cell efficiency. Therefore, strategies have been proposed to solve the CO₂ poisoning problem. Cifrain and Kordesch¹⁰ found that the negative effects of CO₂ poisoning can be partly reduced by circulating the electrolyte. Nowadays, most of the current strategies for solving the CO₂ poisoning issue in AFC are still in their early stages and inadequate for commercialization.

It has been proposed that the use of an anion exchange membrane (AEM) in place of liquid KOH – creating so-called anion exchange membrane fuel cells (AEMFCs) – can eliminate the effect of carbonation because there is no possibility for precipitation to occur. The carbonate anions should be freely transported through the AEM when they are formed.

In AEMFCs, Figure 1.1b, hydrogen reacts with hydroxide anions in the electrolyte to create water and electrons (Equation 1.1). The electrons move through the external circuit
to cathode where they react with oxygen and water to create the OH\(^-\) (Equation 1.2). The latter is supplied through the electrolyte to the anode by migration.

\[
2H_2 + 4OH^- \rightarrow 4H_2O + 4e^- \quad (1.1)
\]

\[
O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (1.2)
\]

Researchers have aimed to prepare AEMs with high anion (hydroxide) conductivity, long-term stability in alkaline media at fuel cell operating temperature, robust mechanical properties for overcoming in-use pressure differences, as well as proper water uptake and swelling, which facilitate ion transport within the electrodes and membrane. Early development of AEMFCs was hindered by AEMs with very poor alkaline stability\(^{11}\) and very poor performance, with typical peak power densities well below 0.5 W cm\(^{-2}\). The combination of low achievable power and limited durability\(^{12,13}\) made AEMFCs uncompetitive with PEMFCs for years. However, the fact that AEMFCs struggled with low performance and poor durability compared to PEMFCs was confusing because each of the individual components of the cell (membrane, catalyst, etc.) showed very strong ex-situ performance. For instance, there have been several reports of AEMs with hydroxide conductivity of over 100 mS/cm (60°C to 80°C)\(^{14-16}\) and recent reports of AEMs with conductivity over 200 mS/cm (at 80°C).\(^{17}\) More facile kinetics of the ORR in alkaline media than in acidic media allows the replacement of expensive and scarce Pt-based electrocatalyst with a class of non-precious metal including transition metal oxides. Peng et al. reported that nitrogen-doped carbon–CoO\(_x\) has high intrinsic activity and achieved 1.05 W cm\(^{-2}\) peak power density used as AEMFC cathode. The N-C-CoO\(_x\) cathode even showed good stability over 100 hours of operation with a voltage decay of only 15 % at 600 mA cm\(^{-2}\) under H\(_2\)/air (CO\(_2\)-free) reacting gas feeds.\(^{18}\)
What our group discovered was that the reason for the lower performance in an operating cell than would be expected from the component-level properties was poor control over water in the cell and electrodes. Therefore, our group has focused on improving operational protocols including controlling temperature, pressure, reacting gas dew points, etc. to manipulate the cell-level water dynamics. Our group has also focused on component fabrication techniques, most notably tight control over the ionomer:carbon:catalyst loading and hydrophilicity/hydrophobicity of the anode and cathode electrodes. This allowed our team to routinely achieve high AEMFC performance (> 2000 mW/cm\(^2\) peak power densities) and long life (> 1000 h with minimal loss in operating voltage at 600 mA/cm\(^2\)). State-of-the-art AEMFCs even have the ability to achieve peak power densities over 3 W cm\(^{-2}\) operating on H\(_2\)/O\(_2\) gas feeds. Huang et.al reported AEMs consisting of composite poly(norbornene) with record high hydroxide conductivity, 198 mS/cm, and very high peak power density in a hydrogen/oxygen fuel cell, 3.4 W/cm\(^2\) at 80°C. 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%)\(^{19,21-23}\).

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, such as operating on real air, which contains CO\(_2\). Though AEMs are able to freely transport carbonates, and do avoid the salting that plagued AFCs, it is unknown to what the extent carbonation might occur in operating cells or if carbonation will lead to performance losses.
It is widely known that when CO\textsubscript{2}-containing air is fed to the AEMFC cathode, the OH\textsuperscript{-} anions that are produced from the oxygen reduction reaction (ORR), Equation 1.2, react with CO\textsubscript{2} to produce carbonate and/or bicarbonate anions, Equations 1.3-1.4.

\[
\text{CO}_2 + \text{OH}^- \rightleftharpoons \text{HCO}_3^-
\]

(1.3)

\[
\text{HCO}_3^- + \text{OH}^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}_2\text{O}
\]

(1.4)

As (bi)carbonate anions are produced, they are transported towards the anode by migration, resulting in a “carbonation” of the AEM and the ionomer in the electrodes (especially the anode). The presence of carbonate anions decreases the conductivity of the AEM and therefore the AEMFC performance. It is because they have a larger ionic radius than that of OH\textsuperscript{-}, and therefore, have lower diffusion coefficients and lower mobility. As in aqueous solutions, OH\textsuperscript{-}, CO\textsubscript{3}\textsuperscript{2-} and HCO\textsubscript{3}\textsuperscript{-} have ionic mobilities of 20.64, 7.46, and 4.61 \texttimes 10\textsuperscript{8} \text{m}^2\text{V}^{-1}\text{s} \textsuperscript{-1} respectively.\textsuperscript{24} Kiss et al.\textsuperscript{25} developed a mathematical model for ion transport in AEMs and calculated that the ion-membrane diffusion coefficient of OH\textsuperscript{-} was up to 1.3 times higher than that of the CO\textsubscript{3}\textsuperscript{2-}-coefficient and 1.5 times higher than that of HCO\textsubscript{3}\textsuperscript{-}. With the transport of carbonate from cathode to anode, carbonate accumulates in the anode, resulting in a lower pH. The pH gradient reduces the cell voltage, approximated as 70 mV per pH unit over most of the pH range.\textsuperscript{26} This thermodynamic effect from carbonation can result in a severe reduction in the operating cell voltage, with carbonate-related overpotentials as high as 400 mV.\textsuperscript{27} Rheinhardt et al.\textsuperscript{28} also proposed an electrochemical capture or release device of CO\textsubscript{2} by controlling pH: an increase in pH at the cathode helps uptake CO\textsubscript{2}, trapped CO\textsubscript{2} (as carbonate species) move towards the anode by electromigration, and regenerated CO\textsubscript{2} will come out of the acidic anode.
Several experimental groups have also investigated the CO\textsubscript{2} poisoning issue in AEMFCs. Suzuki et al. found that the flux of CO\textsubscript{2} in the anode exhaust of AEMFCs increased with CO\textsubscript{2} concentration in the cathode and with cell current density\textsuperscript{29}. They found that the increasing of Ohmic resistance was noticeable by the supply of CO\textsubscript{2} to cathode but not obvious when CO\textsubscript{2} was fed to the anode. Kimura and Yamazaki\textsuperscript{24} measured an increase in ex-situ conductivity of an AEM exposed to CO\textsubscript{2}. Shiau et al.\textsuperscript{30} found by modeling that as the current increases, the flux of CO\textsubscript{2} from the anode outlet increases, which means that less CO\textsubscript{2} might be accumulated in the AEM; suggesting that carbonate buildup will minimize the purging effect. Fukuta et al.\textsuperscript{31} believed almost all CO\textsubscript{3}\textsuperscript{2-} was released at the higher current density by self-purging, and small pH change caused big difference in anode catalytic activity. However, the extent to which self-purging could be used to decarbonate active cells has not been confirmed experimentally and the carbonation dynamics are poorly understood. Watanabe et al.\textsuperscript{32} found that the ion ratio (OH\textsuperscript{-}, CO\textsubscript{3}\textsuperscript{2-} and HCO\textsubscript{3}-) depended on current density.

The literature work discussed above suggests that there are many parameters that will affect the carbonation of AEMFCs and influence their behavior during operation. These include: current density, CO\textsubscript{2} concentration, temperature, flow rate, reacting gas dew points, etc. Though theoretical studies have tried to shed some light on this phenomena\textsuperscript{33,34}, unfortunately, essentially all of these models have not been validated by any experimental work. This is likely because there exists a very small body of experimental work in the literature quantifying the impact of CO\textsubscript{2} and determining the root causes behind the extensive performance drop for AEMFCs when CO\textsubscript{2} is present.
Therefore, the purpose of this study is to establish a resolute understanding of the influence of CO$_2$ on the performance of AEMFCs. Herein, the 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. An extensive collection of carbonation data as a function of current density and CO$_2$ concentration at the cathode is presented. The level of carbonation is linked to electrochemical performance. Then, this work explores the lower limits of CO$_2$ exposure to determine whether or not there is a baseline CO$_2$ tolerance in AEMFCs, which informs the field to what degree oxidant gas scrubbing might be needed. Finally, CO$_2$ is fed to the anode to simulate fuel impurities or the use of organic fuels. Subsequently, the effect of flowrates and hydration level on carbonation in AEMFC were studied. Finally, the application of AEMFCs operating with carbon dioxide in cathode feed is discussed.
Chapter 2

Experimental

2.1 Electrode preparation

The electrodes in this work were prepared using a method that has been detailed in previous publications from our group. 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, ion-exchange capacity IEC = 1.24 mmol g\(^{-1}\)) into a mortar and grinding it with a pestle by hand for 10 min. The catalyst powder, additional Vulcan carbon (XC-72R, Cabot), and 1 mL of Millipore deionized (DI, Type 1 18.2 M\(\Omega\) cm resistivity) water 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 mass fraction of carbon was maintained at 0.48 for both electrodes. Next, the catalyst-AEI slurry was transferred to a centrifuge tube. 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 °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 N₂) to create gas diffusion electrodes (GDEs). The target catalyst loading on the GDEs was 0.6 ± 0.1 mgPt cm⁻².

2.2 AEMFC assembly and break-in procedure

Before cell assembly, the GDEs were soaked in 1 M aqueous KOH solutions (made 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 μm thick (fully swollen in water) ETFE-BTMA-based radiation-grafted AEM 37, which was used for the CO₂ dosing experiments at 60 °C. The second AEM was a 25 μm thick LDPE-(low density polyethylene)-BTMA-based radiation-grafted AEM 38. 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 CO₂-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 cm² Scribner hardware between two single pass serpentine flow graphite 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 CO₂ measurements were made, all cells underwent a break-in procedure. First, the cell was brought to its operating temperature under N₂ flow on both sides of the cell at 100% relative humidity (RH). Then, the feed gases were switched to Ultra High Purity H₂ and O₂ (Airgas) at the anode and cathode, respectively. Then, the cell was operated chronoamperometrically 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. The optimized reacting gas dew points were very repeatable from cell-to-cell, 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⁻²) and allowed to equilibrate for at least 30 min before CO₂ exposure was initiated. Multiple cells (no less than three) were constructed and tested for each measurement.

2.3 AEMFC carbon dioxide measurements

Following the break-in procedure and 30 min equilibration, the cell current was held constant and CO₂ was parametrically added to the Ultra High Purity O₂ cathode stream. CO₂ was added to O₂ instead of air in order to simplify observations and isolate the effects of CO₂ on performance, since air has additional O₂ mass transport impact (e.g. N₂ dilution) during cell operation, which is largely eliminated by utilizing O₂ as the reacting gas. The flowrate for O₂ and H₂ in all experiments was 1 L min⁻¹. CO₂ cathode concentrations as low as 2 ppm and as high as 3200 ppm were tested. Typically, after CO₂ 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 CO₂ concentrations took longer to reach steady-state). After 30 min operation at constant current, CO₂ 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$_2$ level and no CO$_2$ emission was measured at the anode (shown in Figure 2.1); or ii) more typically, to reduce the time between CO$_2$ trials, the cell potential was pulsed down to 0.1 V for 1 min (Figure 2.2), after which no CO$_2$ emission was measured in the anode stream. When CO$_2$ was fed to the cathode, the concentration of CO$_2$ being emitted from the anode and cathode were both constantly monitored in real time using a PP Systems WMA-5 non-dispersive infrared CO$_2$ 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$_2$ at concentrations between 2 and 400 ppm was added to the anode instead of the cathode. This was meant to simulate two possible scenarios: i) CO$_2$ accumulation in the anode; and ii) CO$_2$ exposure at the anode from the oxidation of carbonaceous fuels (through reforming or direct alcohol oxidation). When CO$_2$ was fed to the anode, the concentration of CO$_2$ being emitted from the anode and cathode was constantly monitored in real time using the WMA-5. The cathode data is not shown since CO$_2$ concentration was always below the detection limit during operation (though a very small amount of CO$_2$ was observed in the cathode exhaust when the cell current was turned off due to diffusion across the AEM, which is shown).

The third set of experiments investigated the effects of temperature on CO$_2$-related voltage losses. CO$_2$ 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
Figure 2.1 Voltage recovery from 400 ppm CO$_2$ exposure when fed to a) anode b) cathode under constant current operation at 1 A cm$^{-2}$.
Figure 2.2. Rapid recovery of AEMFC performance through forced decarbonation by pulsing the operating voltage to 0.1V for 2 min. The concentration of the carbonate that was in the AEMFC can be calculated from the measured transient CO$_2$ concentration in the anode effluent during the pulse (not shown).
used for these temperature studies was LDPE-BTMA (IEC = 2.5 mmol g⁻¹), and not ETFE-BTMA (IEC = 2.05 ± 0.05 mmol g⁻¹), because of its superior thermomechanical stability.

The fourth set of experiments investigated the effects of flowrate on AEMFC performance. The flowrate for O₂ or H₂ in experiments was varied from 0.2 to 1 L min⁻¹, meanwhile keeping constant 400 ppm CO₂ concentration in cathode feed and 0 ppm CO₂ in the anode feed. LDPE-BTMA was used. The final set of experiments investigated the effects of hydration level on AEMFC operating with 400 ppm CO₂ in cathode. Here, the dew points of both electrodes were systematically modified in order to change the hydration state of the cell; however, all other variables and operating procedures were identical to the description above.
Chapter 3

Results and discussions

In a typical analysis of fuel cell performance, it is often assumed that the cell voltage ($V_{cell}$) can be represented by Equation 3.1:

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

(3.1)

where $V_{OCV}$ is the open-circuit voltage, $i$ is the cell current, $R_\Omega$ is the Ohmic resistance to ion transport, $R_{ct}$ is the charge transfer resistance and $R_{mt}$ is the mass transport resistance. In PEMFCs, it is typically assumed that $R_{ct}$ 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\(^\text{39}\). Therefore, discussion regarding charge transfer resistance should take into consideration both the ORR and HOR, which can be denoted as $R_{ct,ORR}$ and $R_{ct,HOR}$, respectively. PEMFCs also assume that $R_{mt}$ is dominated by oxygen diffusion, which is likely to hold in AEMFCs as well (can be denoted as $R_{mt,ORR}$), though this can often be neglected with high stoichiometry pure O\(_2\) flows). However, the presence of CO\(_2\) and carbonate anions complicates this type of analysis.

The electrochemical production of hydroxide anions in the presence of CO\(_2\) and their subsequent equilibrium reactions were summarized in Equations 1.2 – 1.4. It should be
noted here that \( \text{OH}^-/\text{CO}_3^{2-}/\text{HCO}_3^- \) equilibrium constants exist such that \( \text{OH}^- \) and \( \text{HCO}_3^- \) can never exist together in large quantities. However, \( \text{CO}_3^{2-} \) can exist in high concentrations with either \( \text{OH}^- \) or \( \text{HCO}_3^- \). During cell operation at practical current densities, a significant amount of \( \text{OH}^- \) is produced and \( \text{CO}_2 \) is purged from the cell. Therefore, the two ions that dominate under operating conditions are \( \text{OH}^- \) and \( \text{CO}_3^{2-} \), which has been confirmed through theoretical modeling\textsuperscript{33}. For this reason, the remainder of the discussion in this work will only consider the presence of “carbonate” as \( \text{CO}_3^{2-} \), 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.

After their formation at the cathode, the \( \text{CO}_3^{2-} \) anions are transported through the AEM to the anode by migration, resulting in the “carbonation” of the AEM and the catalyst layer ionomers (Figure 3.1). This carbonation reduces the AEM conductivity since \( \text{CO}_3^{2-} \) has a lower intrinsic mobility than \( \text{OH}^- \)\textsuperscript{40-42}, which increases the area-specific resistance (ASR) relative to \( \text{OH}^- \)-only operation (\( \Delta \text{ASR} \)). However, this effect should not be overstated as it 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\textsuperscript{33,43,44}, 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.
Figure 3.1 Illustration of the carbonate and hydroxide transport and distribution in operating AEMFCs with CO$_2$ present in the cathode reacting gas. The top section of the diagram isolates the CO$_3^{2-}$ behavior in operating cells, with the color gradient representing the concentration gradient. The top section of the diagram shows the OH$^-$ concentration gradient, as well as the directionality for hydroxide migration and diffusion.
The first CO$_2$-related effect is pH related and due to a concentration gradient, that builds up across the cell, as discussed in Chapter 1. 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 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 CO$_2$ concentration in the cathode stream). The resulting CO$_3^{2-}$ concentration gradient provides a driving force for back-diffusion of 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, 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 ($\Delta V_{Nernst}$) according to the Nernst equation during operation, which has been theoretically estimated to be as high as 180 – 350 mV.

The second effect arises from the reduced migrational supply and reduced local concentration of reacting OH$^-$ anions as CO$_3^{2-}$ carries charge from the cathode to the anode and accumulates there. Previous work (and the data in Figure 2.2 for cell pulsing to 0.1 V) has shown evidence that at high anode overpotentials that CO$_2$ is quickly removed from operating AEMFCs – suggesting that carbonate may directly react with H$_2$ at those overpotentials to produce water and CO$_2$ thereby significantly accelerating decarbonization (also supported by data on slide 17 in Ref. 46). However, the long timescales needed to completely decarbonate AEMFCs at typical operating current and higher cell voltages (lower anode overpotentials), such as Figure 3.1, 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 OH- based HOR and ORR reactions (Equations 1.1 and 1.2, respectively). Therefore, when CO$_3^{2-}$ anions carry charge through the AEM, the balance of reacting OH$^-$ that is no longer supplied by migration (due to CO$_3^{2-}$ carbonate conduction) must be compensated for by diffusion, which is an intrinsically slower process.

Therefore, CO$_3^{2-}$ in the anode effectively shuts off catalyst sites with high local CO$_3^{2-}$ concentration due to reduced access to OH$^-$ ions – increasing the effective current density on OH$^-$ accessible anode catalysts. This means that although the presence of carbonate species does not negatively impact the intrinsic HOR electrocatalysis $^{47}$, the high 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 $\Delta R_{ctHOR}$).

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:

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

(3.2)

The assignment of all of the new kinetic overpotential to the anode is supported by experimental work by Matsui et al. $^{48}$ 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$_2$, while the overpotential of the anode increased considerably.

The above-discussed behavior of carbonated AEMFCs is very similar to cation-contaminated PEMFCs $^{49-52}$, though some critical differences do exist. Most important, in
this case the “contaminant”, CO$_3^{2-}$, 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$_3$/NH$_4^+$ couple$^{53}$. For CO$_2$ containing AEMFCs, CO$_3^{2-}$ can be removed during operation by introducing a CO$_2$-free oxidant, activating a “self-purging” mechanism, which has been discussed in Chapter 1$^{27}$. 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$_2$ 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$^-$ and CO$_3^{2-}$, illustrated in Figure 3.1.

In order to minimize the effect of CO$_2$ and carbonation on operating AEMFCs, it is important for the field to better understand how CO$_2$ uptake, membrane carbonation, and CO$_2$ release occur. There are both transient and steady-state concerns with little experimental data to provide insight or support modeling validation. The results presented here quantify the uptake and release rates of CO$_2$, quantify the amount of CO$_2$ within the MEA under different steady-state conditions, and provide data as to the performance and high frequency resistance of AEMFCs under specific CO$_2$ conditions. This first of its kind data provides significant insight into the performance losses and ultimate potential of AEMFCs when exposed to CO$_2$. This work provides direct evidence regarding the extent to which the CO$_2$ 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$_2$ uptake and release, as well as the negative effects of CO$_2$ on performance.

3.1 Dynamic observation of CO$_2$ uptake and transport in operating AEMFCs

To probe the uptake and release of CO$_2$ in AEMFCs, CO$_2$ (100, 200, 400, 800, 1600 and 3200 ppm) was added to cells at open circuit conditions as well as cells operated at 0.2, 0.5, 1.0 and 2.0 A cm$^{-2}$. For the entire data set, the concentration of CO$_2$ leaving both the anode and cathode was measured in real time. The results for 400 ppm CO$_2$ in O$_2$ are shown in Figures 3.2a and b, and the results for all of the other CO$_2$ concentrations are shown as Figures 3.3-3.7. The first condition assessed was steady-state at the open-circuit voltage (OCV, labeled as 0.0 A cm$^{-2}$), which allows the diffusional dynamics of ionomer and membrane carbonation to be observed since there is no current driving the movement of CO$_3^{2-}$ from the cathode to the anode. Though the OCV did not change, in agreement with the work by Inaba et al. $^{54}$, it was clear during the experiment that the AEM and AEI were being converted to the carbonate form since the amount of CO$_2$ leaving the cathode was far below the 400 ppm feed, Figure 3.2b, especially over the first 300 s.

After the CO$_2$ 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$_2$ into the AEM and ionomer and the increase in the CO$_2$ partial pressure in the gas stream (the humidifier and cell lag in the CO$_2$ concentration is denoted as “blank” in Figure 3.2b - determined in a cell containing a Teflon membrane, which does not uptake CO$_2$ and form CO$_3^{2-}$ anions). Comparing the “blank” and 0.0 A cm$^{-2}$ (black dotted line) plots in Figure 3.2b, it was clear that there was rapid CO$_2$ uptake into the AEM because the concentration of CO$_2$ leaving the AEM-containing cell was always lower than with the "blank". By 600 s, the
concentration of CO₂ 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 CO₂.

When CO₂ 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⁻² to 2.0
A cm⁻²), after a brief time lag, the cell operating voltage precipitously declined, the ASR
increased, and CO₂ was emitted at the anode; this is shown in Figures 3.2a 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⁻², it took approximately 31 s for CO₂ to
be measured in the anode stream (from the time that the reacting gas CO₂ concentration
increased). It took another 96 s after CO₂ was initially measured in the anode gas before a
quasi-steady-state was achieved. When the current was halved to 1.0 A cm⁻², the time for
CO₂ 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⁻²
and 0.2 A cm⁻².

The CO₂ 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 CO₂ 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⁻², 1.0 A cm⁻², 0.5
A cm⁻², and 0.2 A cm⁻², 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 has an
IEC of 2.05 ± 0.05 mmol g⁻¹ with ca. 43 µmol of charge-carrying, covalently-bound
positively-charged, groups in the 5 cm² membrane active area). The fact that the
breakthrough time for CO\textsubscript{2} is 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\textsubscript{2} 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 Equations 1.3-1.4). This explains the lag in the CO\textsubscript{2} release as well as provides an explanation as to why breakthrough occurs earlier at higher currents since CO\textsubscript{3}\textsuperscript{2-} back-diffusion is less effective resulting in critical anode concentrations being reached sooner. At steady-state, the rate of CO\textsubscript{3}\textsuperscript{2-} formation at the cathode will equal the rate of carbonate release (CO\textsubscript{2} emission) at the anode; the transient and steady-state fluxes for CO\textsubscript{3}\textsuperscript{2-} reaction and CO\textsubscript{2} emission at several current densities and CO\textsubscript{2} concentrations to the cathode are given in Figure 3.2c.

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\textsubscript{3}\textsuperscript{-} and CO\textsubscript{3}\textsuperscript{2-} (see as Figure 3.8).

Hence, the quantity of CO\textsubscript{2} that has been taken up into the cell by the AEM and AEI is the integrated area between these two plots. From here, the degree of carbonation (DOC, % of charge groups converted to the carbonate form) can be calculated by:

\[
\text{DOC} = \frac{(\text{Charge per CO}_2)(\mu\text{mol CO}_2)}{(\text{Charge per group})(\mu\text{mol AEM groups}+\mu\text{mol AEI groups})} = \frac{(2)(38.2)}{(1)(42.8+25.5)} = 1.11 = 111%
\]

This number being higher than 100% validates literature data on membranes that were carbonated outside of operating cells with no current flowing where the balance in the membrane is a mixture of both carbonate and bicarbonate. The data above could be used to make a rough calculation of the ratio of carbonate to bicarbonate since bicarbonate
Figure 3.2. Uptake of 400 ppm CO$_2$ fed to both the anode and cathode of H$_2$/O$_2$ AEMFCs operating at 60°C and discharging at 0.00 (load off), 0.20, 0.50, 1.0 and 2.0 A cm$^{-2}$ current densities.  a) voltage decrease and ASR increase upon introduction of CO$_2$ into the cathode reacting gas; b) CO$_2$ emission from the anode (solid lines) and cathode (dotted lines) when 400 ppm CO$_2$ is fed to the cathode; c) CO$_2$ flux fed to the cell and released from the anode (solid lines) and cathode (dotted lines) when 400 ppm CO$_2$ is fed to the cathode; d) voltage decrease and ASR increase upon introduction of CO$_2$ into the anode reacting gas; e) CO$_2$ emission from the anode (solid lines) and cathode (dashed line) when 400 ppm CO$_2$ is fed to the anode; f) CO$_2$ molar flux fed to the cell and released from the anode (solid lines) and cathode (dashed line) when 400 ppm CO$_2$ is fed to the anode.  AEM used was an ETFE-TMA (IEC = 2.05 mmol g$^{-1}$).
Figure 3.3. Uptake of 100 ppm CO₂ fed to the cathode of H₂/O₂ AEMFCs operating at 60°C and discharging at 0 (load off), 0.20, 0.50, 1.0 and 2.0 A cm⁻² current densities. a) voltage decrease and ASR increase upon introduction of CO₂ into the cathode reacting gas; b) CO₂ emission from the anode (solid lines) and cathode (dotted lines) when 100 ppm CO₂ is fed to the cathode; c) CO₂ flux fed to the cell and released from the anode (solid lines) and cathode (dotted lines) when 100 ppm CO₂ is fed to the cathode.
Figure 3.4. Uptake of 200 ppm CO₂ fed to the cathode of H₂/O₂ AEMFCs operating at 60°C and discharging at 0 (load off), 0.20, 0.50, 1.0 and 2.0 A cm⁻² current densities. a) voltage decrease and ASR increase upon introduction of CO₂ into the cathode reacting gas; b) CO₂ emission from the anode (solid lines) and cathode (dotted lines) when 200 ppm CO₂ is fed to the cathode; c) CO₂ flux fed to the cell and released from the anode (solid lines) and cathode (dotted lines) when 200 ppm CO₂ is fed to the cathode.
Figure 3.5. Uptake of 800 ppm CO\textsubscript{2} fed to the cathode of H\textsubscript{2}/O\textsubscript{2} AEMFCs operating at 60°C and discharging at 0 (load off), 0.20, 0.50, 1.0 and 2.0 A cm\textsuperscript{-2} current densities. a) voltage decrease and ASR increase upon introduction of CO\textsubscript{2} into the cathode reacting gas; b) CO\textsubscript{2} emission from the anode (solid lines) and cathode (dotted lines) when 800 ppm CO\textsubscript{2} is fed to the cathode; c) CO\textsubscript{2} flux fed to the cell and released from the anode (solid lines) and cathode (dotted lines) when 800 ppm CO\textsubscript{2} is fed to the cathode.
Figure 3.6. Uptake of 1600 ppm CO₂ fed to the cathode of H₂/O₂ AEMFCs operating at 60°C and discharging at 0 (load off), 0.20, 0.50, 1.0 and 2.0 A cm⁻² current densities. a) voltage decrease and ASR increase upon introduction of CO₂ into the cathode reacting gas; b) CO₂ emission from the anode (solid lines) and cathode (dotted lines) when 1600 ppm CO₂ is fed to the cathode; c) CO₂ flux fed to the cell and released from the anode (solid lines) and cathode (dotted lines) when 1600 ppm CO₂ is fed to the cathode.
Figure 3.7. Uptake of 3200 ppm CO$_2$ fed to the cathode of H$_2$/O$_2$ AEMFCs operating at 60°C and discharging at 0 (load off), 0.20, 0.50, 1.0 and 2.0 A cm$^{-2}$ current densities. a) voltage decrease and ASR increase upon introduction of CO$_2$ into the cathode reacting gas; b) CO$_2$ emission from the anode (solid lines) and cathode (dotted lines) when 3200 ppm CO$_2$ is fed to the cathode; c) CO$_2$ flux fed to the cell and released from the anode (solid lines) and cathode (dotted lines) when 3200 ppm CO$_2$ is fed to the cathode.
Figure 3.8. Comparison of CO\textsubscript{2} concentration leaving the AEMFC (fed at 400 PPM) when an AEMFC MEA is present and when Teflon is placed between the flowfields with no electrodes.
cannot exist with significant quantities of OH\(^-\) and CO\(_3^{2-}\) due to the equilibrium constraints.

If it is assumed that the ionomeric materials are completely carbonated, then the average charge per CO\(_2\), \(\varepsilon\), can be found by:

\[
\frac{(\phi)\,(38.2)}{(42.8+25.5)} = 1.00
\]

Here, \(\varepsilon = 1.79\), meaning that 79% of the charge groups are in the CO\(_3^{2-}\) form and 21% are in the HCO\(_3^-\) form at open circuit.

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 3.1). To calculate the quantity of carbonate anions in the operating cell at steady state for any operating condition, the number of CO\(_2\) molecules taken up by the cell were quantified. The data in Figure 3.2c and Figures 3.3c-3.7c provide a pathway to do this because it gives the molar flux of CO\(_2\) that is entering the cell when no uptake occurs ("blank"). It also provides the CO\(_2\) flux that is leaving from both the anode and cathode with time until the cell reaches steady state. From this data, the three curves ("blank" vs. time, anode exhaust vs. time, and cathode exhaust vs. time) can be integrated and the total number of moles of CO\(_2\) (\(N_{CO2}\)), and hence \(\text{CO}_3^{2-}\), can be calculated by:

\[
N_{CO2} = \int \text{"blank"(t) dt} - \int \text{"anode exhaust"(t) dt} - \int \text{"cathode exhaust"(t) dt}
\]

From here, the DOC was also calculated from the equation above.

As expected, there was a greater amount of CO\(_3^{2-}\) present in the system with higher concentrations of CO\(_2\) in the cathode stream. It was also found that the total amount of CO\(_3^{2-}\) in the system decreased with increasing current density. The change in the total
number of CO$_3^{2-}$ anions in the system with current density and cathode CO$_2$ concentration clearly explains the trends in the ASR.

Another interesting point in the dataset where it would be informative to know how much carbonate was in the system is after the CO$_2$ was removed from the cathode and the cell has reached the new quasi steady state. Figure 3.11a showed a set of typical carbonation + decarbonation experiments, where the cell was exposed to a known amount of CO$_2$ for 30 min and then the CO$_2$ was removed from the cathode gas stream. Cell decarbonation happened in 2 stages. The first stage was when the cell was operated for 30 min at the same current density. The second stage occurred after this 30 min of operation, when the cell voltage was pulsed down to 0.1 V. Here, the CO$_2$ coming out of the anode came out in a large slug that quickly decayed over 1-2 minutes. After that, the cell voltage was allowed to come back to steady state at the initial operating current and “complete” decarbonation was assumed if the steady state voltage was equal to the pre-CO$_2$ exposed operating voltage.

The amount of carbonate left after the ~10 min new quasi steady state can be found by integrating the area under the slug of CO$_2$ that was measured with time at 0.1V. This calculation was also done for every current density and cathode CO$_2$ concentration and the resulting values are tabulated in Table 3.1. From here, the DOC was calculated from the equation above.

However, one interesting observation was that a plot of the total carbonate in the system vs. the change in the ASR (Figure 3.9) did not yield a single straight line for all conditions, but there were trends as a function of current density and CO$_2$ concentration. To understand this, it should be noted that the HFR measurement by the fuel cell test station is only measuring the two closest points separated by the ionomer; in other words, it is essentially
Table 3.1. Degree of carbonation of operating AEMFCs (AEM+AEI) as a function of current density and CO₂ concentration in the cathode.

<table>
<thead>
<tr>
<th>Current Density (A cm⁻²)</th>
<th>PPM CO₂ in Cathode</th>
<th>Carbonate in AEMFC (umol) during CO₂ exposure</th>
<th>DOC during CO₂ exposure (%)</th>
<th>Carbonate remaining in AEMFC (umol) after CO₂ removed, @ new quasi steady state</th>
<th>DOC, after CO₂ removed, and new quasi steady state established after ~10 min (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>13.5</td>
<td>39.5</td>
<td>5.7</td>
<td>16.6</td>
</tr>
<tr>
<td>1.0</td>
<td>100</td>
<td>4.7</td>
<td>13.9</td>
<td>7.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>11.1</td>
<td>32.4</td>
<td>8.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>18.0</td>
<td>52.8</td>
<td>7.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>28.1</td>
<td>82.2</td>
<td>6.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1600</td>
<td>38.8</td>
<td>113</td>
<td>7.9</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>100</td>
<td>20.7</td>
<td>60.1</td>
<td>10.3</td>
<td>30.0</td>
</tr>
<tr>
<td>0.2</td>
<td>100</td>
<td>25.4</td>
<td>74.4</td>
<td>14.4</td>
<td>41.9</td>
</tr>
<tr>
<td>0.0 (no current)</td>
<td>400</td>
<td>38.2</td>
<td>111</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>
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 (Figure 3.2b), at least at the high flowrates investigated in this work; 2) the decrease in the cell voltage (Figure 3.2a) 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 (Figure 3.2a); 4) the steady-state ASR was realized before the steady-state voltage was achieved and \( \text{CO}_2 \) was measured in the anode effluent (Figure 3.2a and b); 5) the steady-state ASR increased with decreasing current density (Figure 3.2a); 6) increasing current density decreased the amount of \( \text{CO}_3^{2-} \) present in the system at steady-state (Table 3.1); and 7) even at the highest current density and lowest \( \text{CO}_2 \) concentration (2.0 A 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 cm\(^{-2}\) and 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 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 CO₂ concentration in the anode H₂ reacting gas was also 400 ppm. The results of these experiments are shown in Figures 3.2d and e. The first thing that should be noted is that while current was flowing, no measurable CO₂ was ever found leaving the cathode, which can be attributed to the high net anionic flux relative to typical diffusion rates. Simply, CO₃²⁻ cannot diffuse and accumulate to a critical concentration at the cathode faster than migration pushes it to the anode under the conditions tested. Therefore, Figure 3.2d only shows the CO₂ concentration of the anode effluent and Figure 3.2e only shows the anode CO₂ flux. Like the cathode, there was approximately a 45 s lag between the time that CO₂ was turned on and its measurement (Figure 3.3). In this set of experiments, the dynamic CO₂ concentration in the effluent (before steady-state) increased with increasing current density, suggesting lower CO₂ uptake and CO₃²⁻ formation at higher currents. Also, the overall voltage decrease and ASR increase were both lower (but only slightly so) when CO₂ was fed to the anode vs. the cathode, most likely because of reduced carbonation stemming from the direction of ion transport.

3.2 Deconvolution of carbonate-related losses in operating AEMFCs

Though the previous two sections have established some basic parameters for the behavior of CO₃²⁻ 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 and over a wide range of cathode CO₂ concentrations. The response of a steady-state AEMFC operating at 1 A cm⁻² to the introduction of 100, 200, 400, 800, 1600, 3200 ppm CO₂ to the cathode reacting gas is shown in Figure 3.2a, and equivalent data for AEMFCs operating at 0.2, 0.5 and 2.0 A cm⁻² are provided in Figures 3.11a – c. Between each tested CO₂ concentration, the cell was decarbonated as described in the Experimental section. The data shown in Figures 3.10a and 3.11a – c show one hour of AEMFC behavior at each CO₂ concentration – the first 30 min segment shows the carbonation event and the re-establishment of a new steady-state. The second 30 min segment shows the initial response following CO₂ removal (where pure O₂ is again fed).

As discussed earlier, the introduction of CO₂ 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 (ΔASR), increasing the anode charge transfer resistance (ΔRctHOR) and increasing the thermodynamic anode potential (ΔVNernst). The challenge here is to find a systematic way to use the CO₂ exposure and removal data in Figure 3.10a, 3.11 to quantify the contribution of each of these resistances to the total CO₂-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 CO₂ at 1.0 A cm⁻² is given here for illustrative purposes, and then the summary of all the calculated parameters is shown in Figures 3.10b – d.
Figure 3.9. ASR changes vs. quantity of carbonate in the cell as a function of current density and cathode CO2 concentration. As discussed earlier, the fact that these plots do not fall on a single line suggests that more of the carbonates are in the anode electrode than the AEM with increasing current density.
Figure 3.10. Deconvolution of CO\textsubscript{2} overpotential a) Response of an AEMFC operating at 1.0 A cm\textsuperscript{-2} to various concentrations of CO\textsubscript{2} in the cathode reacting gas; b) Summary of the change in the ASR at various current densities and CO\textsubscript{2} concentrations; c) AEMFC anode Nernstian voltage loss as a function of current density; d) Increase in anode charge transfer resistance with increasing CO\textsubscript{2} concentration and decreasing current density. All cells were operated at 60°C with an ETFE-BTMA AEM (IEC = 2.05 ± 0.05 mmol g\textsuperscript{-1}).
Figure 3.11. Response of an AEMFC operating at a) 0.2, b) 0.5 and c) 2.0 A cm$^{-2}$ to various concentrations of CO$_2$ in the cathode reacting gas.
Before adding any CO$_2$ to the AEMFC operating at 1.0 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 Equation 3.1. What this means is that the CO$_2$-free steady-state operating voltage already contains $R_{\Omega,OH}$, $R_{\text{ct,ORR}}$ and $R_{\text{ni,ORR}}$; hence, the deviation of the operating voltage after adding CO$_2$ will only come from $\Delta V_{\text{Nernst}}$, $\Delta ASR$ and $\Delta R_{\text{ct,ORR}}$, as shown in Equation 3.2. After adding 400 ppm CO$_2$ to the cell, the new steady-state voltage that was reached was 0.44 V – meaning that the total CO$_2$ overpotential was ca. 280 mV. While the stoichiometries used in these experiments were high, leading to high CO$_2$ dosages, the observed performance losses (in combination with the total CO$_2$-related overpotential of ~260 mV for a cell operating at 2.0 A cm$^{-2}$ with 400 ppm CO$_2$) suggest that the “self-purging” mechanism has a relatively modest effect in decarbonating the cell, and reducing CO$_2$-related voltage losses to an acceptable level during operation on ambient air will be a significant challenge, and may not be possible at all.

The first CO$_2$-related loss that was calculated was $\Delta ASR$. The ASR as a function of time is shown in Figure 3.2a, and under this operating condition, $\Delta ASR$ was 25 m$\Omega$ cm$^2$. Assuming this $\Delta ASR$ resulted in proportional Ohmic losses, at 1 A/cm$^2$ this would result in an Ohmic loss of 25 mV. For completeness, it is acknowledged 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$^{49,50}$. 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 which remains a small percentage of total overpotential loss (<10%). Perhaps what is most important is that this
observation clearly shows that the ASR change caused by the emergence and transport of \( \text{CO}_3^{2-} \) through the AEM represents a very small portion of the overall \( \text{CO}_2 \) overpotential.

For the AEMFC operating at 1.0 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 \textit{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 re-achieved is for all of the \( \text{CO}_3^{2-} \) to be removed, either by waiting for many hours (Figure 2.1), or by accelerated decarbonation at 0.1 V (Figure 2.2). However, it is important to consider what is happening phenomenologically in the AEMFC. When \( \text{CO}_2 \) is removed from the cathode, no new \( \text{CO}_3^{2-} \) anions are generated at the cathode and the concentration of \( \text{CO}_3^{2-} \) at that electrode drops towards zero as \( \text{OH}^- \) continues to be produced and that 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 Figure 3.10a) 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 \( \text{HOR} \) to occur.

Therefore, the voltage increase during this 10 min establishment of the new quasi steady-state after \( \text{CO}_2 \) removed can be mostly attributed to the relaxation of the kinetic limitations described by \( \Delta R_{\text{HOR}} \) (though the new ASR acting on charge transport needs to
be corrected for as well). At the condition above, 1.0 A cm$^{-2}$ with 400 ppm CO$_2$ in the cathode, $\Delta R_{ctHOR}$ was calculated by Equations 3.3 and 3.4.

$$\Delta V_{ctHOR} (mV) = [0.544 V - 0.443 V] \times 1000 - (1.0 \text{ A cm}^{-2})(83.5 \text{ m}\Omega \text{ cm}^2 - 75.3 \text{ m}\Omega \text{ cm}^2) = 93.7 \text{ mV} \quad (3.3)$$

$$\Delta R_{ctHOR} (m\Omega) = \frac{93.7 \text{ mV}}{(1.0 \text{ A cm}^{-2})(5 \text{ cm}^2)} = 18.7 \text{ m}\Omega \quad (3.4)$$

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 Equations 3.3 and 3.4 are likely a lower limit for $\Delta R_{ctHOR}$, 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 mV - 25 mV - 94 mV = 162 mV). Because the estimate for $\Delta R_{ctHOR}$ is a lower bound, 162 mV is an upper bound for $\Delta V_{Nernst}$, 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 CO$_2$ concentrations can yield values for the total CO$_2$-related overpotential, $\Delta ASR$, $\Delta R_{ctHOR}$, and $\Delta V_{Nernst}$ as well as the Ohmic voltage loss ($\Delta V_{Ohmic}$) and the CO$_2$-related kinetic polarization ($\Delta V_{ctHOR}$) at every condition. All of these values are given in Table 3.2. Performing the data deconvolution over such a wide range of current densities and cathode CO$_2$ concentrations yielded some very revealing trends and important insight into the behavior of carbonated AEMFCs. Not too surprisingly, the total CO$_2$-related overpotential
was increased with decreasing current density and increasing CO₂ concentration in the cathode (Table 3.2). However, understanding why this happened requires digging into the trends in ΔASR, ΔR_{eHOR}, and ΔV_{Nernst} more extensively.

Figure 3.10b presents the ΔASR values at all conditions. As the concentration of CO₂ in the cathode reacting gas was decreased, there less of a negative impact on the ASR. This makes sense from the transient and steady-state experimental results (Table 3.1) which showed that the total amount of CO_3^{2-} in the AEMFC was lower at lower CO₂ concentration in the cathode and increased current density. As discussed earlier, the overall trends in the ASR with current density and cathode CO₂ concentration (Figure 3.11) led to the conclusion that increasing the current density shifts the CO_3^{2-} concentration gradient toward the anode electrode. Hence, with increasing current density, relatively less and less CO_3^{2-} is present in the AEM (though the total CO_3^{2-} flux is higher, Figure 3.2c), resulting in a lower ASR.

The fact that the concentration gradient shifts toward the anode with current density might lead to the assumption that ΔV_{Nernst} (Figure 3.10c) 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 ΔV_{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 CO_3^{2-} concentration, as illustrated in Figure 3.1, and it is possible for that one specific location to be close to saturation over a wide range of conditions. ΔV_{Nernst} appeared to decrease with increasing current density, though the values at current densities ≤ 1.0 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 $\Delta V_{Nernst}$ at the lower current densities, ~165 mV. The effective alkalinity of AEMFC cathode is between pH 13 – 14. It is also known that $\text{CO}_3^{2-}$ is overwhelmingly the dominant carbon-based charge carrier and this can only happen in water at pH values > 11. Therefore, the maximum pH shift that could possibly be expected at the anode in an operating cell would be 3, resulting in a $\Delta V_{Nernst,max}$ of 177 mV. The only data point in Figure 3.10c where $\Delta V_{Nernst}$ is markedly lower is at very high current, 2.0 A cm$^{-2}$, where $\Delta V_{Nernst}$ is ~125 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 OH$^-$ ions being released throughout the anode as CO$_2$ is evolved through the reverse of Equations 1.3-1.4, though the root cause for this behavior will likely need to be teased out through computational modeling. It is also noteworthy that the $\Delta V_{Nernst}$ was completely unaffected by the cathode 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 in $\Delta R_{c\text{HOR}}$, Figure 3.10d. At higher overall carbonate content, increased cathode CO$_2$ concentration and/or lower current density, $\Delta R_{c\text{HOR}}$ was also higher, sharply increasing over the entire scale of tested concentrations. At a constant $\text{CO}_3^{2-}$ concentration (same ppm CO$_2$ in the cathode stream), $\Delta R_{c\text{HOR}}$ actually decreased with increasing current, even though the total amount of carbonate in the anode electrode was higher at higher current. This observation yields important insight into the location of carbonate in electrodes, suggesting that higher current densities compress the volume
Table 3.2. Summary of the CO$_2$-related resistances and overpotentials as a function of current density and cathode CO$_2$ concentration (in O$_2$). The AEMFC was operated at 60°C with an ETFE-BTMA AEM. Gas flowrates were 1 L min$^{-1}$ at both the cathode and anode (H$_2$).

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<th>Total CO$_2$-related overpotential (mV)</th>
<th>∆ASR (mΩ cm$^2$)</th>
<th>R$_{clHOR}$ (mΩ)</th>
<th>∆V$_{Ohmic}$ (mV)</th>
<th>∆V$_{Nernst}$ (mV)</th>
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occupied by carbonates to the outermost portion of the anode, which effectively allows more catalyst sites to have easy access to reacting OH⁻.

3.3 AEMFC response at low CO₂ concentrations

A practical interpretation of the experiments shown in Figure 3.10 is that the polarization losses from AEMFC carbonation are significant at all current densities and near-ambient CO₂ concentrations, and that AEMFCs will likely require pre-scrubbing of CO₂ from the operating air. Additionally, the dynamics of CO₂ uptake (fast) and release (slow) mean that even if CO₂ could be quickly removed from the anode stream to avoid significant accumulation, losses would still be high. One sensible approach to reducing CO₂-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 CO₂ scrubber is less of a concern than it is for mobile or transportation applications. Figure 3.12a explores the response of an AEMFC operating at 1 A cm⁻² with 5 – 50 ppm CO₂ in the cathode reacting gas. Though the voltage loss was less than at higher concentrations, even down to 5 – 10 ppm CO₂ in the cathode the CO₂-related polarization was significant, approximately 140 mV.

Figure 3.12b shows the response of an AEMFC operating at 1 A cm⁻² with 5 – 50 ppm CO₂ added to the anode H₂ reacting gas. The behavior of low-level CO₂ in the anode is very similar to the cathode; at 10 ppm, the total CO₂-related voltage loss was 136 mV. For CO₂ present in both the cathode and anode, Figure 3.12 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).
3.4 Influence of temperature on CO$_2$-related polarization losses at 400 ppm

Figure 3.12 showed that simply removing a portion of the CO$_2$ in ambient air will not be sufficient to eliminate the CO$_2$-related losses in operating AEMFCs. In fact, the above work demonstrated that even at 5 ppm CO$_2$ significant performance losses occurred. Therefore, it is important for researchers to identify other fundamental and operational properties of the system that can be manipulated to reduce the AEMFC sensitivity to CO$_2$. One pathway to reducing the amount of carbonate accumulated in the system is to increase the cell operating temperature. Increasing temperature would have several positive impacts on carbonate: i) CO$_2$ has lower solubility in water as the temperature is increased;\textsuperscript{57} ii) the kinetics for CO$_2$ release (reverse of Equations 1.3 and 1.4) at the anode will improve; iii) the mass transport rate of evolved gaseous CO$_2$ from the anode will increase; and iv) the intrinsic kinetics for the ORR and HOR will improve.

Figure 3.13 summarizes the response of AEMFCs with a LDPE-BTMA membrane operating at 0.2, 0.5, 1.0 and 2.0 A cm$^{-2}$ and several temperatures (60, 65, 70, 75, 80 °C) following the introduction of 400 ppm CO$_2$ to the cathode and anode. Regardless of where the CO$_2$ was introduced, increasing the temperature simultaneously decreased the total CO$_2$ overpotential and the ASR (Figures 3.13a – 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\textsuperscript{33}. One possible explanation for the increased performance is that less CO$_2$ was apparently taken up into the system. Figure 3.13b shows that the concentration of CO$_2$ being emitted from the anode side of the cell decreased with increasing temperature. At steady-state, this means that less CO$_2$ was absorbed at the cathode. Figure 3.13d shows that when CO$_2$ was fed to the anode, increasing the
Figure 3.12. Exploring the existence of a lower threshold concentration for CO₂ present in the a) cathode and b) anode compartments. The AEMFCs were operated at an operating current density of 1.0 A cm⁻² at 60 °C with the ETFE-BTMA AEM.
temperature resulted in lower CO₂ uptake at that electrode as well, which is shown by the increasing concentration of CO₂ in the anode effluent. It should also be noted in Figures 3.13b 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 CO₂ tolerance of operating AEMFCs; however, the CO₂-related overpotential is still too high for many practical applications. A combination of lower CO₂ concentration, more modest air stoichiometry, and elevated temperature can further reduce the total CO₂ overpotential. For instance, it was observed that an AEMFC operating at 1 A cm⁻² and 80°C with 10 ppm CO₂ fed to the cathode (the same LDPE-BTMA membrane) had a total CO₂ overpotential of only 90 mV.

Deconvoluted data for AEMFCs operating at different temperatures but at a constant current of 1 A cm⁻² and constant cathode CO₂ concentration of 400 ppm to find ΔASR, ΔV_{Nernst} and ΔR_{cHOR} can be found in Table 3.3. 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 CO₃²⁻ anions were carrying the charge through the AEM, supported by the results of accelerated decarbonation experiments at 0.1 V as Table 3.4, which led ΔR_{cHOR} to be fairly constant with temperature as well. Therefore, the primary impact of an overall reduced number of CO₃²⁻ 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, ΔV_{Nernst} was the most dependent on temperature, decreasing by nearly 50% from 60 – 80 °C.
Figure 3.13. Impact of temperature on the total CO$_2$-related overpotential, HFR and anode CO$_2$ exhaust with 400 ppm CO$_2$ fed to the cathode at multiple current densities. Total CO$_2$ overpotential (solid lines) and ASR (dashed lines) when CO$_2$ was fed to the a) cathode and c) anode. CO$_2$ concentration in the anode effluent when CO$_2$ was fed to the b) cathode and d) anode. An LDPE-BTMA AEM (IEC = 2.5 mmol g$^{-1}$) was used in these experiments.
Table 3.3. Calculated values for $\Delta$ASR, $\Delta$V\textsubscript{Nernst} and $R_{ctHOR}$ as a function of operating temperature for AEMFCs operating at a constant current of 1 A cm$^{-2}$ and constant cathode CO$_2$ concentration of 400 PPM. It should be noted that the membrane here was LDPE-BTMA, so the absolute values can’t really be compared with Table 3.2, but can be inter-compared to determine the impact of temperature on the behavior.

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>$\Delta$ASR (m$\Omega$ cm$^2$)</th>
<th>$\Delta$V\textsubscript{Ohmic} (mV)</th>
<th>$\Delta$V\textsubscript{Nernst} (mV)</th>
<th>$R_{ctHOR}$ ((\Omega))</th>
<th>$V_{ctHOR}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>22.6</td>
<td>22.6</td>
<td>226</td>
<td>17.0</td>
<td>84.8</td>
</tr>
<tr>
<td>65</td>
<td>17.6</td>
<td>17.6</td>
<td>177</td>
<td>18.0</td>
<td>90.2</td>
</tr>
<tr>
<td>70</td>
<td>16.9</td>
<td>16.9</td>
<td>150</td>
<td>18.2</td>
<td>91.1</td>
</tr>
<tr>
<td>75</td>
<td>18.2</td>
<td>18.2</td>
<td>134</td>
<td>17.7</td>
<td>88.5</td>
</tr>
<tr>
<td>80</td>
<td>15.9</td>
<td>15.9</td>
<td>113</td>
<td>17.2</td>
<td>85.9</td>
</tr>
</tbody>
</table>
Table 3.4. Degree of carbonation (AEM+AEI) as a function of temperature for AEMFCs with LDPE AEM operating at 1 A cm$^{-2}$ and constant cathode CO$_2$ concentration of 400 ppm.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>60</th>
<th>65</th>
<th>70</th>
<th>75</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonate in AEMFC (µmol)</td>
<td>17.87</td>
<td>12.44</td>
<td>12.41</td>
<td>11.51</td>
<td>11.37</td>
</tr>
<tr>
<td>Degree of Carbonation, DOC (%)</td>
<td>33.98</td>
<td>23.66</td>
<td>23.60</td>
<td>21.88</td>
<td>21.61</td>
</tr>
</tbody>
</table>
In summary, with regards to temperature, 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, though there is promising work ongoing in this area. What this really points to is that improving the CO₂ tolerance of AEMFCs will 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.

3.5 Influence of flowrate on AEMFC performance with 400 ppm cathode CO₂

Research about the effect of reacting gases flowrate is rare. Gerhardt et al. modeled the carbonation behavior along the flow channel as changing flow type and flow rate, and found that an optimum flow rate existed to balance oxygen transport loss with CO₂ related performance loss.

The effect of oxygen gas flowrate on the behavior of a carbonated AEMFC is shown in Figure 3.14. As shown in Figure 3.14a, the CO₂ overpotential increased (approximately linearly) with the increasing O₂ flow rate, showing that the total dosing of the cell by CO₂ plays an important role in carbonation. Hence, the carbonate concentration inside of operating cells is clearly increased with increased oxidant flowrate. Table 3.5 shows the carbonation degree of fuel cell at different cathode flow rates; the calculation follows the procedure described in Chapter 3.1. The rate of carbonate removal from the cell as CO₂ also increased with increasing cathode flowrate, Figures 3.14b and 3.14c. Likely due to the higher concentration in the cell, increasing cathode flow rate also led to a shorter breakthrough time at anode exhaust. This makes sense because the driving force for CO₂ release is the accumulation of carbonate in the cell, which eventually leads to the
thermodynamic shift from $\text{CO}_3^{2-}$ to $\text{HCO}_3^-$ and then $\text{CO}_2$ as the concentration in the anode increases. Also interesting, Figure 3.14b shows that AEM-like devices can also act as $\text{CO}_2$-separators that also simultaneously generate, not consume, power. Figure 3.14d shows the deconvolution of the $\text{CO}_2$-related polarization losses with changing cathode flowrates. It was found that lowering the oxygen flowrate did not appreciably impact the Nernst loss. What this shows is that the outermost part of the anode remains nearly saturated at all flowrate. The most severe increase is in the charge transfer resistance. The kinetic resistance increases with increasing flowrate at the same Nernst loss showing that the overall carbonate content of the anode is higher in this case (Table 3.5); hence at higher flowrate, more of the anode is “shut off” by carbonation – leading to higher voltage losses.

Interestingly, when both flowrates are lowered equally, the dosing and removal track very well shown as Figure 3.15. Lower flowrates have higher overpotentials, even when the amount of carbonate in the cell is similar at steady state, suggesting the carbonation is slower than the removal rate at higher flowrates. Also seen in Table 3.6, the rate of carbonate “decomposition” to $\text{CO}_2$ (the “removal amount”) is a function of anode flowrate (removing gas flowrate). As flowrates increase, fuel cell system takes in more $\text{CO}_2$ (hence the $\text{R}_{\text{chHOR}}$ goes up) but there is less carbonate in the anode due to an increase in the rate of $\text{CO}_2$ removal. The Nernstian voltage loss is increasing as decreasing of both flowrates.

The effect of hydrogen gas flowrate on the behavior of a carbonated AEMFC is shown in Figure 3.16. In general, the anode flowrate did not have a severe an impact on carbonation as the cathode flowrate. Figure 3.16a shows that the $\text{CO}_2$ overpotential increased with the decreasing $\text{H}_2$ flowrate. This was not due to a significant increase in the amount of carbonate in the membrane, as evidenced by the similar HFR for all cases and
the total cell carbonation being similar (Table 3.7). This suggests that the main reason for increased polarization is increased carbonate concentration in the anode, particularly right at the anode/GDL interface, which is evidenced by larger Nerstian losses at lower flowrates.

An additional observation was that as the anode flowrate was decreased, the anode exhaust concentration increased. In fact, it was possible for the concentration of CO2 in the exhaust to be significantly higher than the cathode feed, showing that these devices can also be CO2 concentrators. The cathode exhaust nearly always contains 200 ppm CO2 regardless of the H2 flowrate, showing that the extent of carbonation near the cathode is very low, in fact suggesting that the cathode likely sees no resistance to CO2 uptake and carbonate formation.

3.6 Effect of hydration on AEMFC performance with 400 ppm cathode CO2

Next, the effect of water on carbonation was studied by increasing the dew points of the anode and cathode reacting gases. The results are shown in Figure 3.17. As the dew points for the reacting gases fed to the anode and cathode were increased, the hydration level of the AEMFC also increases. This led to a reduced effect of CO2 poisoning on cell performance, meaning that the magnitude of the CO2 overpotential and HFR decreased as the dew points were increased, Figure 3.17a. Interestingly, as the dew points were increased, the concentration of CO2 in the anode exhaust decreased while the concentration leaving the cathode increased, Figure 3.17b. This suggests that increasing the amount of free water in the cell prevents CO2 uptake in the cathode. As the amount of free water increases, the degree of carbonation of the polymer decreases, though the total amount of carbonate in the cells is approximately the same. This suggests that some of the CO2/carbonate is actually present in the liquid water phase and not in the polymer. However, there is a
Figure 3.14 Flowrate effect on carbonation of AEMFC: change of O$_2$ flowrate. AEMFC operating at 1 A/cm$^2$ and 60 °C with 25 um LDPE AEM, 400 ppm CO$_2$ was fed to cathode, using O$_2$ flowrate of 0.2, 0.4, 0.6, 0.8, 1 L/min, constant 1 L/min H$_2$ a) voltage loss and HFR increase as the introduction of CO$_2$, b) CO$_2$ emission from the anode (solid lines) and cathode (dotted lines), c) CO$_2$ flux, d) deconvolution of O$_2$ flowrate effect on CO$_2$ related voltage loss.
Table 3.5 Degree of carbonation as function of cathode flowrate feeding with 400 ppm CO₂.

<table>
<thead>
<tr>
<th></th>
<th>1/1</th>
<th>1/0.8</th>
<th>1/0.6</th>
<th>1/0.4</th>
<th>1/0.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>[carbonate] in FC /μmol</td>
<td>20.8</td>
<td>17.0</td>
<td>13.3</td>
<td>8.3</td>
<td>3.9</td>
</tr>
<tr>
<td>Remaining [carbonate] in FC /μmol</td>
<td>7.8</td>
<td>7.4</td>
<td>7.2</td>
<td>7.5</td>
<td>7.6</td>
</tr>
<tr>
<td>Removal /μmol</td>
<td>13</td>
<td>9.6</td>
<td>6.1</td>
<td>0.8</td>
<td>/</td>
</tr>
</tbody>
</table>
Figure 3.15 Flowrate effect on carbonation of AEMFC: change of H$_2$ and O$_2$ at the same flowrate. AEMFC operating at 1 A/cm$^2$ and 60$^\circ$C with 25 um LDPE AEM, 400 ppm CO$_2$ was fed to cathode, using H$_2$/O$_2$ flowrate of 0.4, 0.6, 0.8 L/min a) voltage loss and HFR increase as the introduction of CO$_2$, b) CO$_2$ emission from the anode (solid lines) and cathode (dotted lines), c) CO$_2$ flux, d) deconvolution of reactant gases flowrates effect on CO$_2$ related voltage loss.
Table 3.6 Degree of carbonation as function of anode/cathode flowrate feeding with 400 ppm CO₂.

<table>
<thead>
<tr>
<th></th>
<th>0.8/0.8</th>
<th>0.6/0.6</th>
<th>0.4/0.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>[carbonate] in FC/umol</td>
<td>14.5</td>
<td>13.9</td>
<td>14.7</td>
</tr>
<tr>
<td>Remaining [carbonate] in FC/umol</td>
<td>7.5</td>
<td>9.3</td>
<td>10.7</td>
</tr>
<tr>
<td>Removal /umol</td>
<td>7</td>
<td>4.6</td>
<td>4</td>
</tr>
</tbody>
</table>
Figure 3.16 Flow rate effect on carbonation of AEMFC: change of H$_2$ flow rate. AEMFC operating at 1 A/cm$^2$ and 60 $^\circ$C with 25 um LDPE AEM, 400 ppm CO$_2$ was fed to cathode, using H$_2$ flow rate of 0.2, 0.4, 0.6, 0.8, 1 L/min, constant 1 L/min O$_2$ a) dynamic voltage and HFR change, b) CO$_2$ emission from the anode (solid lines) and cathode (dotted lines), c) CO$_2$ flux, d) deconvolution of H$_2$ flow rate effect on CO$_2$ related voltage loss.
Table 3.7 Degree of carbonation as function of anode flowrate feeding with 400 ppm CO₂.

<table>
<thead>
<tr>
<th></th>
<th>1 /1</th>
<th>0.8/1</th>
<th>0.6/1</th>
<th>0.4/1</th>
<th>0.2/1</th>
</tr>
</thead>
<tbody>
<tr>
<td>[carbonate] in FC /umol</td>
<td>19</td>
<td>20</td>
<td>20</td>
<td>27</td>
<td>24</td>
</tr>
<tr>
<td>Remaining [carbonate] in FC /umol</td>
<td>11</td>
<td>11</td>
<td>14</td>
<td>14</td>
<td>18</td>
</tr>
</tbody>
</table>
Figure 3.17 Dew point effect on carbonation of AEMFC. AEMFC operating at 1 A/cm² and 60 °C with 25 um ETFE AEM, 400 ppm CO₂ was fed to cathode, increasing the dew points of electrodes a) voltage loss and HFR increase as function of dew points (anode/cathode), b) CO₂ emission from the anode (solid lines) and cathode (dotted lines), and c) CO₂ flux.
Table 3.8 Degree of carbonation as a function of fuel cell hydration states (dew points).

<table>
<thead>
<tr>
<th></th>
<th>50/52</th>
<th>51/53</th>
<th>52/54</th>
<th>53/55</th>
<th>54/56</th>
<th>55/57</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ overpotential</td>
<td>0.277</td>
<td>0.277</td>
<td>0.272</td>
<td>0.261</td>
<td>0.244</td>
<td>0.151</td>
</tr>
<tr>
<td>(V)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>△HFR / mOhm</td>
<td>4.73</td>
<td>4.43</td>
<td>4.37</td>
<td>4.21</td>
<td>3.72</td>
<td>2.66</td>
</tr>
<tr>
<td>[carbonate] in FC</td>
<td>16.6</td>
<td>16.3</td>
<td>13.9</td>
<td>18.3</td>
<td>15.3</td>
<td>16.6</td>
</tr>
<tr>
<td>/umol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Remaining [carbonate] in FC</td>
<td>16.4</td>
<td>15.9</td>
<td>17.1</td>
<td>17.7</td>
<td>17.3</td>
<td>12.1</td>
</tr>
<tr>
<td>/umol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
tradeoff here where very high hydration levels do lead to anode flooding and reduced overall cell performance, which presents itself as fluctuations in the cell voltage for dew points of 55 °C cathode of 57 °C in Figure 3.17. Therefore, it is important to find ways to operate AEMFCs at high hydration levels and avoid electrode flooding.

3.7 Comparison between model prediction and experimental data

In the literature, there have been a few theoretical models proposed that aim to capture the dynamics of AEMFC carbonation. For instance, Shiau et al.\textsuperscript{30} rightfully predicted that as the current increases, the flux of CO\textsubscript{2} from the anode outlet increases, which means that less CO\textsubscript{2} might be accumulated in the AEM; suggesting that carbonate buildup will minimize the purging effect. Setzler et al.\textsuperscript{60} simulated that a dynamic pH gradient profile through the MEA would occur when 400 ppm CO\textsubscript{2} fed to cathode. It showed a steep pH gradient from 9.5-13 crossing AEMFC, and the gradient flattens when low current density was applied. It was only when the anode reaches the lowest pH’s that CO\textsubscript{2} is evolved into the anode, explaining the lag in time from the feed of CO\textsubscript{2} to its detection in Figures 3.2-3.7. Also, increasing cathode or reducing anode flowrate was predicted to increase the level of cell carbonation, in agreement with this thesis. One prediction that has not been yet validated experimentally is AEMFC behavior at very low concentration; Setzler found that even 0.1 PPM CO\textsubscript{2} results in 10 mV performance loss at steady state, 3 ppm CO\textsubscript{2} caused ca. 50mV loss which is close to our experimental results. Finally, Gerhardt et al.\textsuperscript{59} suggested two main reasons for voltage loss – the thermodynamic and anode kinetic overpotentials which were verified by our experimental data. Some models are not consistent with our experiment data. For instance, Krewer et al.\textsuperscript{33} modeled that increasing cell temperature does not have a beneficial effect on the carbonation process which we had
the opposite conclusion. However, one limitation of nearly all computation models regarding CO₂ in the literature is that they have not been experimentally validated. It is suggested that the modeling and experimental groups combine forces, which can yield new insights into this issue that is critically important for AEMFCs.
Chapter 4

Conclusions

Even in highly performing AEMFCs, the addition of CO$_2$ has a severe negative impact, where the cell operating voltage is generally decreased by 200 – 500 mV depending on the reaction conditions. Lower CO$_2$ concentration in the reacting gas, higher current density and higher operating temperature all reduce the voltage penalty, but none have been shown be able to sufficiently minimize the CO$_2$ impact. This experimental work, the first of its kind to systematically investigate carbonation and to deconvolute the root causes for performance decline, has provided new insight into the dynamics of CO$_2$ and CO$_3^{2-}$ in operating AEMFCs.

The formation of carbonates in the AEMFC occurs very quickly and in quasi-equilibrium with the reacting gas in the cathode. Decarbonation of the cell does not occur through direct electrochemical reaction under typical operating conditions – and is hence very slow; however, it is likely that carbonates do directly react with H$_2$ in the anode at very low voltages/very high anode potentials, which can allow for rapid cell decarbonation by pulsing away from typical operating conditions (e.g. 0.1 V or short-circuiting the cell). by diffusion toward the anode reacting gas. Therefore, decarbonation during operation by the so-called “self-purging” mechanism is slow, taking several hours even after only
transient exposure to CO₂. Hence, “self-purging” cannot be relied upon to decarbonate a real system efficiently. Also, although pulsing to low operating voltages can be used for decarbonation, it most likely cannot be practically applied to engineered fuel cell stacks where some individual cells would experience negative voltages. The dominating loss in operating AEMFCs in the presence of CO₂ 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⁻ anions. The CO₂ concentration in the cathode and the current density are both determining factors for the quantity of CO₃²⁻ in the system, and the current density appears to play a primary role in dictating the CO₃²⁻ location and distribution. The HOR charge transfer resistance increases markedly with both increased CO₂ 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 CO₂-related overpotential can be reduced by increasing the temperature – or better yet, through a combination of higher current density, lower CO₂ concentration and higher operating temperature.

With constant 400 ppm CO₂ fed to cathode stream, CO₂ overpotential linearly increases with increasing O₂ flowrate, while decreasing with H₂ flow rate. The carbonation degree of the fuel cell is clearly increased with increased oxidant flowrate. It provides evidence that AEM-like devices can also act as CO₂ separators that simultaneously generate power. CO₂ concentration in the anode exhaust increases with decreasing H₂ flowrate, though the
flux was unchanged, suggesting a CO₂ concentrator application. Digging into the fundamental mechanisms of CO₂-related performance loss, Nernstian change dominates, and is not affected by flow rates. Kinetic resistance increases as increasing O₂ flowrate, decreasing H₂ flowrate. Ohmic resistance increases as reacting gas flow increases. Last but not least, increasing AEMFC hydration decrease CO₂-related losses.

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.
References


52 B. Kienitz, Case Western Reserve University, 2009.


