PERFORMANCE, DURABILITY, AND MODELING OF
HYDROXIDE EXCHANGE MEMBRANE FUEL CELLS

by

Robert B. Kaspar

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering

Fall 2015

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ABSTRACT

2015 marks the first year in which U.S. consumers can buy fuel cell cars like the Toyota Mirai. Instead of combustion engines, these cars are powered by proton exchange membrane fuel cells (PEMFCs), electrochemical devices that convert hydrogen and air directly into electricity and water. Unfortunately, PEMFCs’ reliance on scarce platinum catalyst may preclude the mass production of fuel cell vehicles.

Hydroxide exchange membrane fuel cells (HEMFCs) are an emerging alternative to PEMFCs. Their high-pH operating conditions intrinsically support earth-abundant catalysts like nickel and silver. But at present, HEMFCs perform worse than PEMFCs and their durability is not well understood. In this work, membrane-electrode assemblies (MEAs), the core of a fuel cell, are manufactured with a robotic sprayer. This reproducible, high-volume fabrication process serves as a platform for investigating fuel cell performance and durability, with support from analytical and numerical models.

To study performance, HEMFCs’ distinctive water transport behavior is modeled for the first time. Wetproofing, a common technique for keeping liquid water out of PEMFC electrodes, is shown to make flooding worse in HEMFCs. Electrode patterning is proposed as an unconventional approach to level out the cell water distribution.

To study durability, a degradation mode already known to corrode the PEMFC cathode during device startup and shutdown is identified for the first time in HEMFCs. Anodes made with ruthenium (instead of platinum) significantly resist this corrosion; non-precious-metal catalysts like nickel could provide near-immunity.

Future directions include designing highly porous gas diffusion architectures and screening anode catalysts with low oxygen reduction activity. More broadly, the priority in this field should be to develop novel materials: thermally resistant electrolytes and active, oxidation-resistant, reaction-specific catalysts.
GLOSSARY

AFC  Liquid alkaline fuel cell
CCG  Catalyst-coated gas diffusion layer
CCM  Catalyst-coated membrane
CL   Catalyst layer, where chemical reactions occur in a fuel cell
COR  Carbon oxidation reaction (typically at the cathode)
CV   Cyclic voltammetry, an electrochemical characterization technique
EDS  Energy-dispersive X-ray spectroscopy
GDL  Gas diffusion layer, part of the fuel cell sandwich
HOR  Hydrogen oxidation reaction (at the anode)
Hydroxide cell  Short for “hydroxide exchange membrane fuel cell”
IR   Internal (ohmic) resistance, generally from the electrolyte
MEA  Membrane-electrode assembly, the core of a fuel cell
MPL  Microporous layer, an optional GDL component
OCV  Open-circuit voltage, the resting state of a fuel cell
ODE  Ordinary differential equation
OER  Oxygen evolution reaction, ORR in reverse
ORR  Oxygen reduction reaction (at the cathode)
PPD  Peak power density, a measure of cell performance
Proton cell  Short for “proton exchange membrane fuel cell”
PTFE Poly(tetrafluoroethylene) (trade name Teflon)
RCD  Reverse-current decay, a fuel cell degradation mechanism
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<td>SEM</td>
<td>Scanning electron microscopy</td>
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<td>SGL</td>
<td>SGL Carbon, a German GDL manufacturer</td>
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<td>SHE</td>
<td>Standard hydrogen electrode, the benchmark reference electrode</td>
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<td>TKK</td>
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Chapter 1

INTRODUCTION

1.1 Motivation

This work is a comparison of two types of fuel cells: proton exchange membrane fuel cells (commonly abbreviated “PEMFCs”), and hydroxide exchange membrane fuel cells (sometimes referred to as “alkaline anion exchange membrane fuel cells” or similar\(^1\)). Here, these two devices will be called simply “proton” and “hydroxide” fuel cells.

Proton cells have already shown high performance and acceptable durability but their dependence on scarce catalysts like Pt may prove unsustainable in mass production. As an emerging alternative technology, the hydroxide cell shows increasingly competitive performance\(^2\textsuperscript{-}^5\) and supports earth-abundant catalysts like Ni and Ag\(^6\textsuperscript{,}^7\) as well as cheap, non-fluorinated electrolytes\(^8\textsuperscript{,}^9\).

This year, Toyota releases its first hydrogen fuel cell car the Mirai on the U.S. consumer market, and other major manufacturers prepare to follow suit. These first-generation vehicles are based on proton cells. While it remains uncertain whether fuel cells will overtake pre-existing battery technologies (e.g., Tesla’s), this investment by auto manufacturers provides a clear reason to study the hydroxide cell as a candidate for an inexpensive, sustainable second- or third-generation device.

1.2 Fundamentals of Low-Temperature Hydrogen Fuel Cells

All fuel cells share three components: an anode, an electrolyte, and a cathode. On the anode, a chemical reaction consumes fuel and produces electrons at low potential. Since the electrolyte does not conduct electrons, they are forced outside the cell where they must flow through an external circuit in order to reach the high-potential
cathode. This electron flow provides electrical power. Simultaneously, on the cathode, a chemical reaction consumes the electrons and an oxidant, typically air.

Unbalanced production or consumption of electrons at either electrode, as described above, would lead to unphysical accumulation of charge during steady-state operation. Thus, in addition to electrons, ions are produced at one electrode, migrate through the electrolyte, and are consumed at the other electrode. The direction of flow depends on whether these ions are positively or negatively charged. Together, the external electron path and this internal ion path form a complete, charge-balanced electrochemical circuit.

Beyond these fundamental similarities, differences between the dozens of types of fuel cells can include fuel, oxidant, catalyst, electrolyte, and operating temperature. Proton and hydroxide fuel cells, juxtaposed schematically in Figure 1.1, are remarkably similar in that they differ only by electrolyte.\(^a\) Both consume hydrogen and oxygen, produce water, and operate at low temperature (50-80 °C). In fact, with the same test procedures, fabrication methods, and materials (except for the electrolyte) that have already been developed and optimized for proton cells, a hydroxide cell will function and even show reasonable performance.

However, the choice of electrolyte is still extremely important. Ultimately, it leads to divergence in every aspect of fuel cell behavior, as described in the remainder of this chapter.

1.2.1 Electrolytes

Electrolytes conduct ions. The simplest electrolyte is an aqueous salt solution. Indeed, liquid alkaline fuel cells (AFCs), which can be thought of as an early version of hydroxide cells, utilize concentrated KOH to transport OH\(^-\) from cathode to anode. Under ideal conditions AFCs can be more efficient than any other fuel cell. But when the liquid electrolyte is exposed to CO\(_2\) (\(e.g.\) from the air that flows through the cathode). This assumes that Pt is the desired catalyst. Much of the appeal of hydroxide cells is that Pt is an option rather than a requirement.
Figure 1.1: Schematic comparison of (a) proton and (b) hydroxide fuel cells. The gray region is the anode; white, electrolyte; pink, cathode. See Figure 1.6 for balanced chemical equations.

The cathode during operation), $K_2CO_3$ forms and precipitates, thereby both depleting KOH and physically blocking gas diffusion pathways in the electrodes. This degradation by terrestrial CO$_2$ has largely confined AFCs to niche applications in controlled environments, such as on space shuttles during the 20th century.

By contrast, the class of electrolytes on which proton and hydroxide cells are based is much more resilient toward carbonation. These solid-polymer electrolytes (“polyelectrolytes”) generally have two components: an inert backbone for structural support, and a functional salt$^b$ attached to the backbone for ion conduction (Fig. 1.2). The salt dissociates in water to leave one charged moiety bound to the backbone and a

\[ -NMe_3^+HCO_3^- \]

$^b$ “Salt” here is meant in the broad sense of a molecule with an ionic bond that dissociates to some extent in water. More precisely, in a proton cell the functional group is a solid acid; in a hydroxide cell, a solid base. But in hydroxide cells, particularly while the device is not operating, atmospheric CO$_2$ can convert the base into a carbonate or bicarbonate salt such as $-NMe_3^+$ HCO$_3^-$. 

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second oppositely charged moiety freely mobile (but still subject to the overall system constraint of electroneutrality). The mobile counterion should have the same charge as the species to be conducted; ideally, they are the same ion.

For example, to transport OH$^-$ in a hydroxide cell, instead of liquid K$^+$ OH$^-$ the electrolyte might consist of a solid poly(sulfone) backbone modified with quaternary ammonium groups (e.g., $-\text{NMe}_3^+$ OH$^-$). Attaching the cations to a polymer matrix in this fashion both slows diffusion of CO$_2$ into the electrolyte and renders any subsequent carbonation reversible. No precipitate forms since the electrolyte is already a solid, and any conversion of OH$^-$ counterions to HCO$_3^-$ will ultimately be undone at high current density once the cathode generates sufficient OH$^-$ replacements (a phenomenon known as self-purging).

In contrast with the preceding examples of anion conductors, the archetypal polymer electrolytes are perfluorosulfonic acid cation conductors, in particular Nafion, whose discovery in the 1960s revolutionized applied electrochemistry and spurred interest in fuel cells in particular. Half a century later, it remains the state of the art for proton fuel cells. Nafion consists of a PTFE backbone and pendant $-\text{SO}_3^-\text{H}^+$ groups
Figure 1.3: Chemical structure of Nafion. As drawn, the H$^+$ counterion is bound to the sulfonate group.

(Fig. 1.3), which conduct H$^+$ from anode to cathode in a proton cell. In brief: Nafion's combination of hydrophobic backbone and hydrophilic pendant group limits water swelling without sacrificing ion conductivity. At present there is no equivalent anion conductor that can match Nafion's performance and stability. (This is an area of active research.) However, Nafion is expensive and shows high gas permeability compared to non-fluorinated polymer membranes.

To explain why gas permeability matters in fuel cells, the role of the electrolyte must be described in more detail. In fact, a proton or hydroxide cell contains two different polymer electrolytes.

The first type of electrolyte, the membrane, is sometimes called the bulk electrolyte because of its position at the center of the cell and its high thickness (typically 10-50 µm). Its purpose is not only to conduct ions as described above, but also to physically separate the anode and cathode compartments. An excessively permeable membrane can impact both the lifetime and performance of the cell. When H$_2$ mixes with O$_2$ it is likely to combust, destroying the cell and posing an obvious hazard. More subtly, crossover is the first of four ways in which cell voltage – the primary indicator of fuel cell performance for a given current density – can be lost (Fig. 1.4).

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The hydroxide-conducting electrolytes we employ in this work are proprietary (Tokuyama, Inc.); their chemical structure will not be disclosed or discussed here.
Specifically, a molecule of H$_2$ that crosses the membrane effectively shorts the electrodes by bypassing the usual electrochemical circuit. Its electrons are harvested on the cathode where they immediately reduce oxygen, generating heat instead of useful work. This crossover can be mitigated by switching to a thicker membrane. But since ionic resistance, like electrical resistance, is proportional to thickness, according to Ohm’s law a thicker membrane will yield more voltage losses (the third mechanism depicted in Fig. 1.4). Thus, membrane thickness represents a key performance tradeoff between crossover losses and ohmic losses (not to mention cost and durability).

The second type of electrolyte in a fuel cell is the ionomer. The chief purpose

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$^d$ A related mechanism is true electronic shorting, which arises because the membrane has a finite electrical conductivity. Normally gas crossover is more significant, particularly when the cell is operated at elevated pressure (as in part of this work).

$^e$ Ohmic losses in a fuel cell can also result from electrical resistance, since electrons must travel through the catalyst layer and current collector before leaving/entering the device. Generally electrical conductivity is high enough that these losses are negligible, and in fact, some in-situ measurement techniques are only capable of detecting resistance between the electrodes (i.e., membrane resistance and membrane-electrode interfacial resistance). However, electrode degradation can lead to significant electrical resistance, as will be discussed in Chapter 5.
of the ionomer is, again, to conduct ions, but it also acts as a binder to hold catalyst particles together. Technically it is possible to construct a cell without an ionomer, relying on the membrane alone as electrolyte, but as will be shown in Chapter 3 the performance of such a cell suffers greatly. The reason a second electrolyte is needed is that the hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR) only occur on the “triple-phase boundary” where the following phases meet: gas pores (to supply reactants), electrolyte (to supply/remove ions), and catalyst (to supply/remove electrons and provide a surface on which the reaction can occur more quickly). With only a membrane pressed against an electrode (to form a “membrane-electrode assembly”, or MEA), the contact between the electrolyte phase (membrane) and the gas & catalyst phases (electrode) is limited to the geometric area of their interface. There are no ionic channels in the electrode, so regardless of the total electrode thickness only the top layer is active; the catalyst is under-utilized. To activate more of the electrode, ionomer is mixed into the catalyst ink before MEA fabrication. The result is increased penetration of ionic connections into the electrode, a larger triple-phase boundary, and higher cell performance.

1.2.2 Catalysts

The most popular hydrogen fuel cell catalyst is active metal nanoparticles (∼10 nm) supported on inactive carbon nanoparticles (∼100 nm). The C support separates the smaller metal particles, maximizing their exposed surface area while still providing electrical connectivity.

The electrolyte governs which active metals may be used. Proton conductors like Nafion (as in a proton cell) are effectively\(^\dagger\) acidic, while hydroxide conductors (in

\(^\dagger\) This qualification is important because pH is undefined for solids. The protons bound to Nafion are less available for chemical reaction than those of a free liquid acid. However, the analogy is still valid, particularly at high current when many high-energy ions are flowing through the cell. Concentrated acid (or base, for hydroxide cells) is a popular model of the cell environment for ex-situ durability testing.
a hydroxide cell) are effectively basic. Non-precious metals tend to corrode in acid, so the basicity of a hydroxide cell offers more flexibility in choosing a catalyst.

Quantitatively: whether a metal M will oxidize at a given potential $E$ depends on the standard electrode potential $E^\circ$ of its first oxidation reaction (e.g., $M \rightarrow M^{n+} + ne^-$. If $E > E^\circ$, M will eventually oxidize (and subsequently dissolve); according to the Tafel equation, the greater this “overpotential”, the exponentially faster the oxidation. The relevance of pH is that it changes $E$. Take for example HOR on Pt, as in a fuel cell anode. At pH 0, $E \equiv 0$ V vs. the standard hydrogen reference electrode (SHE). But for every unit of pH increase, $E$ drops by ca. 59 mV. Thus, the overpotential that drives oxidation of the anode catalyst is 827 mV lower at pH 14 than at pH 0. The upshot is that there are many anode catalysts – and similarly, many cathode catalysts – to choose from for hydroxide cells (Fig. 1.5). By contrast, Pt and its alloys are virtually the only catalysts used in both electrodes for proton cells.

Compared to the HOR catalyst on the anode, oxidation is even more problematic at the higher potentials the ORR catalyst must face on the cathode. Fortunately, in a hydroxide cell, Ag has already shown in-situ ORR performance on par with Pt.
(whereas with $E^\circ = 800$ mV it would be thermodynamically unstable in a proton cell). Thus, current research focuses instead on HOR catalysts suitable for the anode. Essentially all monometallic options are already ruled out (due to cost, performance, or stability), but recently, binary and ternary systems have shown promise. A Pt-Ru alloy significantly outperformed Pt despite the somewhat lower cost of Ru. An inexpensive Co-Ni-Mo alloy showed comparable performance ex situ, though durability may be an issue.

Aside from durability, the other critical characteristic of a catalyst is its activity, the rate at which it catalyzes HOR or ORR. For both proton and hydroxide cells, the most active catalyst for either electrode is Pt (or one of its alloys). But even Pt, whose cost and availability are major barriers to fuel cell commercialization, shows far from ideal activity. This departure from ideality manifests as a catalyst “activation loss”, the second loss mechanism shown in Figure 1.4. Activation losses impact cell performance even at very low current loads; the catalyst surface cannot turn over quickly enough to keep up with the queue of waiting reactants.

1.2.3 Flooding

Kinetic, ohmic, and crossover losses correspond to nonideal catalysts (low activity) and electrolytes (low conductivity, high permeability), as already discussed. A final mode of performance loss is flooding, a more complex system-level phenomenon rather than a fundamental material property.

The chemical product of a fuel cell is water. In proton cells, water is produced on the cathode; in hydroxide cells, on the anode (Fig. 1.6). The higher the current, the more the water produced. Ideally, some of this water diffuses into the electrolyte to maintain high ion conductivity, and any excess is advected to the cell outlet by the passage of gas through the flow channels. Additionally, in a hydroxide cell, water is consumed on the cathode by ORR, so significant back-diffusion from the anode is necessary for the cell to function.
However, at high current (typically >1 A cm\(^{-2}\); see the rightmost region of Fig. 1.4) these water disposal mechanisms are no longer adequate, and liquid water accumulates on the electrode where it was produced. Droplets block pores in the electrode, impeding transport of \(\text{H}_2\) or \(\text{O}_2\) to the catalyst surface.

The consequence of this flooding is not only lower performance, but also less-stable performance. Under constant-voltage operation, the current will oscillate. Initially, flooding decreases current, leading to slower water production. With slower production the liquid water will dissipate until the current rises and flooding begins again. Thus, cell performance under heavy flooding can be unstable.

Because flooding prevents reactants from reaching the catalyst surface, it is commonly referred to as a mass transport loss mechanism. Other types of mass transport losses are also possible. For example, if the \(\text{H}_2\) flow rate is too low – as might be desirable under realistic operation, to maximize fuel utilization – then \(\text{H}_2\) consumption along the flow channel becomes important, and concentration can be significantly higher at the anode entrance than at the anode exit, resulting in “hot spots” and “cold
spots”. In theory, for a hydroxide cell, mass transport losses are not restricted to H₂ and O₂, since on the cathode water is also a reactant. This possibility will be discussed in Chapter 4.

In proton cells, a common flooding control strategy is to wetproof the gas diffusion layer (GDL), a component of the fuel cell sandwich that lies directly outside the MEA and whose fine pore structure ensures an even distribution of the reactant gases across the catalyst layer (CL). In short, wetproofing is thought both to trap water in the cell under dry conditions and to keep water out of parts of the GDL by a capillary effect, guaranteeing passage of gases to the CLs even under wet conditions. The appropriateness of wetproofing for hydroxide cells will be discussed in Chapters 4 and 6.

1.2.4 Degradation

Sustained fuel cell operation introduces new performance losses. The two classic modes are electrolyte degradation and catalyst degradation. For the electrolyte, the same acidity (in a proton cell) or basicity (hydroxide cell) that facilitates ion transport can also facilitate chemical attack of the membrane, or especially of the ionomer. Whereas Nafion is relatively inert in acid, for hydroxide-conducting electrolytes stability under basic conditions continues to pose a challenge. Additionally, some catalysts generate radical species that can accelerate electrolyte degradation.

Specific degradation mechanisms of a polymer electrolyte vary depending on its chemical structure. The typical point of failure is the salt, the active ion-conducting group. But degradation of the polymer backbone is also known, and in hydroxide cells, the linkage between the salt and the backbone is especially vulnerable. Degradation of the salt cripples the functionality of the electrolyte, decreasing ion-exchange capacity

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9 In this work, relatively high flow rates minimize such losses.

h Thus, the most popular backbones are chemical- and heat-resistant, such as poly(sulfone) or poly(phenylene oxide) for hydroxide-conducting electrolytes and fluorinated aliphatic chains for proton-conducting ones.
and exacerbating ohmic losses. Degradation of the backbone can be even more serious, particularly in the bulk membrane: as molecular weight decreases due to this “cutting up” of the polymer, the film’s integrity becomes compromised. A membrane that cracks in this manner may not lose much ion conductivity, but sudden mixing of hydrogen and oxygen could ensue, resulting in permanent cell failure or even an explosion.

For the catalysts, a wide variety of physical and chemical degradation mechanisms are known, such as dissolution, Ostwald ripening, and surface poisoning. Of particular interest here are metal oxidation and carbon corrosion. Noble metals such as Pt tend not to oxidize irreversibly at the potentials encountered in a fuel cell. However, as described already in Section 1.2.2 and later in Chapter 5, non-precious metals do oxidize, even at anode potentials. For most metals this oxidation cannot easily be undone and renders the catalyst inert and/or soluble, limiting the feasible choices that are available – especially for proton cells, which operate at higher (more oxidative) potentials than hydroxide cells.

The second type of catalyst degradation of interest here is corrosion of the carbon support via the carbon oxidation reaction (COR). Thermodynamically, whether in acid or base, COR begins at just a few hundred millivolts above the reversible hydrogen electrode (RHE):\(^{23}\)

\[
\begin{align*}
C + 2H_2O & \rightarrow CO_2 + 4H^+ + 4e^- \quad (+0.21 \text{ V}_{\text{SHE}} \text{ in acid}) \\
C + 6OH^- & \rightarrow CO_3^{2-} + 3H_2O + 4e^- \quad (-0.44 \text{ V}_{\text{SHE}} \text{ in base})
\end{align*}
\]

But the kinetics is so slow that in practice, in proton cells little corrosion is observed until \(\sim 0.9 \text{ V}_{\text{RHE}}\). (In hydroxide cells, COR has not been studied.) Thus, in continuous operation, COR effectively occurs only on the cathode and only near open-circuit conditions; indeed, somewhat counter-intuitively, a common practice in industry is to assess proton MEA lifetime in an “accelerated” open-circuit test during which the device never bears a load.

\(^i\) Since HOR occurs at \(-0.83 \text{ V}_{\text{SHE}}\) in a hydroxide cell, the standard potential for COR translates to \(+0.39 \text{ V}_{\text{RHE}}\) after pH correction.
However, during proton cell startup and shutdown, the cathode can experience higher-than-open-circuit potentials through a reverse-current decay (RCD) mechanism, greatly enhancing COR. Despite its short duration (on the order of one second per startup/shutdown event) and relatively recent discovery in 2005, RCD may be the most important fuel cell degradation mechanism. Nissan reports that it accounts for 44% of all system degradation over the course of a fuel cell car lifetime (typically 5000 h).\textsuperscript{24,25} RCD will be discussed in more detail in Chapter 5.
Chapter 2

METHODS

2.1 Experimental

All of the experimental work is on hydroxide cells. No proton cell results are shown here.

2.1.1 Fabrication of the membrane-electrode assembly

MEAs were fabricated by depositing 5 cm$^2$ electrodes onto both sides of a membrane (Tokuyama Corp. A201 or A901) with a robotic sprayer (Sono-Tek ExactaCoat). The frame used to mask the non-electrode area is shown in Figure 2.1. The electrode ink was prepared by adding catalyst (typically 120 mg$_{\text{metal}}$) and ionomer (Tokuyama Corp. AS-4, typically 20 wt% of the total solids content of the ink$^a$) to 10 g of water and 10 g of isopropanol, followed by sonicating for 1 hour. A typical catalyst loading was 0.4-0.5 mg$_{\text{metal}}$ cm$^{-2}$.

All of the catalysts used in this work were supported on C.$^b$ The benchmark for both anode and cathode was Pt (Tanaka Kikinzoku Kogyo, or TKK, 50% Pt on

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$^a$ In retrospect, an improvement is possible. In striking a balance between pore size and the connectivity of both the ion- and electron-conducting networks, volume is a more relevant descriptor than weight. Since the metal is much denser than its support, it does not contribute significantly to the volume the catalyst occupies in the electrode. Thus, C weight should be used instead of total catalyst weight to more precisely describe ionomer content. This concept is especially important when catalysts of different metal loadings are being compared.

$^b$ Unsupported catalysts are sometimes used in fuel cells, but in general they require higher loadings (1-5 mg cm$^{-2}$) – and even then, they tend to perform worse. Large C particles form a better electron-conducting network than small metal ones. Further, decoration of small particles on a large support mitigates aggregation, increasing the available metal surface area.
high-surface-area C). Additionally, some non-Pt anode catalysts were explored: 20% Ir, Pd, or Ru on Vulcan XC-72 (Premetek). For one experiment, C black (AkzoNobel Ketjenblack) alone was used as cathode catalyst. This C black is similar to the high-surface-area TKK support.

The sandwich was completed by adding a PTFE-coated fiberglass gasket, a GDL (typically Toray TGP-H-060; sometimes SGL 25 BA or SGL 25 BC), and a graphite flow field (typically ElectroChem; sometimes Fuel Cell Technologies) to each side of the MEA (Fig. 2.2). The complete system, assembled and ready for testing, is shown in Figure 2.3. Hot pressing was not necessary. The Toray GDLs were used as received: typically unwetproofed, sometimes wetproofed with 5, 10, 20, or 50 wt% PTFE. The manufacturer wetproofed the Toray paper by dipping into a PTFE suspension followed by high-temperature drying.
Figure 2.2: Exploded view of a fuel cell sandwich. Only the bottom half is shown; above the MEA there is a second GDL, gasket, flow field, and current collector. The reactant gas enters the cell via an inlet bored into the graphite block, whence it flows through serpentine channels flush against the MEA before exhausting via an outlet on the other side of the block.

2.1.2 Fuel cell testing

MEAs were evaluated with a fuel cell test system equipped with a back pressure module (Scribner 850e or 890e). After conditioning (breaking in) the MEA, performance was recorded by scanning current, scanning voltage, holding current constant, or holding voltage constant. Internal resistance (IR) was monitored continuously by a current interrupt method built into the test system. Note that since IR decreases with water production, it is preferable always to measure IR at the same current density, e.g. 500 mA cm\(^{-2}\); ideally, conditioning (on a current basis) would also be the same across tests to precisely control the amount of accumulated water in the cell. (This is not always possible when the performance of the MEAs being compared is very different.)

Conditioning significantly affects cell performance, yet apparently has not been studied extensively in the literature, even for proton cells. The purpose of conditioning is to hydrate the electrolyte without flooding the electrodes or damaging any part of the cell. Thus, the most important parameters are current density and the temperatures of
Figure 2.3: Fuel cell testing setup. The green box in the background is a mass flow controller. The black tanks are bubble humidifiers wrapped in insulation. The black and red lines connect humidified H\textsubscript{2} and O\textsubscript{2} feeds, respectively, to the fuel cell enclosure, which is supported on wooden blocks. Exhaust streams, which lead to back-pressure regulators below, are partially visible on the bottom of the enclosure. The red patch on the outside of the enclosure is a heating pad. The metal plate is the cathode current collector; there is an identical one on the anode side (not visible). The graphite flow fields, gaskets, GDLs, and MEA lie between the current collectors. Load cables, potential-sensing cables, and thermocouple are not shown.
the cell and humidifiers. Obviously, hotter humidifiers are more effective, but if $T_{\text{hum}}$ exceeds $T_{\text{cell}}$, water from the saturated feeds will precipitate in the flow channels instead of penetrating into the MEA as vapor. At high cell temperature, more water vapor can be introduced without precipitation, but the electrolyte may begin to degrade. At high current, more water is produced overall; ohmic losses are lower, but the risk of flooding is higher and electrolyte degradation also appears to increase with current.\(^c\)

Conditioning procedures were tailored to the experiment. When maximizing performance, the cell was conditioned by scanning current,\(^d\) beginning at zero and ending when the voltage dropped below 150 mV. This approach was also used in the water manipulation project (Sections 4.1 and 4.2). It provides continuous monitoring of the peak power density (PPD) of the cell: once the power density levels off or starts to decrease, the tradeoff between electrolyte hydration and flooding/degradation has become unfavorable and the final performance should be recorded. For experiments in which one or both sides of the cell were completely unhumidified, high-current conditioning was used instead to generate more water: the cell voltage was fixed at 50 mV for 20 minutes. Similarly, when the goal was to detect flooding, as in the electrode patterning project (Section 4.3), the cell was ramped down to a low voltage (in this case, 10 min decreasing from 0.5 to 0.1 V followed by a 15 min hold at 0.1 V) prior to the performance scans to ensure that liquid water was present. For the reverse-current decay (RCD) project (Chapter 5), the constant-voltage tests of interest doubled as conditioning to minimize cell degradation; since performance was not critical, no separate conditioning step was performed.

\(^c\) This is intuitive, since $\text{OH}^-$ is known to degrade the electrolyte and the current dictates the $\text{OH}^-$ flux. In contrast to proton cells whose degradation (primarily of the catalysts, not the electrolyte) is most severe at low loads (high cathode potential), in hydroxide cells the longest known durability test (showing 50% performance loss after 5000 hrs) was conducted at just 100 mA cm\(^{-2}\).\(^{26}\)

\(^d\) Various scan rates were used, typically in the range of 10 to 50 mA cm\(^{-2}\) s\(^{-1}\).
2.1.3 *In-situ* cyclic voltammetry

After certain fuel cell tests the anode was characterized by cyclic voltammetry (CV). The cell and humidifiers were allowed to cool to 30 and 50 °C, respectively, over 3 h while the cathode was flushed with N\textsubscript{2} to remove residual O\textsubscript{2}.\textsuperscript{e} Then the N\textsubscript{2} flow rate was reduced from 0.2 to 0.05 L/min\textsuperscript{27} and the electrodes were connected to a potentiostat (Princeton Applied Research VMP2). Prior to the reported measurements, the potential was repeatedly cycled from 0 to 1.2 V vs. the H\textsubscript{2} anode.

*Ex-situ* CV with a traditional three-electrode setup is one of the most widely used electrochemical techniques. *In situ*, in a fuel cell, only two electrodes are available. (Here, the anode is the reference electrode and the cathode is the working electrode.) The reason it is possible to dispense with the counter electrode is that the current CV requires is so small (∼10 mA cm\textsuperscript{−2}). Normally, the counter electrode balances any current that the working electrode generates or consumes. If the counter electrode were absent and current were instead routed through the reference electrode, losses like those shown in Figure 1.4 would alter the reference potential and any electrochemical measurements would be unreliable. However, fuel cell electrodes are much thicker than disk electrodes, and the direct use of gaseous H\textsubscript{2} and O\textsubscript{2} feeds circumvents solubility constraints that can induce mass transport losses in an aqueous setup. Compared to the normal performance a Pt/C fuel cell anode is capable of (>1 A cm\textsuperscript{−2}), *in-situ* CV current is negligible. At such a low load the anode is still an approximately accurate reference. On the other hand, more-demanding techniques such as *in-situ* HOR or ORR activity tests would not be possible without a third electrode.

\textsuperscript{e} The cathode was flushed for such a long time because the humidifier tanks are so large. After 30 min of flushing, enough O\textsubscript{2} residue remained in the cathode feed that the CV was still noticeably tilted: at high potential the O\textsubscript{2} had little effect, but at low potential significant ORR current interfered with the CV scan.
2.1.4 Scanning electron microscopy

Scanning electron microscopy (SEM) was performed with a JSM-7400F microscope equipped with an ultra-thin-window energy-dispersive X-ray spectrometer (EDS). Micrographs and EDS spectra were obtained at an accelerating voltage of 10 kV. Deviations given in the summary of EDS data (Table 5.1) indicate one standard error.

2.2 Theoretical

Two theoretical models were applied in this work. The first is an original but heavily simplified water transport model based on Fick’s law. The second is more sophisticated: an extension of a previously published RCD model. In both cases the model plays a supporting role, either motivating or clarifying the experimental work that is the focus of this dissertation. More details about these models (including equations, parameter values, and the complete Mathematica/Python code) can be found in Appendices A and B, respectively.

2.2.1 Water transport model

To model the water distribution within a hydroxide cell, Fick’s laws of diffusion were applied piecewise on the membrane, GDLs, and catalyst layers (CLs), with source and sink terms in the CLs and an electro-osmotic drag term in the membrane and CLs, yielding a second-order ordinary differential equation (ODE) for each region. The external boundary conditions were fixed concentration at the flow channels depending on humidification, and the interfacial boundary conditions were continuity of concentration and flux. Thanks to the model’s simplicity, the ODEs were integrated directly. The integration constants were found by applying the boundary conditions and solving the resultant linear system.

The most important limitation of the model is that all water is assumed to exist in the gas phase. Equilibrium with a liquid phase was ignored for simplicity. Additionally, electro-osmotic drag was summarized in a single constant parameter despite
known dependence on hydraulic pressure and back-diffusion rate.\textsuperscript{37} Other assumptions include: that current is generated evenly in the CLs, that diffusion coefficient is not a function of position within each region, and that the cell is isothermal.

In light of these limitations, the model should be treated only as semi-quantitative. It is too simplistic to apply predictively without validation. Here, the model only illustrates and supports arguments that are based primarily on experimental evidence.

2.2.2 Reverse-current decay model

Reiser et al. applied a charge conservation balance to model the electrolyte potential of a Pt-based proton cell during startup/shutdown, as described in the original work.\textsuperscript{28} They solved the resultant second-order ODE by a finite difference method. We reproduced their work, and here provide some computational details so that others may more easily follow the same approach.

The governing second-order ODE is highly nonlinear, representing a sum of the five Butler-Volmer processes shown in Figure 5.1 (anode: HOR or ORR; cathode: ORR, COR, or the oxygen evolution reaction, OER). Since the region of interest is the hydrogen-air front on the anode, the model domain is only a small segment of the flow channel, centered on the interface. On the boundary of this segment the derivative of the electrical potential is zero.

We solved the ODE with a finite difference method. However, on our first try, the solver diverged immediately because of the ODE’s nonlinearity (which manifests itself as a discontinuity in the center of the domain; see Fig. 5.7a). To improve the stability of the system we used parameter continuation as follows. First, a simplified linear version of the problem was solved. Then, a small amount of nonlinearity was introduced and the problem was solved again. The nonlinearity was increased incrementally in this fashion until the original nonlinear problem was recovered, yielding the final solution.
Before studying an electrochemical device scientifically, it is important to optimize for reproducibility and performance. Otherwise any conclusions that are reached, however interesting, may be unreliable or irrelevant to the state of the art. While of little scientific interest \textit{per se}, this chapter provides a framework within which finer aspects of fuel cell behavior may be studied.

3.1 Reproducibility

The electrochemically active part of a fuel cell is the MEA. The vast majority of fundamental fuel cell research focuses on the membrane/ionomer, catalysts, or electrode architecture, all components of the MEA. Typical MEA fabrication consists roughly of the following steps: the polymer electrolyte and catalysts are prepared separately; most of the electrolyte is cast into a solid membrane, the catalyst and remaining polymer are suspended in a water-based ink, two electrodes are fabricated from the ink, and the membrane is pressed between the electrodes.

The step that has received the most attention is the electrode fabrication step, for which many techniques are available. Three broad categories are catalyst-coated membrane (CCM), catalyst-coated GDL (CCG), and the decal method. In CCM, the catalyst ink is deposited directly onto the membrane by painting, spraying, or doctor blading. In CCG, the same techniques are applied with the GDL instead of the membrane as substrate. GDL porosity must be taken into account so that the ink does not simply pass through the GDL before drying; typically, only GDLs with microporous layers (MPLs) are suitable for CCG. In the decal method, the same techniques are
applied onto a PTFE “blank” substrate, after which the membrane and blank are pressed together to transfer the electrode to the membrane.

Whether by the CCG, CCM, or decal method, and whether by painting, spraying, or doctor blading, electrode fabrication at the laboratory scale is often done by hand. Manual fabrication presents two issues. First, it is time-consuming. Ideally, for a uniformly porous structure, the electrode should be built up (tediously) of many identical layers, each of which must dry before the next is deposited. High-volume studies like those presented in the following chapters would not be feasible without multiple dedicated technicians. Second, it is prone to human error and variability. Poor reproducibility further increases the number of test replicates that must be performed to achieve statistical significance. Additionally, for a given catalyst loading, cell performance is maximized when the catalyst is distributed uniformly over the electrode. Heavy-deposition regions lead to poor catalyst utilization; light-deposition regions are limited by available catalyst surface area.

Therefore, in this work, electrodes were fabricated with the help of a robotic sprayer (Fig. 3.1). Typically, each electrode was built up gradually over 100 passes for a total thickness of 5-15 µm. Three serpentine spraying patterns were offset to flatten the Gaussian deposition profile a single pattern would yield. Typically, each batch of ink produced four identical 5 cm² electrodes (though more complicated patterns were also explored; see Fig. 2.1 and Section 4.3). Overall, this automation improved MEA reproducibility, production efficiency, and performance compared to the airbrush spraying that was employed by hand previously.

3.2 Performance

Aside from choice of catalysts and electrolyte, dozens of less obvious factors influence cell performance. An abbreviated list follows, presented roughly in decreasing order of importance: gasket thickness, ionomer loading, cell and humidifier temperatures, air vs. O₂ as oxidant, back pressure, catalyst loading, flow rates of fuel and oxidant, presence/absence of CO₂ in the feeds, pattern of the flow channels, gasket
Figure 3.1: Robotic sprayer for fabricating membrane-electrode assemblies.

material, and electrical conductivity of the GDL.\(^a\) Here I will discuss just two of the most critical factors, gasket thickness and ionomer loading.

Gasket thickness matters because all of a fuel cell’s components must be in tight contact for efficient operation. The cell is compressed during assembly to ensure such contact, providing some leeway, but this is irrelevant if the gasket thickness is completely wrong.\(^b\) If the gaskets are too thick, an air gap between the current collector (e.g., graphite flow field) and the electrically conductive GDL can increase the IR of the cell by one or two orders of magnitude. If the gaskets are too thin, assembly over-compresses the GDLs and causes cracking; for the carbon-paper GDLs used in this study, the fibers may puncture the MEA, compromising the membrane’s role as gas

\(^a\) Other more important GDL properties will be examined in Chapter 4.

\(^b\) A related parameter is the pressure (or screw torque) with which the fuel cell sandwich is assembled. A mismatch between gasket thickness and MEA-plus-GDL thickness often can be corrected by adjusting the assembly pressure.
Choosing an appropriate ionomer loading in the catalyst layer (CL) is also critical to cell performance. We prepared MEAs by the CCM method, with ionomer loading ranging from 10 to 30 wt%, and found a clear optimum near 20% (Fig. 3.2) in agreement with Yang et al.\textsuperscript{29} This optimum loading results from a tradeoff: too little ionomer lowers catalyst utilization due to insufficient ion-conducting channels, while too much reduces both mass transport due to pore clogging and electrical conductivity due to separation of catalyst particles. Additionally, the hydrophilic ion-conducting groups may affect the water distribution in the cell, but in Chapter 4 we will fix the ionomer loading at 20% to study other factors that control water transport: GDL wetproofing and humidification.
Figure 3.3: High-temperature performance. Solid circles indicate the polarization curve and open circles indicate the power density curve. Materials: Tokuyama A901 membrane, ionomer loading of 20% Tokuyama AS-4, catalyst loading of 0.4 mgPt cm$^{-2}$ TKK 50% Pt/C, 5% PTFE in Toray GDLs. Test conditions: cell at 80 $^\circ$C, anode and cathode humidifiers at 85 $^\circ$C, H$_2$ and O$_2$ flow rates of 0.2 L/min and back pressures of 250 kPag.

Overall, following the approaches for reproducibility and high performance outlined in this chapter, an MEA based on 20% ionomer loading and low-PTFE GDLs showed a high peak power density (PPD) of 737 mW cm$^{-2}$ (Fig. 3.3). This performance is among the highest reported in the literature (Table 3.1).$^{2-5,30-32}$
Table 3.1: High-performance hydroxide fuel cells in the literature.

<table>
<thead>
<tr>
<th>Source</th>
<th>PPD</th>
<th>Cell temperature (°C)</th>
<th>Back pressure (kPag)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wang et al. (2015)</td>
<td>1000</td>
<td>60</td>
<td>100</td>
</tr>
<tr>
<td>Mamlouk et al. (2012)</td>
<td>823</td>
<td>60</td>
<td>0</td>
</tr>
<tr>
<td>This work</td>
<td>737</td>
<td>80</td>
<td>250</td>
</tr>
<tr>
<td>Isomura et al. (2012)</td>
<td>730</td>
<td>80</td>
<td>- a</td>
</tr>
<tr>
<td>Li et al. (2013)</td>
<td>550</td>
<td>60</td>
<td>100</td>
</tr>
<tr>
<td>This work</td>
<td>459</td>
<td>60</td>
<td>250 c</td>
</tr>
<tr>
<td>Piana et al. (2010)</td>
<td>400</td>
<td>50</td>
<td>- a, b</td>
</tr>
<tr>
<td>Zhao et al. (2013)</td>
<td>338</td>
<td>60</td>
<td>50</td>
</tr>
<tr>
<td>Isomura et al. (2011)</td>
<td>330 e</td>
<td>50</td>
<td>- b, d</td>
</tr>
</tbody>
</table>

a Not reported  
b CO₂-free air instead of O₂ as oxidant  
c 0% relative humidity (RH) in anode feed  
d 0% RH in cathode feed  
e Approximate value (estimated from plot)
Whereas proton cells have been modeled and optimized meticulously,\textsuperscript{35–37} hydroxide cell materials and operating conditions are still under active investigation. Because the two systems seem to differ only in minor ways, it is natural to apply general findings from the more mature proton cell to hydroxide cell development. For example, in proton cells hydrophobized GDLs with MPLs were introduced in part to mitigate cathode flooding at high current.\textsuperscript{38} In hydroxide cells HOR produces water so in principle the anode is analogously susceptible to flooding; yet, while GDL thickness has been studied in the hydroxide cell literature,\textsuperscript{4} there is little discussion of hydrophobic treatment or MPLs.\textsuperscript{3,30,39,40} Cathode drying is also a potential concern for hydroxide cells because ORR consumes water (Fig. 1.6).\textsuperscript{40}

Surprisingly, water management strategies have been adopted in which cathode humidification is eliminated\textsuperscript{32} or greatly reduced\textsuperscript{40} (despite potential cathode drying) and instead only the anode is fully humidified (despite potential anode flooding). It has been shown that the resultant concentration gradient increases water flux through the cathode,\textsuperscript{32} but an explanation has yet to be published for why these indirect approaches should be more effective than humidifying the drying-prone cathode directly.

Here we present a high-performance hydroxide cell made from commercially available materials. We demonstrate flooding and drying by manipulating humidification and GDL wetproofing. We show that wetproofing is detrimental because it floods the anode, and that dry-anode operation leads to higher performance than dry-cathode
operation. We describe flooding and drying behavior semi-quantitatively through a simplistic water diffusion model.

4.1 By Wetproofing

Identical MEAs were fabricated with an automated sprayer, assembled with macroporous-only Toray GDLs of various wetproofing levels (0, 5, 10, 20, or 50 wt% PTFE), and tested. High PTFE levels drastically reduced performance, in particular when applied on the anode side, and even low levels had a noticeable negative effect (Fig. 4.1). In proton cells, surface hydrophobization of GDL pores normally prevents water from accumulating at the electrodes,\textsuperscript{38,41} so the obvious interpretation of Figure 4.1 is that wetproofing dries out the cell, resulting in ohmic losses from low electrolyte hydration and potentially cathode mass transport losses from insufficient water availability for ORR.

To test this interpretation, we measured the cell IR. IR is sensitive to flooding and drying because the electrolyte only conducts well in the presence of water, whose solvating effect frees the hydroxide ions to migrate through the cell. Surprisingly, for the 21 MEAs tested in Figure 4.1 the IR did not vary substantially (84-108 mΩ cm$^{-2}$). The corresponding variation in ohmic losses (42-54 mV) accounts for only 2% of the observed variation in performance (114-746 mV) at a current density of 500 mA cm$^{-2}$. This IR uniformity indicates that the electrolyte was adequately hydrated in all cases, likely due to the high level of humidification ($T_{\text{hum}} = T_{\text{cell}} + 10 \degree C$), and rules out the possibility that wetproofing significantly dries out the electrolyte.

To investigate further, we performed controlled-current tests with relatively low humidification ($T_{\text{hum}} = T_{\text{cell}} - 2 \degree C$) over a long time period to ensure that the cell reached steady state. Three conditions were studied: no wetproofing, 50% anode GDL wetproofing, and 50% cathode GDL wetproofing. To avoid possible differences between individually fabricated MEAs, a single MEA was used for both wetproofed conditions: by switching the feeds and load cables, the wetproofed GDL was effectively transferred from one electrode to the other with no need for cell reassembly. When no wetproofing
Figure 4.1: Impact of GDL wetproofing on cell performance. (a) Each dot represents the average peak power density of MEAs tested with equal wetproofing on both GDLs (black), wetproofing only on the anode GDL (red), or wetproofing only on the cathode GDL (green). Error bars indicate ±1 standard error (n = 3). (b) Representative polarization curves. Materials: Tokuyama A901 membrane, ionomer loading of 20% Tokuyama AS-4, catalyst loading of 0.4 mgPt cm$^{-2}$ TKK 50% Pt/C. Test conditions: cell at 60 °C, anode and cathode humidifiers at 70 °C, H$_2$ and O$_2$ flow rates of 0.2 L/min and back pressures of 250 kPag.
was present the IR quickly stabilized at constant current (Fig. 4.2a, black curves). Similar behavior was observed with cathode wetproofing (green curves). By contrast, with anode wetproofing the IR continued to drop over time (red curves). Thus, anode wetproofing does not dry out the cell but acts as a water-retaining barrier, lowering IR and reducing ohmic losses. However, after a few minutes other losses outweighed these ohmic gains (Fig. 4.2b), suggesting that anode wetproofing can induce flooding even at moderate current densities (170 mA cm\(^{-2}\)) under partial humidification.

While wetproofing the anode GDL dramatically lowered performance (Figs. 4.1 and 4.2, red coloring), wetproofing the cathode GDL had little impact (green coloring). Since hydrophobicity is unlikely to change after the pore walls are completely coated (approx. 10% PTFE),\(^{42}\) we instead explain this discrepancy mainly through GDL pore size effects,\(^{43}\) in two ways. First, if flooding occurs chiefly on the anode, where water is produced, then shrinking the pores by coating the walls with PTFE should only exacerbate flooding when applied to the anode GDL.

Second, the total water content of the cell, and in turn the extent of flooding, is more sensitive to diffusivity changes in the anode GDL than in the cathode GDL. Since the anode produces more water than the cathode consumes, at steady state the net direction of water transport is out of the cell. Under equal humidification, the water concentration and diffusive potential are higher at the anode than at the cathode.\(^{44}\) Thus, decreasing the effective water diffusion coefficient of the GDL on the anode side, in this case by shrinking pores through wetproofing, leads to more water retention than decreasing diffusivity on the cathode.

We illustrate this water-trapping effect with a single-phase one-dimensional constant-current steady-state isothermal water transport model of the hydroxide cell sandwich that accounts for diffusion, reaction, and electro-osmotic drag. Wetproofing

\(^{a}\) The distinction is not critical. Whether the culprit is surface energy or pore size, the result of wetproofing is an increase in capillary pressure that prevents water from exiting through the GDL.
Figure 4.2: Impact of asymmetric wetproofing on steady-state cell water content. One MEA was assembled without wetproofing (black curves). A second MEA was assembled with one 50% wetproofed and one unwetproofed GDL (colored curves). Each MEA was subjected to five identical one-hour tests (I, II, III, IV, and V), which consisted of a 35 min open-circuit drying period during which the feeds were replaced with dry N₂, a 1 min current ramp from 0 to 170 mA cm⁻², and a 24 min current hold at 170 mA cm⁻². (a) Internal resistance and (b) cell voltage (shown only for Test III, for clarity) were monitored continuously. At t = 2 h and again at t = 4 h, the feeds and load cables were switched, reversing the electrode roles for Tests III and IV. Thus, the wetproofed GDL was on the cathode side for Tests I, II, and V (green), and on the anode side for Tests III and IV (red). Materials: Tokuyama A201 membrane, ionomer loading of 20% Tokuyama AS-4, catalyst loading of 0.4 mgPt cm⁻² TKK 50% Pt/C, 0 or 50% PTFE in Toray GDLs. Test conditions: cell at 30 °C, anode and cathode humidifiers at 28 °C, H₂ and O₂ flow rates of 0.2 L/min at ambient pressure. Similar results were obtained at 60 °C cell and 70 °C humidifier temperatures (not shown). For clarity, the high IR measured at the beginning of each test (typically 2000 mΩ cm²) is omitted.
was represented by a lower water diffusion coefficient in the GDL\textsuperscript{b} and humidification entered as the water concentration on the system boundary. Predicted cell water profiles for different combinations of wetproofed and unwetproofed GDLs are shown in Figures 4.3a-4.3d. When both GDLs are wetproofed, water concentration is higher throughout the cell (Fig. 4.3a vs. 4.3d). However, the electrode contributions are unequal: anode wetproofing accounts for most of the profile upshift (Fig. 4.3b) while cathode wetproofing alone has almost no effect (Fig. 4.3c). This trend confirms our experimental observation that increasing anode GDL capillary pressure via wetproofing induces catastrophic flooding. The model suggests that although cathode wetproofing is harmless on its own, the marginal impact is magnified when a large amount of water is already present at the cathode, for example due to anode wetproofing.

In proton cells, a common strategy to reduce cathode flooding is to add an MPL to the cathode GDL, which acts as a barrier and reroutes excess water to exit through the anode.\textsuperscript{38,41,45–47} Surprisingly, we find that the analogous strategy in hydroxide cells, namely adding an MPL to the anode to reroute water to the cathode, is ineffective. The commercial SGL GDLs 25 BA and 25 BC feature identical macroporous layers (190 $\mu$m, 5 wt\% PTFE), but 25 BC has an additional MPL (45 $\mu$m, 10 wt\% PTFE). We tested these GDLs with identical MEAs (Fig. 4.4) in the same manner as in Figure 4.1. Our data corroborate the finding of Piana et al. that in the activation and ohmic regions, MPLs have little effect on polarization behavior.\textsuperscript{30} But as with the Toray paper wetproofing, an MPL on the anode GDL substantially reduces performance in the region of mass transport control. It is tempting to conclude that MPLs are inherently ineffective in hydroxide cells, according to the same pore size and capillary

\textsuperscript{b} This is a simplification. In reality the effect of wetproofing is more complex (even when surface energy is ignored). For example, decreasing the porosity causes a larger pressure drop across the GDL, affecting fluid flow. This effect may be neglected by assuming that the total pressure is constant throughout the sandwich so that diffusion (based on partial pressure differences) dominates convection. An operational constraint partly justifies this assumption: the anode and cathode compartments of the cell must be near mechanical equilibrium lest the membrane rupture.
Figure 4.3: Cell water profiles predicted by a simplistic model. Curves a-d show the impact of GDL wetproofing, with full 70 °C humidification in all cases: a, water diffusivity is decreased in both GDLs to simulate 50% wetproofing; b, only the anode GDL is wetproofed; c, only the cathode GDL is wetproofed; and d, neither GDL is wetproofed. Curves d-f show the impact of decreased humidification, with no wetproofing in all cases: d, both feeds are humidified at 70 °C; e, only the anode feed is humidified; and f, only the cathode feed is humidified. Unhumidified feeds are completely dry (0% RH). The GDLs are abridged because they are over 10 times thicker than the other sandwich components. MPLs were not considered.
Figure 4.4: Impact of the MPL on cell polarization. Black circles indicate tests in which neither or both GDLs contained MPLs; green diamonds, only the cathode GDL had an MPL; and red squares, only the anode GDL had an MPL. Materials: Tokuyama A901 membrane, ionomer loading of 20% Tokuyama AS-4, catalyst loading of 0.4 mg_{Pt} cm^{-2} TKK 50% Pt/C. Test conditions: cell at 60 °C, anode and cathode humidifiers at 70 °C, H_{2} and O_{2} flow rates of 0.2 L/min and back pressures of 250 kPag.

pressure arguments presented above. There is also an alternative explanation: that since MPLs are denser than macroporous layers (here, 0.92 vs. 0.27 g cm^{-3}, excluding PTFE), even a low PTFE weight percentage translates to a high absolute loading. Water management in hydroxide cells could require novel low-PTFE MPLs.

Still, it is unclear why PTFE seems to impact hydroxide cells more strongly than proton cells, for which at least a small amount in the GDL and/or MPL is widely considered beneficial.\textsuperscript{38,41–43,45–49} Hydroxide cells operate at lower temperature due to the limited stability of currently available electrolytes,\textsuperscript{1} resulting in less evaporation and more liquid water.\textsuperscript{50} The hydrophobic effect of wetproofing is also stronger at
low temperature\textsuperscript{42} since the surface energy barrier to wetting is more significant when less thermal energy is available. Additionally, for a given current density, local water production is twice as fast on the hydroxide cell anode as on the proton cell cathode, which could increase the total amount of liquid in the cell if the water consumed in ORR on the relatively dry cathode is predominantly in the vapor phase. After heavy wetproofing, the initially macroporous Toray GDLs used in this study may begin to resemble MPLs, which when free of cracks have also been found to limit liquid water transport in proton cells.\textsuperscript{42,51}

4.2 By Humidification

Our results appear to conflict with strategies in which only the anode feed is humidified. Specifically, we claim that the intrinsically higher water concentration on the anode can lead to flooding (Figs. 4.2 and 4.3a-4.3d), while Isomura et al. obtained good performance (a peak power density, or PPD, of approx. 330 mW cm\textsuperscript{-2}) when only the anode feed was humidified, and did not report performance under cathode-only humidification.\textsuperscript{32} We performed both experiments with our setup and observed slightly better performance with a dry anode than a dry cathode (Fig. 4.5).

In agreement with this experimental result, our model predicts a more uniform water profile for a dry anode, with improved hydration on the cathode and alleviation of any flooding on the anode, which should reduce ohmic and mass transport losses (Figs. 4.3e and 4.3f). Additionally, we found previously that cathode overhumidification can improve performance.\textsuperscript{8} Overall, our findings confirm the conclusion of Isomura et al. that high performance is possible with a dry cathode feed, and additionally show that a dry anode feed is equally tenable. However, anode-only humidification may be more attractive for other practical reasons, such as improved fuel utilization via anode dead-ending.\textsuperscript{40,c}

\textsuperscript{c} Dead-ending brings water issues of its own. Ideally, with no available exit on the anode, all of the water produced in the cell would exit through the cathode. But in practice the anode still floods. Periodically, water must be purged from the anode by
Figure 4.5: Performance when one feed is dry. For the orange circles, the anode was humidified (humidifier temperature: 70 °C) and the cathode was dry (0% RH); for the blue squares, the cathode was humidified and the anode was dry. Solid symbols indicate polarization curves and open symbols indicate power density curves. Materials: Tokuyama A901 membrane, ionomer loading of 20% Tokuyama AS-4, catalyst loading of 0.4 mg Pt cm$^{-2}$ TKK 50% Pt/C, unwetproofed Toray GDLs. Test conditions: cell at 60 °C, H$_2$ and O$_2$ flow rates of 0.2 L/min and back pressures of 250 kPag. A test was also performed with both feeds dry, but the performance was too low to measure reliably ($< 2$ mW cm$^{-2}$; not shown).
4.3 By Electrode Patterning

The preceding results suggest that hydroxide cell performance is particularly sensitive to the internal distribution of water. The anode floods under innocent-looking conditions, while the extent to which the cathode dries out is unknown. In this section we introduce electrode patterning as a method to enhance back-diffusion of water from anode to cathode.

As discussed in Section 1.2 and implied in the foregoing modeling work, membrane thickness plays a key role in the hydroxide cell water distribution. Thicker membranes present higher resistance against water transport by diffusion and electrosmosis; the highest-performance membranes are very thin (~10 µm). But the CLs where water is produced or consumed may themselves act as barriers to water transport. The idea behind electrode patterning is to alternate between normal active electrode area and inactive water diffusion channels that consist of bare membrane. While the channels do not directly generate electricity, they alleviate flooding and/or drying by equalizing any water concentration gradients between cathode and anode, boosting the performance of nearby electrode area (Fig. 4.6).

This approach is especially well-suited to hydroxide fuel cells. Proton cells do not appear to suffer as severely from the water imbalances identified earlier in this chapter. In addition, fluorinated proton exchange membranes tend to be thicker than hydroxide exchange membranes. Clearing off part of the CL in a proton cell might have little effect on the water distribution if a thick membrane already acts as a significant barrier to transport. By contrast, the higher ionic resistance and lower gas permeability of non-fluorinated hydroxide exchange electrolytes drive the membrane down to nearly the same thickness as the CLs.

Here we study MEAs based on five types of Pt/C electrodes (see Fig. 4.7) and two membranes (Tokuyama A201 and A901). The electrodes are identically composed and differ only by the mask with which they are fabricated. We hypothesize that the briefly opening the outlet and greatly increasing the hydrogen flow rate. Presumably, the fuel losses during these purges are small enough to justify dead-ending.
Figure 4.6: Illustration of enhanced water diffusion in patterned MEAs. The anode side of the fuel cell sandwich is shown, corresponding to (a) the >5 cm\(^2\) electrode, (b) the 5 cm\(^2\) electrode, or (c) a 3.5 cm\(^2\) patterned electrode from Figure 4.7. The gasket and GDL are not to scale; in reality, each is about 20 times thicker than the membrane or CL. Dashed blue arrows indicate transport routes whereby water on the anode must pass through both the CL and membrane to reach the cathode side. Solid arrows indicate preferred routes that utilize water channels (white), macroscopic gaps in the CL. In (a), there are no such gaps because the electrode is too large for the gasket opening. In (b), small gaps are present between the electrode perimeter and the gasket. In (c), additional channels are introduced deliberately.
Figure 4.7: Non-standard electrode patterns to improve water back-diffusion. Active electrode area is shown in black, with bare membrane in white. The dashed red lines indicate an area of 5 cm$^2$, the size of the flow fields and gasket windows used to test the MEAs. The electrode areas shown are (a) >5 cm$^2$; (b) 5 cm$^2$, the same size used elsewhere in this work; and (c-e), a total of 3.5 cm$^2$ each, not counting the channels between the electrode islands, distributed in a single-square, 2 x 2, or 4 x 4 pattern. A photograph of an MEA fabricated with the pattern from (e) is also shown. If the hypothesis is correct that water channels improve performance, then after normalizing to the active electrode area (i.e., the total black area contained within the dashed line), (a) should perform worst and (e) best.
performance per active area should correlate with the perimeter between the electrode and any water channels. Further, the performance enhancement should be more pronounced in MEAs based on the thinner A901 membrane, for which the CLs account for a greater proportion of the total resistance to water transport.

To test these hypotheses, MEAs were fabricated with masks based on the designs in Figure 4.7 and tested under identical conditions. To guarantee the best possible comparison, four of the five masks were applied together (Fig. 2.1) and sprayed simultaneously with the same batch of ink.

Preliminary results suggest a relationship between electrode perimeter and performance. With a thick membrane (A201, 28 µm) no relationship is visible (Fig. 4.8, black circles). (If a relationship does exist, the resolution of this experiment is too limited to detect it.) However, as expected, with the thinner A901 membrane (10 µm) a significant trend emerges (red triangles). Representative polarization curves are shown in Figure 4.9. Whereas all of the MEAs behave similarly at low current, at high current in the mass transport regime the patterned electrodes generally perform better, indicating that the water diffusion channels are effective in controlling flooding and/or drying.

Interestingly, the trend is not monotonic: increasing the degree of patterning beyond 2 x 2 hurts performance. This may be an artifact of the small sample size, but the error bars are sufficiently tight that some further speculation is warranted. The decrease in performance for the 4 x 4 patterned cell could represent gas crossover losses, an issue specific to thin membranes like A901. Just as the CL acts as a barrier to water transport, it also supplements the membrane in separating H₂ on the anode from O₂ on the cathode. Removing part of the CL is expected to increase crossover. The trouble with this explanation is that crossover losses are normally visible even at open circuit (Fig. 1.4), yet for these data the patterned and unpatterned MEAs behave identically

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Safety note: all of these tests were conducted at standard pressure. To avoid explosive crossover, extreme caution should be exercised when testing patterned MEAs at elevated pressure.
until a relatively high load is applied. Further, it is unclear why redistributing a given amount of channel area should affect crossover losses; intuitively, many small channels should result in the same amount of gas crossover as few large ones.

Despite these concerns, as additional evidence of greater gas crossover for 4 x 4 vs. 2 x 2 patterning, we measured the open-circuit voltage (OCV) immediately after connecting the cell to the H\textsubscript{2} and O\textsubscript{2} feeds. This measurement differs from the normal OCV point at the beginning of a polarization scan in that the cell has not yet been conditioned. No water has been generated inside the cell and too little time has passed for the humidified feeds to wet the electrolyte. Without the swelling that results from wetting, the volume of hydrophilic regions in the membrane and CLs is lower, so hydrophobic regions occupy a larger fraction of the total volume. Thus, both because the total volume is lower and because transport of nonpolar gases is faster through hydrophobic media, conductance of H\textsubscript{2} and O\textsubscript{2} through the electrolyte should be highest just after the feeds are connected. This initial OCV can be thought of as an especially sensitive crossover measurement. Indeed, under these conditions the OCV is much lower for highly patterned A901 MEAs (Fig. 4.10), consistent with the hypothesis that crossover is more significant at high levels of patterning. As expected, when A201 is used instead, patterning makes no difference because the thick membrane already blocks virtually all gas crossover.

Overall, electrode patterning does appear to slightly increase cell performance as long as the membrane is thin (or has a high water diffusivity) compared to the CLs. However, at high levels of patterning the tradeoff between enhanced crossover and enhanced water diffusion leads to a performance optimum. At best, the electrode patterns proposed here could increase cell performance by several percent. Such a small improvement is unlikely to be practical when the water channels could instead be filled in with additional electrode area.\textsuperscript{e} However, this small effect size could limited

\textsuperscript{e} Speculatively, this sort of improvement could matter in scenarios where fuel is expensive and efficiency is more important than capital cost, or where the catalyst is extremely expensive compared to other device components.
Figure 4.8: PPDs of conventional and patterned MEAs made with thin A901 or thick A201 membranes. Error bars indicate ±1 standard error (n = 3). The five x-values correspond to Figure 4.7. For the large (>5 cm²) electrode, the perimeter-to-area ratio is zero because there is no exposed membrane in the active 5 cm² gasket window.

Figure 4.9: Polarization of conventional and patterned MEAs made with thin A901 membranes. The data are taken representatively from the same tests as Figure 4.8.
Figure 4.10: OCV of patterned MEAs before testing. Error bars indicate ±1 standard error (n = 3). The data are from the same tests as Figure 4.8.

by materials, equipment, and processing. If a thin membrane with high resistance to both gas and water transport can be developed, then ideally, patterned MEAs would be prepared with channel sizes on the same order of magnitude as the CL thickness – but this is not remotely feasible without a laser cutter. Additionally, during electrode spraying, micron-sized mask openings could be too small to allow cohesive water-based ink droplets to pass through to the membrane. In the future, the experiments reported here should be repeated with more sophisticated mask designs and fabrication methods.
Chapter 5

REVERSE-CURRENT DECAY

(Based on Kaspar, Wittkopf, Woodroof, Armstrong, and Yan (2015).)

5.1 Introduction and Mechanism in Proton Fuel Cells

A reverse-current mechanism of proton cell degradation was discovered in 2005. We summarize it as follows. After a period of inactivity, a proton cell anode contains only air due to equilibration with the atmosphere. As hydrogen is introduced during device startup, distinct hydrogen and air regions form on the anode (Fig. 5.1a). In the hydrogen region, the device operates normally: HOR occurs on the anode while across the membrane, ORR occurs on the cathode. Since the two anode regions are electrically connected, electrons produced by HOR in the hydrogen region can move to the stagnant air region and react with protons supplied by the electrolyte to reduce oxygen. Removing positive charge from the electrolyte in this manner lowers the electrolyte potential, ultimately generating an interfacial potential difference sufficient to drive the COR and OER on the cathode in the stagnant air region. This mechanism is called reverse-current decay (RCD) because reduction occurs on the anode where hydrogen is normally oxidized while oxidation occurs on the cathode where oxygen is normally reduced. Related decay processes take place during shutdown and whenever hydrogen is maldistributed on the anode. Over the course of many startup/shutdown cycles, corrosion of the cathode carbon support leads to significant performance loss.

Strategies to mitigate RCD include maintaining hydrogen pressure in the anode after shutdown or flushing with an inert gas, shorting the electrodes to depress the
Figure 5.1: Mechanism of reverse-current decay during startup in (a) proton cells (known) and (b) hydroxide cells (proposed). Stagnant air (white regions) is displaced by flowing hydrogen and air (shaded regions). While (b) indicates that COR produces CO$_2$, in reality at high pH the aqueous equilibrium favors HCO$_3^-$ and/or CO$_3^{2-}$.
cathode potential, replacing carbon with a corrosion-resistant support, and mixing OER catalysts into the cathode to reduce selectivity for COR. However, these strategies add to system complexity or treat symptoms instead of resolving the underlying problem.

The key issue responsible for RCD in proton cells is that the anode and cathode catalysts are the same. Pt is the best catalyst available for both HOR and ORR. When a mixture of gases is present at the anode, Pt catalyzes HOR as intended, but also catalyzes ORR. A direct way to stop RCD is to eliminate the interfacial potential buildup altogether by replacing Pt with a specialized anode catalyst that has no ORR activity.

Unfortunately, because proton cells operate under harsh acidic conditions, many metals oxidize and subsequently dissolve at anode potentials (Fig. 1.5). Thus, efforts to date to reduce ORR activity have focused on modifying Pt. Genorio et al. completely suppressed the ORR activity of Pt at low overpotential by covering the surface with the organic macrocycle calix[4]arene. However, they reported only half-cell measurements; it is unclear whether this surface modification approach would be practical in a real device.

By contrast, because hydroxide cells operate under basic conditions, they intrinsically support earth-abundant non-Pt anode catalysts (Fig. 1.5), such as Ni. Until now RCD has never been studied in hydroxide cells, but it could present an even more serious issue than in proton cells. In a basic environment, CO₂ produced by COR reacts further to the stabler CO₃²⁻ form, increasing the energetic favorability of corrosion. A carbon durability test designed to mimic fuel cell conditions yielded 18 times higher corrosion current in 1 M NaOH than in 1 M H₂SO₄. Furthermore, the tendency of the hydroxide cell anode to flood (Chapter 4) may exacerbate hydrogen maldistribution during closed-circuit operation. Despite these differences, we expect the basic mechanism of RCD in hydroxide cells to be similar to that of proton cells (Fig. 5.1b). We aim to determine whether RCD affects hydroxide cells, and if so, whether it can be mitigated by choosing specialized anode catalysts with low ORR activity.
5.2 In Hydroxide Fuel Cells

Here we demonstrate for the first time that hydroxide cells undergo RCD. We adapt the model of Reiser et al.\textsuperscript{28} to predict an inverse relationship between anode ORR activity and RCD driving force. We test several monometallic catalysts and confirm that cathode corrosion is slower for anode catalysts with low ORR activity.

5.2.1 Evidence of RCD with platinum electrodes

Our experimental RCD protocol (Fig. 5.2a) is analogous to that of Reiser et al. To simulate startup/shutdown conditions without cycling, we employ two cells: a “driver” and a “performer”. Hydrogen and oxygen are allowed to flow through the driver as usual, while the performer inlets and outlets are simply exposed to stagnant air. Shorting the cells together achieves a perpetual startup-like configuration.

To determine whether degradation took place in an RCD test, we evaluated the performer cell beforehand and afterward by connecting it to hydrogen and oxygen feeds, controlling the cell voltage, and measuring IR and current (Fig. 5.3). To minimize sources of degradation other than RCD, we chose mild test conditions (moderate temperature and full humidification) and used different MEAs, prepared identically with a robotic sprayer (Sono-Tek), for each test.

Initially, we limited our experiments to Pt-based electrodes to determine whether RCD affects hydroxide cells. Evaluation of a Pt/C performer before and after a 2 h RCD test (Fig. 5.4a) shows a clear performance drop (from 1310 to 336 mA cm\textsuperscript{2}) and IR increase (from 0.129 to 0.477 Ω cm\textsuperscript{2}), consistent with the loss of electron- and ion-conducting pathways that is expected to accompany electrode corrosion. \textit{In-situ} CV of the cathode showed that RCD rendered the Pt surface inaccessible (Fig. 5.5). After a 6 h test, SEM revealed cathode thinning (approx. from 13 to 6 µm, Fig. 5.6), and despite the disappearance of the Pt peak in the CV, EDS revealed Pt enrichment in the cathode (from 44 to 82 wt%, Table 5.1), both signatures of RCD in proton cells. We conclude that RCD does affect hydroxide cells.
Figure 5.2: Experimental configurations for (a) normal and (b) inverted RCD tests. The hydroxide cell shown in Fig. 5.1b is split along the vertical dotted line into two separate cells. In each test, the cells are connected by two wires. The H\textsubscript{2}/O\textsubscript{2} cell is termed the driver because it provides the low hydrogen potential required to induce ORR in the performer cell. The performer is the air/air cell whose performance degrades over the course of the RCD test. For all tests, identical Pt/C electrodes, with 0.5 mg\textsubscript{Pt} cm\textsuperscript{-2} and 20% ionomer loading, were used for both driver electrodes and for the performer electrode where COR occurs (i.e., the cathode in a normal test or the anode in an inverted test). The catalyst in the remaining electrode is used to identify the performer cell (e.g., a “Ru/C performer” consists of a Ru/C anode and a Pt/C cathode).

Table 5.1: Elemental composition of CLs in a Pt/C performer cell after a 6 h RCD test.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Abundance (wt%)</th>
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<tbody>
<tr>
<td></td>
<td>Pt</td>
</tr>
<tr>
<td>Anode</td>
<td>43.6 ± 2.6</td>
</tr>
<tr>
<td>Cathode</td>
<td>82.2 ± 0.9</td>
</tr>
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Figure 5.3: Four-step structure of an RCD experiment.

(a) Evaluate the performer before RCD. The performer is connected to humidified H$_2$ and O$_2$ feeds and the cell voltage is decreased from 0.5 to 0.1 V over 10 min, then held at 0.1 V for 20 min to measure current and IR. This step also functions to activate the performer. The performer is then disconnected from the feeds and allowed to cool to room temperature in air.

(b) Activate the driver. The driver is connected to the feeds and activated in the same manner as the performer.

(c) Execute the RCD test. The load is removed from the driver to return to open-circuit conditions. The driver and performer are shorted as shown in Figure 5.2. The OCV drops immediately after shorting, typically from about 1.05 V to about 0.98 V (see also Fig. 5.9). A 1 h duration is indicated but the test may be lengthened as desired.

(d) Evaluate the performer after RCD. The wires shorting the cells are removed. The performer is connected to the feeds and evaluated as before, concluding the experiment. Test conditions: cells at 50 °C while connected to feeds (room temp. otherwise), anode and cathode humidifiers at 55 °C, H$_2$ and O$_2$ flow rates of 0.2 L/min. For a Ru/C performer, in steps (a) and (d) the cell voltage is maintained at 0.5 V throughout (dashed lines) to avoid catalyst oxidation.
Figure 5.4: Evaluation of (a) a Pt/C performer and (b) an inverted C black performer before and after a 2 h RCD test. Solid symbols indicate initial evaluation; open symbols, final evaluation; triangles, current density; and circles, IR. In (b), some IR points at t < 5 min are missing because the current was too low to perform the measurement. (a) Materials: catalyst loading of 0.5 mgPt cm$^{-2}$ Pt/C with 20% ionomer for both anode and cathode. (b) Materials: catalyst loading of 0.5 mgPt cm$^{-2}$ Pt/C with 20% ionomer for the anode, and 1.0 mg cm$^{-2}$ C black with 30% ionomer for the cathode. Test conditions: cell at 50 °C, anode and cathode humidifiers at 55 °C, H$_2$ and O$_2$ flow rates of 0.2 L/min.
Figure 5.5: *In-situ* CVs of a Pt/C performer cathode before (black) and after a 1 h (blue) or 2 h (red) RCD test. Different but identically prepared MEAs were used for all three tests. Materials: same as Figure 5.4a. CV conditions: cell at 30 °C, humidifiers at 50 °C, scan rate of 10 mV s\(^{-1}\), anode (reference electrode) flow rate of 0.2 L/min H\(_2\), cathode (working electrode) flow rate of 0.05 L/min N\(_2\).
Figure 5.6: Scanning electron micrograph of a Pt/C performer MEA after a 6 h RCD test. Before the test (not shown), the anode and cathode were the same thickness. Six regions visible in this micrograph, three from each electrode, were further characterized by EDS (Table 5.1).
We confirmed this conclusion by running a control: a 2 h test in which the driver and performer were never shorted together so that no RCD took place (not shown). The Pt performer showed minor current loss (1350 to 1150 mA cm\(^{-2}\)) and IR gain (0.128 to 0.138 Ω cm\(^2\)), suggesting little or no corrosion as expected.

We selected IR as the preferred indicator of RCD. Compared to current density, IR is more directly comparable across catalysts. Prior to RCD, the IR should be roughly similar regardless of catalyst choice as long as the same membrane and ionomer are used, whereas current density varies widely due to differences in HOR activity. However, IR is still an imperfect indicator of RCD, since loss of electrical conductivity in the cathode is not the only way in which a fuel cell’s IR may increase. Two additional ways should be mentioned. First, the membrane may degrade during normal operation through mechanisms unrelated to RCD, for example via nucleophilic attack by hydroxide ions. Second, if the cell performance drops for any reason, including but not limited to RCD, the membrane may dehydrate as a result. At low current density the cell produces less water, so the membrane becomes a less efficient ion conductor. These additional mechanisms explain the small IR increase observed in the control, which we term “baseline degradation”.

5.2.2 Catalyst specialization as mitigation strategy

To test our claim that reducing anode ORR activity mitigates RCD, we reproduced Reiser et al.’s Pt-based open-circuit proton cell startup/shutdown model (Fig. 5.7a, orange curve). The left half of the electrolyte potential profile shows the hydrogen region, where the cell operates normally. Although the electrolyte is in contact with both the anode and the cathode, its potential is nearer to HOR equilibrium (≡0 V\text{RHE}) than to ORR equilibrium (1.23 V\text{RHE}) because HOR is much faster. The right half of the profile shows the air region of the anode, where ORR can occur. Proton consumption by ORR lowers the electrolyte potential to about −0.6 V\text{RHE}, at which point ORR on the anode is balanced by COR and OER on the cathode.
Figure 5.7: Impact of anode ORR activity on electrolyte potential during proton cell startup predicted by Reiser et al.’s RCD model. (a) Electrolyte potential versus position. The profile labeled “Pt” is calculated with the original parameters of Reiser et al.; other labels indicate the number of orders of magnitude by which the anode ORR exchange current density was increased or decreased. (b) Electrolyte potential averaged over the air region versus anode ORR activity. The average interfacial potential that drives RCD is the cathode potential of ca. 0.85 V_{RHE} minus the average electrolyte potential shown (e.g., for Pt, 0.85 V − (−0.6 V) = 1.45 V).
Then, we modified the model to predict the effect of increasing and decreasing the ORR exchange current density of the anode catalyst (Fig. 5.7a, all curves). When the anode catalyst is completely inactive, the electrolyte potential profile is essentially flat, indicating that the driving force for RCD is gone: startup and shutdown are no different from normal open-circuit conditions. As activity increases, the electrolyte potential drops monotonically as expected, resulting in a higher difference between the cathode potential (measured to be approx. 850 mV under RCD conditions\textsuperscript{28}) and the electrolyte potential, and thus more overpotential to drive OER and COR on the cathode. This trend is quantified in Figure 5.7b, a plot of average electrolyte potential in the air region versus ORR activity. The large negative slope seen between $-12$ and $-3$ on the x-axis is related in part to the curvature of the profiles. At high activity, a sharp transition is predicted at the hydrogen-air front, but as the activity is decreased, the potential drop becomes not only shallower but also smoother. Since only a 1 mm section of the anode flow channel is shown, the effect of this smoothing is minor during startup/shutdown when the entire length is considered, but it does indicate that a somewhat smaller region of the cell is maximally affected when ORR activity is low. Overall, the model predictions support our claim that reducing the ORR activity of the anode catalyst mitigates RCD in proton cells. Without reparameterizing the model, we assume that this result transfers qualitatively to hydroxide cells.

For hydroxide cells, there are many possible choices for the anode catalyst. Aside from cost, typical selection criteria are high oxidative stability and high HOR activity. To avoid the issue of oxidation, we consider here only four of the most thermodynamically stable catalysts shown in Figure 1.5 (Ru, Pd, Ir, and Pt), all of which also have some HOR activity. Ru is an especially exciting option because a PtRu/C anode catalyst recently showed exceptional hydroxide cell performance.\textsuperscript{2}

We propose that in addition to high stability and HOR activity, low ORR activity is also desirable. Literature measurements of the ORR activities of these catalysts are shown in Table 5.2.\textsuperscript{63–69} Based on the modeling results above, if we control for HOR activity, we hypothesize that differences in ORR activity of these anode catalysts will
Table 5.2: ORR activities of hydroxide cell anode catalysts measured ex situ by RDE (2000-6100 rotations per minute), standardized to RHE.

<table>
<thead>
<tr>
<th>Disk material</th>
<th>Source</th>
<th>Potential at 0.5 mA cm$^{-2}$ Reported (V)</th>
<th>$V_{\text{RHE}}$</th>
<th>Electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>Vracar et al.$^63$</td>
<td>0.07 vs. SHE</td>
<td>0.85</td>
<td>1 M LiOH</td>
</tr>
<tr>
<td>Pt</td>
<td>Tarasevich$^{64-66}$</td>
<td>0.06 vs. SHE</td>
<td>0.83</td>
<td>(pH 13)$^a$</td>
</tr>
<tr>
<td>IrO$_2$$^b$</td>
<td>Chang and Wen$^67$</td>
<td>−0.19 vs. Ag/AgCl</td>
<td>0.82</td>
<td>1 M KOH</td>
</tr>
<tr>
<td>Ru</td>
<td>Anastasijevic et al.$^68$</td>
<td>−0.23 vs. Hg/HgO</td>
<td>0.71</td>
<td>0.1 M NaOH</td>
</tr>
<tr>
<td>C</td>
<td>Taylor and Humffray$^69$</td>
<td>−0.40 vs. Ag/AgCl</td>
<td>0.62</td>
<td>0.8 M NaOH</td>
</tr>
</tbody>
</table>

$^a$ Not reported

$^b$ IrO$_2$-coated Ti disk

dictate the extent of cathode carbon degradation in an experimental RCD test.

Accordingly, we repeated the RCD test for performers with Ru/C, Pd/C, and Ir/C anodes. In all cases the performer cathode and both driver electrodes were still Pt/C. Differences in HOR activity did not affect the RCD test since an identical Pt/C driver anode was exposed to hydrogen each time, and the IR increases observed may be compared across tests since the degradation occurred in identical Pt/C performer cathodes. Thus, we attribute the observed differences in cathode degradation rate to differences in anode ORR activity.

Pd/C and Ir/C performers degraded similarly to the Pt/C performer after a 2 h RCD test ($\Delta\text{IR} = 0.3-0.5 \, \Omega \, \text{cm}^2$, Table 5.3), as expected from their similar ORR activities. Ru/C, the most promising candidate based on its low ORR activity, was compared to Pt/C in greater detail. After a 6 h RCD test, the Ru/C performer showed six times lower IR than the Pt/C performer (1.02 vs. 6.01 $\Omega \, \text{cm}^2$, Fig. 5.8, solid lines). Additionally, during the RCD test itself when the performer and driver cells were shorted together, the OCV of the two-cell system was higher for the Ru/C performer (Fig. 5.9). This indicates slower corrosion; an RCD-immune performer would not decrease the driver’s OCV at all.

Note that to prevent oxidation, the Ru/C performer was evaluated at a higher cell voltage (0.5 vs. 0.1 V). This inconsistency does not compromise the results: the
Figure 5.8: Summary of long-term RCD tests with various performer catalysts. Each point represents the evaluation of performer MEAs before ($t = 0$) or after ($t > 0$) an RCD test. The dashed gray line indicates that for one 6 h test the Pt/C performer was evaluated under the same conditions as a Ru/C performer, at 0.5 instead of 0.1 V. The dashed blue line indicates an inverted RCD configuration for the C black performer (Figs. 5.2b and 5.4b). Fresh driver and performer MEAs were used for every data point past $t = 0$. IR values were obtained by averaging over the final 10 min of the 30 min evaluation. The loading for all electrodes was the same (0.5 mg$_{metal}$ cm$^{-2}$ with 20% ionomer), except for the metal-free C black electrode (1.0 mg cm$^{-2}$ and 30% ionomer). See Figure 5.3 for test conditions.
Table 5.3: Summary of short-term RCD tests with various performer anode catalysts.

<table>
<thead>
<tr>
<th>Performer anode</th>
<th>IR (Ω cm$^2$)</th>
<th>$t = 0$</th>
<th>$t = 2$ h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C</td>
<td>0.130</td>
<td>0.477</td>
<td></td>
</tr>
<tr>
<td>Pd/C</td>
<td>0.152</td>
<td>0.668</td>
<td></td>
</tr>
<tr>
<td>Ir/C</td>
<td>0.107</td>
<td>0.401</td>
<td></td>
</tr>
<tr>
<td>Ru/C</td>
<td>0.465</td>
<td>0.798</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.9: OCV of shorted two-cell systems undergoing RCD. Only the average OCV from the first hour of each test is considered ($n = 6$, error bars indicate ±1 standard error). The data are from the same tests as Figure 5.8.
RCD test itself was unchanged, and in a 6 h test the IR of a Pt/C performer increased similarly whether evaluated at 0.5 or 0.1 V (Fig. 5.8, dashed gray line). But it does explain why the Ru/C cell showed a high IR even before RCD (t = 0). At a higher cell voltage, the current is lower, so the cell produces less water and the electrolyte is less hydrated during evaluation.

Water production is also important in the final evaluation regardless of the cell voltage chosen. After RCD the cell is corroded, and so performs worse and produces less water. In turn the electrolyte dries out, which decreases conductivity and additionally may facilitate chemical degradation of the electrolyte, since water functions as a diluent. Accelerated degradation of the membrane is apparent in Figure 5.4a: whereas in the initial evaluation IR remained constant between t = 10 min and t = 30 min, in the final evaluation IR increased by 80 mΩ cm² over the same time period. The effect is even more pronounced after a longer RCD test or with a low-performance catalyst.

5.2.3 Role of carbon support on the anode

All of the anode catalysts we tested are supported on carbon. Unlike in acid, carbon in base is known to have appreciable ORR activity (Table 5.2). Therefore, it is conceivable that a carbon support alone is sufficient to catalyze ORR on the hydroxide cell anode, regardless of the active metal. To check this possibility we eliminated the metal and tested C black as the catalyst. However, because carbon has no HOR activity, a hydroxide cell with a carbon-only anode would be impossible to evaluate as a fuel cell. Thus, we modified our experimental setup and performed an inverted RCD test as follows. A performer was prepared with a Pt/C anode and a C black cathode. After the initial evaluation, for the RCD test the performer was wired to a driver in a cross configuration with anode connected to cathode and vice-versa, so that the Pt/C performer anode would corrode instead of the C black performer cathode (Fig. 5.2b). The validity of this inverted RCD approach was confirmed in an additional experiment: a Pt/C performer that underwent a 6 h inverted RCD test and one that underwent a
6 h normal RCD test showed similar degradation, suggesting that normal and inverted tests are comparable.

For the C black performer, evaluation after a 2 h inverted RCD test revealed performance and conductance losses (Fig. 5.4b) which we attribute primarily to carbon corrosion of the Pt/C anode. However, we also partly attribute these losses to baseline degradation, which is more significant for a C black performer than for a Pt/C performer since the former produces less water. Specifically, the IR of a control C black performer that was never connected to a driver increased from 0.557 to 0.703 Ω cm$^2$ after 2 h, suggesting that the baseline accounts for about 30% of the degradation observed in the inverted RCD test. The remaining 70% still indicates significant corrosion, so we conclude that the ORR activity of carbon is sufficient to trigger RCD. Extending the inverted RCD test length to 6 h yielded another moderate IR increase (Fig. 5.8, dashed blue line). Overall, our results show that like Ru/C, C black alone is ORR-active enough to drive RCD, but at a greatly reduced rate compared to Pt/C.

In summary, the extent of RCD as judged by IR followed the ORR activity trend from Table 5.2. Pd/C, Ir/C, and Pt/C anodes all caused similar cathode degradation as expected from their similar ORR activities. Catalysts with lower ORR activity, namely a Ru/C anode and, in an inverted test, a C black cathode, caused significantly less degradation than Pt/C.

We report that hydroxide cells, like proton cells, undergo RCD during startup-like conditions. RCD can be curtailed directly without increased system complexity by replacing Pt with an ORR-inactive anode catalyst. Hydroxide cells stand to benefit more than proton cells from this approach because their lower operating potential supports a wider range of non-Pt HOR catalysts, many of which have low ORR activity. Ru is one promising option but its tendency to oxidize may limit its practical application. Due to its enhanced ORR activity in base, we find that the anode carbon support alone suffices to induce ORR, albeit slowly.

Anode catalysts for hydroxide cells are in constant development with the goal of achieving low cost, high stability, and high HOR activity. To mitigate RCD and
improve durability at the cell level, we recommend low ORR activity as an additional catalyst design consideration. Ultimately, carbon-free or supportless anode catalysts may be needed.
Chapter 6

CONCLUSION AND FUTURE WORK

6.1 Conclusion

In summary, hydroxide fuel cells were compared to the more mature proton cell technology. Reproducible, high-performance hydroxide cells were fabricated in order to study water transport and startup/shutdown degradation. Analytical and numerical models supported the experimental findings.

Like the proton cell cathode, the hydroxide cell anode suffers from flooding at high current. Liquid water accumulates on the anode, providing excellent electrolyte hydration but, more importantly, blocking the flow of hydrogen into the cell. Surprisingly, wetproofing the gas diffusion media with poly(tetrafluoroethylene) only makes matters worse, even at low loadings (5-10%). The reason may be the high stoichiometry of local water production, which calls for more aggressive anti-flooding measures. Ideally liquid water would be rerouted to the cathode where it can be consumed to reduce oxygen, for example by introducing water transport channels between active electrode islands.

As in proton cells, the hydroxide cell cathode experiences high interfacial potential during startup/shutdown conditions, corroding the cathode carbon support. A variety of evidence was presented as proof of this corrosion. Scanning electron microscopy indicated thinning of the cathode, consistent with loss of carbon. Energy-dispersive X-ray spectroscopy detected a relative enrichment of platinum in the cathode, which is expected because during corrosion the absolute amount of platinum stays the same while the amount of carbon decreases. In-situ cyclic voltammetry showed that the platinum surface was inaccessible after corrosion due to loss of electrical conductivity.
in the cathode. Most tellingly, this loss of conductivity also resulted in low fuel cell performance due to extremely high ohmic losses (up to 10 Ω cm²).

Since hydroxide cells’ high pH supports a wider range of materials, it is possible to choose anode catalysts like ruthenium with low oxygen reduction activity, knocking out a necessary step in the reverse-current decay mechanism and in turn mitigating cathode corrosion. The main appeal of the hydroxide cell is thought to be the cost savings of non-precious metals, but this same transition from multi-purpose platinum to specialized, distinct anode and cathode catalysts could automatically circumvent one of the most serious modes of fuel cell degradation.

6.2 Recommendations for Future Work

In addition to the electrode patterning route discussed in Section 4.3, another approach to solving the flooding issue in hydroxide cells is to redesign the GDL architecture. The issue with GDLs that were designed for proton cells may be that the wetproofed pores are too small to handle the larger amounts of water present in hydroxide cells. In proton cells, hydrophobic small pores repel water by capillary action ensuring that gas can reach the CL, while large pores and cracks provide paths for liquid water to exit the cell (Fig. 6.1a). But in hydroxide cells, the large pores may not be big enough to for adequate water removal. Wetproofing only makes the pores smaller and less favorable for water flow, leading to the flooding exacerbation shown in Figure 4.2. A possible solution is to design new GDLs with larger pores. Ideally, some small hydrophobic pores would also be present to facilitate reactant delivery under flooded conditions (Fig. 6.1b), but the focus should be on extending the water exit pathways.

There are several natural directions for the reverse-current decay work. First, our catalyst screening was quite limited. Clever experimental design could extend the tests to include metals like Ni that are more prone to oxidation but show even lower ORR activity. Second, while only degradation of the cathode support was considered
Figure 6.1: Illustration of pore size distribution in the GDL (a) before and after wet-proofing and (b) with the large-pore design proposed to improve the water exit pathways in a hydroxide cell.

here, under hydrogen starvation conditions the cell voltage may reverse (i.e., the positive electrode becomes negative and vice-versa). This reversal can corrode the anode support, a phenomenon yet to be studied in hydroxide cells. Third, the role of C on the anode is not completely clear. It should be verified whether C alone is sufficient to trigger RCD on the cathode, by performing our inverted test (Fig. 5.2b) under different conditions and by comparing supported and unsupported anode catalysts.

More broadly, the fundamental challenges the hydroxide fuel cell technology faces are at the materials level. Catalysts should be the primary research focus. Good ORR catalysts like Ag are already available but more work is needed to find a suitably active alternative to Pt for HOR. While they may be ideal for avoiding RCD, non-precious-metal catalysts are in some ways intrinsically less stable than the noble metals and their electrochemical degradation is not well understood.

Electrolytes should be the secondary focus. In bits and pieces, membranes and ionomers have been developed with high conductivity, high resistance to nucleophilic
attack, and good mechanical properties, but no single material shares all of these attributes. Perhaps the most important limitation is the thermal stability of the electrolyte. Typically hydroxide cells operate at 50-60 °C, since at higher temperatures the electrolyte degrades. But if stabler electrolytes were developed for 80 °C operation, the vapor-liquid balance would shift substantially toward the vapor phase, greatly simplifying the flooding and drying issues identified in this work.
REFERENCES


34. R. B. Kaspar and Y. S. Yan, in preparation.


Appendix A

ANALYTICAL WATER MODEL

A.1 Equations and Parameters

The governing equation for water concentration in a hydroxide cell is

$$\frac{dc}{dt} = s - \frac{d}{dx} (J_{\text{diffusion}} + J_{\text{electro-osmosis}}), \quad (A.1)$$

where the flux terms are

$$J_{\text{diffusion}} = -D \frac{dc}{dx} \quad (A.2)$$

$$J_{\text{electro-osmosis}} = n \Phi(x), \quad (A.3)$$

c is water concentration, t is time, s is a source for HOR or sink for ORR, D is the effective diffusion coefficient, x is position (increasing from 0 at the anode to L at the cathode), and n is the number of water molecules each hydroxide ion carries. The value of $\Phi$, the flux of hydroxide ions, varies with position: in the GDLs, which contain no electrolyte, it is zero; in the membrane, constant (proportional to the current density); and in the CLs between the GDLs and membrane, a linear ramp function (see assumptions below).

At steady state integrating twice yields

$$c = \frac{1}{D} \left[ n \int \Phi(x) \, dx - \frac{s}{2} x^2 + \alpha x + \beta \right] \quad (A.4)$$

piecewise for each region. The integration constants $\alpha$ and $\beta$ were found by solving the model equations and boundary conditions

$$c(0) = \text{const.} \quad (A.5)$$
Table A.1: Water model parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effective diffusion coefficient of water in:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Membrane</td>
<td>$5.00 \times 10^{-7}$ m$^2$ s$^{-1}$</td>
<td>44,70,71$^a$</td>
</tr>
<tr>
<td>Unwetproofed GDL</td>
<td>$3.00 \times 10^{-7}$ m$^2$ s$^{-1}$</td>
<td>72</td>
</tr>
<tr>
<td>50% wetproofed GDL</td>
<td>$1.50 \times 10^{-7}$ m$^2$ s$^{-1}$</td>
<td>72$^b$</td>
</tr>
<tr>
<td>CL</td>
<td>$1.50 \times 10^{-7}$ m$^2$ s$^{-1}$</td>
<td>c</td>
</tr>
<tr>
<td>Source term in anode CL</td>
<td>$1.87 \times 10^5$ g m$^{-3}$ s$^{-1}$</td>
<td>d</td>
</tr>
<tr>
<td>Source term in cathode CL</td>
<td>$-9.37 \times 10^4$ g m$^{-3}$ s$^{-1}$</td>
<td>d</td>
</tr>
<tr>
<td>Number of water molecules each OH$^-$ carries</td>
<td>4.00</td>
<td>73,74$^a$</td>
</tr>
<tr>
<td>Thickness of membrane</td>
<td>$1.00 \times 10^{-5}$ m</td>
<td>Tokuyama</td>
</tr>
<tr>
<td>Thickness of CL</td>
<td>$5.00 \times 10^{-6}$ m</td>
<td>e</td>
</tr>
<tr>
<td>Thickness of GDL</td>
<td>$1.90 \times 10^{-4}$ m</td>
<td>Toray</td>
</tr>
<tr>
<td>Water concentration in humidified feed</td>
<td>$1.96 \times 10^2$ g m$^{-3}$</td>
<td>f</td>
</tr>
<tr>
<td>Water concentration in unhumidified feed</td>
<td>0</td>
<td>N/A</td>
</tr>
</tbody>
</table>

$^a$ See notes in text  
$^b$ Wetproofing is assumed to lower porosity as described in Section 4.1  
$^c$ Assumed to be similar to the wetproofed GDL  
$^d$ Calculated from a current density of 500 mA cm$^{-2}$  
$^e$ Typical value; see for example Gasteiger et al.$^{75}$  
$^f$ Calculated assuming passing through a 70 °C humidifier saturates the feed

\[
c(L) = \text{const.} \quad (A.6)
\]

together as a linear system, with the boundary values determined by the saturation pressure of water inside humidifiers at the temperatures of interest.

Table A.1 shows the values of the model parameters.$^{44,70-74}$ A high value was chosen for the effective diffusion coefficient in the membrane ($5 \times 10^{-7}$ m$^2$ s$^{-1}$ vs. $10^{-10}$ to $10^{-9}$ m$^2$ s$^{-1}$). With lower values, a large concentration drop is predicted and the cathode concentration falls below the boundary humidification level, which would contradict the observation of Zhang et al. that both outlets contain liquid water regardless of current density.$^{44}$
A.2 Mathematica Code

(* Run in Mathematica 10.1 *)

ps = {{Black, Thickness[.005]}, (* *)
   {Green, Thickness[.005]}, (* Plot 4 lines corresponding *)
   {Red, Thickness[.005]}, (* to curves a–d in the figure. *)
   {Black, Thickness[.005]}};

pr = {{11 - 15*10^-6, 14 + 15*10^-6}, (* Plot range for x & y axes *)
   {0, 600}};

n = {4, 4, 4, 4}; (* Electro-osmotic drag coeff. (one entry per plot) *)

(* Diffusion constants, all in m^-2 s^-1 *)
hi = 3*^-7; (* High: unwetproofed *)
lo = 1.5*^-7; (* Low: wetproofed *)
cl = 1.5*^-7; (* Catalyst layer *)
d = 5*^-7; (* Membrane *)

d1 = {lo, hi, lo, hi}; (* *)
d2 = {cl, cl, cl, cl}; (* Diffusion constants in the 5 cell regions. *)
d3 = {d, d, d, d}; (* For a–d, parameterization differs only in *)
d4 = {cl, cl, cl, cl}; (* the GDLs; for e & f, d1 = d5 = {hi, hi}. *)
d5 = {lo, lo, hi, hi}; (* *)

(* Partial pressure of water in the feeds, either high or low *)

pa = {ph, ph, ph, ph}; (* e & f: {ph, pl} *)
pc = {ph, ph, ph, ph}; (* e & f: {pl, ph} *)

j1 = {}; b1 = {}; a2 = {}; b2 = {}; j3 = {}; b3 = {}; a4 = {}; b4 = {}; j5 = {}; b5 = {};
w = {0, 0, 0, 0};

For[i = 1, i <= Length[ps], i++,
    Clear[x, j1s, b1s, a2s, b2s, j3s, b3s, a4s, b4s, j5s, b5s,
       d1s, d2s, d3s, d4s, d5s, pas, pcs, ws, s2s, s4s];
    j = 5000; (* Current density, A m^-2 = 0.5 A cm^-2 *)}
\( F = 96485; \) (*Faraday constant, s A mol\(^{-1}\)*)

\( w[[i]] = n[[i]] \ast j/F; \) (*Electro-osmotic drag, mol m\(^{-2}\) s\(^{-1}\]*)

\( l\text{GDL} = 190 \ast 10^{-6}; \) (* *)

\( l\text{Elec} = 5 \ast 10^{-6}; \) (* Thickness of each region, m. *)

\( l\text{Mem} = 10 \ast 10^{-6}; \) (* *)

\( p_l = 0.; \) (*mol m\(^{-3}\]*)

\( p_h = 10.9; \) (*mol m\(^{-3}\]*)

\( s = 10400/2; \) (*mol m\(^{-3}\) s\(^{-1}\]*)

\( s_2 = 2 \ast s; \) (*Source term in anode CL*)

\( s_4 = -1 \ast s; \) (*Sink term in cathode CL*)

10 = 0; (* *)

11 = l\text{GDL}; (* Location on the *)

12 = l\text{GDL} + l\text{Elec}; (* x-axis for the *)

13 = l\text{GDL} + l\text{Elec} + l\text{Mem}; (* beginning of each *)

14 = l\text{GDL} + 2 l\text{Elec} + l\text{Mem}; (* region. *)

15 = 2 l\text{GDL} + 2 l\text{Elec} + l\text{Mem}; (* *)

**Do**

\( \text{Evaluate}[ j[[1]]] = j[[2]][[1]] ];

\( \{ j, \{\{d1s, d1\}, \{d2s, d2\}, \{d3s, d3\}, \{d4s, d4\}, \{d5s, d5\}, \{pas, pa\}, \{pcs, pc\}, \{ws, w\}\}\};

s = **Solve**[( (*Solve the linear system A x = b*)

\( \{-11/d1s, 1, -11, -1, 0, 0, 0, 0, 0, 0\}, \)

\( \{1, 0, d2s, 0, 0, 0, 0, 0, 0, 0\}, \)

\( \{0, 0, -12, -1, -12/d3s, 1, 0, 0, 0, 0\}, \)

\( \{0, 0, d2s, 0, 1, 0, 0, 0, 0, 0\}, \)

\( \{0, 0, 0, 0, -13/d3s, 1, -13, -1, 0, 0\}, \)

\( \{0, 0, 0, 0, 1, 0, d4s, 0, 0, 0\}, \)

\( \{0, 0, 0, 0, 0, -14, -1, -14/d5s, 1\}, \)

\( \{0, 0, 0, 0, 0, d4s, 0, 1, 0\}, \)

\( \{0, -1, 0, 0, 0, 0, 0, 0, 0, 0\}, \)

\( \{0, 0, 0, 0, 0, 0, 0, 0, 0, 15/d5s, -1\} \}

) (* { j1s },

75
\[
\begin{align*}
\{b1s\}, \\
\{a2s\}, \\
\{b2s\}, \\
\{j3s\}, \\
\{b3s\}, \\
\{a4s\}, \\
\{b4s\}, \\
\{j5s\}, \\
\{b5s\}
\end{align*}
\]

\[
\{−s2 \, 11 \, \text{⋯} / (2 \, d2s) + \text{ws} \, 11 \, \text{⋯} 2 / (2 \, s2s * (12 - 11))\},
\{s2 \, 11\},
\{−s2 \, 12 \, \text{⋯} 2 / (2 \, d2s) + \text{ws} \, 12 / d3s
+ (\text{ws} / d2s) * (11 \, 12 - 12 \, \text{⋯} 2 / 2 / (12 - 11))\},
\{s2 \, 12\},
\{−s4 \, 13 \, \text{⋯} 2 / (2 \, d4s) + \text{ws} \, 13 / d3s
- (\text{ws} / d4s) * (13 + 13 \, \text{⋯} 2 / 2 \, s2(14 - 13))\},
\{s4 \, 13\},
\{−s4 \, 14 \, \text{⋯} 2 / (2 \, d4s)
- (\text{ws} / d4s) * (14 - (14 \, \text{⋯} 2 / 2 - 13 \, 14) / (14 - 13))\},
\{s4 \, 14\},
\{−pcs\},
\{−pas\}
\}
\), \{j1s, b1s, a2s, b2s, j3s, b3s, a4s, b4s, j5s, b5s\};

\text{AppendTo}[j1, \text{N}[\text{First}[j1s, s]]];
\text{AppendTo}[b1, \text{N}[\text{First}[b1s, s]]];
\text{AppendTo}[a2, \text{N}[\text{First}[a2s, s]]];
\text{AppendTo}[b2, \text{N}[\text{First}[b2s, s]]];
\text{AppendTo}[j3, \text{N}[\text{First}[j3s, s]]];
\text{AppendTo}[b3, \text{N}[\text{First}[b3s, s]]];
\text{AppendTo}[a4, \text{N}[\text{First}[a4s, s]]];
\text{AppendTo}[b4, \text{N}[\text{First}[b4s, s]]];
\text{AppendTo}[j5, \text{N}[\text{First}[j5s, s]]];
\text{AppendTo}[b5, \text{N}[\text{First}[b5s, s]]];
c = 18 (*Last-minute conversion factor: mol m$^{-3}$ to g m$^{-3}$*);

(*Messy code to show plots piece by piece! No time to clean it up.*)

Show(*5 cell regions * 4 plots = 20 plot pieces*)

Plot[c*(-(j1[[1]])/d1[[1]])*x + b1[[1]]], {x, 11 - 10*10^{-6}, 11},
PlotStyle -> ps[[1]]],
Plot[c*(-(s2/d2[[1]])*x^2/2 + a2[[1]]*x + b2[[1]]
- (w[[1]]/d2[[1]])*(x^2/2 - 11*x)/(12 - 11)),
{x, 11, 12}, PlotStyle -> ps[[1]]],
Plot[c*(-((j3[[1]] + w[[1]])/d3[[1]])*x + b3[[1]]], {x, 12, 13},
PlotStyle -> ps[[1]]],
Plot[c*(-((j1[[2]])/d1[[2]])*x + b1[[2]]], {x, 11 - 10*10^{-6}, 11},
PlotStyle -> ps[[2]]],
Plot[c*(-(s2/d2[[2]])*x^2/2 + a2[[2]]*x + b2[[2]]
- (w[[2]]/d2[[2]])*(x^2/2 - 11*x)/(12 - 11)), {x, 11, 12},
PlotStyle -> ps[[2]]],
Plot[c*(-((j3[[2]] + w[[2]])/d3[[2]])*x + b3[[2]]], {x, 12, 13},
PlotStyle -> ps[[2]]],
Plot[c*(-(j5[[1]])/d5[[1]])*x + b5[[1]]],
{x, 14, 14 + 10*10^{-6}, PlotStyle -> ps[[1]]],
Plot[c*(-(j1[[2]])/d1[[2]])*x + b1[[2]]], {x, 11 - 10*10^{-6}, 11},
PlotStyle -> ps[[2]]],
Plot[c*(-(s2/d2[[2]])*x^2/2 + a2[[2]]*x + b2[[2]]
- (w[[2]]/d2[[2]])*(x^2/2 - 11*x)/(12 - 11)), {x, 11, 12},
PlotStyle -> ps[[2]]],
Plot[c*(-((j3[[2]] + w[[2]])/d3[[2]])*x + b3[[2]]], {x, 14, 14 + 10*10^{-6}},
PlotStyle -> ps[[2]]],
Plot[c*(-(j5[[2]])/d5[[2]])*x + b5[[2]]], 
{x, 14, 14 + 10*10^{-6}, PlotStyle -> ps[[2]]],
Plot[c*(-((j1[[3]])/d1[[3]])*x + b1[[3]]], {x, 11 - 10*10^{-6}, 11},
PlotStyle -> ps[[3]]],
Plot[c*(-(s2/d2[[3]])*x^2/2 + a2[[3]]*x + b2[[3]]
- (w[[3]]/d2[[3]])*(x^2/2 - 11*x)/(12 - 11)), {x, 11, 12},
PlotStyle -> ps[[3]]],
Plot[c*(-((j3[[3]] + w[[3]])/d3[[3]])*x + b3[[3]]], {x, 12, 13},
PlotStyle -> ps[[3]]]
PlotStyle -> ps[[3]]]},
Plot[c*(-(s4/d4[[3]])*x^2/2 + a4[[3]]*x + b4[[3]]
- (w[[3]]/d4[[3]])*(x - (x^2/2 - 13*x)/(14 - 13))),
{x, 13, 14}, PlotStyle -> ps[[3]]],
Plot[c*(-(j5[[3]]/d5[[3]])*x + b5[[3]]), {x, 14, 14 + 10*10^-6},
PlotStyle -> ps[[3]]],
Plot[c*(-(j1[[4]]/d1[[4]])*x + b1[[4]]), {x, 11 - 10*10^-6, 11},
PlotStyle -> ps[[4]]],
Plot[c*(-(s2/d2[[4]])*x^2/2 + a2[[4]]*x + b2[[4]]
- (w[[4]]/d2[[4]])*(x^2/2 - 11*x)/(12 - 11)), {x, 11, 12},
PlotStyle -> ps[[4]]],
Plot[c*(((j3[[4]] + w[[4]])/d3[[4]])*x + b3[[4]]), {x, 12, 13},
PlotStyle -> ps[[4]]],
Plot[c*(-(s4/d4[[4]])*x^2/2 + a4[[4]]*x + b4[[4]]
- (w[[4]]/d4[[4]])*(x - (x^2/2 - 13*x)/(14 - 13))),
{x, 13, 14}, PlotStyle -> ps[[4]]],
Plot[c*(-(j5[[4]]/d5[[4]])*x + b5[[4]]), {x, 14, 14 + 10*10^-6},
PlotStyle -> ps[[4]]],
PlotRange -> pr,
AxesOrigin -> {11 - 15.*10^-6, 0},
Axes -> {False, True},
ImageSize -> 975,
LabelStyle -> Directive[FontFamily -> "Helvetica", FontSize -> 30],
AxesStyle -> Thick,
AspectRatio -> .7}
Appendix B
NUMERICAL REVERSE-CURRENT DECAY MODEL

B.1 Equations and Parameters

The governing equation for electrolyte potential in a proton cell during start-up/shutdown is

$$\Phi''(x) = \sum_{i=1}^{5} \beta_i e^{\gamma \Phi(x)},$$  \hspace{1cm} (B.1)

where $\Phi$ is electrolyte potential, $x$ is position on the anode (see x-axis of Fig. 5.7a), and $\beta$ and $\gamma$ are constants. Each term in the summation represents a Butler-Volmer process corresponding to Figure 5.1a. Specifically, for each reaction,

$$\beta = \frac{i_0 L A p}{n k t_m}$$  \hspace{1cm} (B.2)

$$\gamma = \frac{\alpha n F (V_{\text{equilibrium}} - V_{\text{electrode}})}{RT},$$  \hspace{1cm} (B.3)

where $i_0$ is the exchange current density, $L$ is the catalyst loading, $A$ is the specific surface area of the catalyst, $p$ is the partial pressure of the reactant gas (if applicable; for example, the only reactants in COR are solid carbon and water or hydroxide ions), $n$ is the number of electrons transferred, $\alpha$ is the transfer coefficient, $V_{\text{electrode}}$ is the potential of the electrode where the reaction takes place, and $V_{\text{equilibrium}}$ is the equilibrium potential. $F$ is the Faraday constant, $k$ is the ionic conductivity, $t_m$ is the thickness of the membrane, $R$ is the gas constant, and $T$ is temperature, which are the same for all reactions. Additionally, the sign of $\beta$ depends on whether the reaction is a reduction or oxidation process. On the boundary, $\Phi'(x) = 0.$
Table B.1: Reverse-current decay model parameters. Physical parameters are taken from Reiser et al.\textsuperscript{28}

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Physical:</strong></td>
<td></td>
</tr>
<tr>
<td>Anode potential</td>
<td>0.00 V</td>
</tr>
<tr>
<td>Cathode potential</td>
<td>0.85 V</td>
</tr>
<tr>
<td>Pt loading in CL</td>
<td>$4.00 \times 10^{-4}$ g cm(^{-2})</td>
</tr>
<tr>
<td>Pt electrochemical surface area</td>
<td>$6.00 \times 10^5$ cm(^2) g(^{-1})</td>
</tr>
<tr>
<td>C loading in CL</td>
<td>$4.00 \times 10^{-4}$ g cm(^{-2})</td>
</tr>
<tr>
<td>C electrochemical surface area</td>
<td>$6.00 \times 10^6$ cm(^2) g(^{-1})</td>
</tr>
<tr>
<td>Membrane thickness</td>
<td>$1.50 \times 10^{-5}$ m</td>
</tr>
<tr>
<td>Membrane conductivity</td>
<td>0.10 S cm(^{-1})</td>
</tr>
<tr>
<td>Temperature</td>
<td>338 K</td>
</tr>
<tr>
<td>Length of modeled domain</td>
<td>$1.00 \times 10^{-3}$ m</td>
</tr>
<tr>
<td>COR equilibrium potential</td>
<td>0.50 V</td>
</tr>
<tr>
<td>COR exchange current density</td>
<td>$6.06 \times 10^{-19}$ A cm(_{\text{C}}^2)</td>
</tr>
<tr>
<td>COR transfer coefficient</td>
<td>0.25</td>
</tr>
<tr>
<td>COR number of electrons</td>
<td>4.00</td>
</tr>
<tr>
<td>HOR equilibrium potential</td>
<td>$\equiv$ 0 V</td>
</tr>
<tr>
<td>HOR exchange current density</td>
<td>$1.00 \times 10^{-3}$ A cm(_{\text{Pt}}^2)</td>
</tr>
<tr>
<td>HOR transfer coefficient</td>
<td>1.00</td>
</tr>
<tr>
<td>HOR number of electrons</td>
<td>2.00</td>
</tr>
<tr>
<td>ORR/OER equilibrium potential</td>
<td>1.23 V</td>
</tr>
<tr>
<td>ORR/OER exchange current density</td>
<td>$1.00 \times 10^{-9}$ A cm(_{\text{Pt}}^2)</td>
</tr>
<tr>
<td>ORR/OER transfer coefficient</td>
<td>0.75</td>
</tr>
<tr>
<td>ORR/OER number of electrons</td>
<td>4.00</td>
</tr>
<tr>
<td><strong>Numerical:</strong></td>
<td></td>
</tr>
<tr>
<td>Number of grid points</td>
<td>200</td>
</tr>
<tr>
<td>Degree of successive <em>under</em>-relaxation</td>
<td>0.10</td>
</tr>
<tr>
<td>Initial nonlinearity $p$ from parameter continuation</td>
<td>$1.00 \times 10^{-6}$</td>
</tr>
<tr>
<td>Relative increase of $p$ per step (fraction of previous value)</td>
<td>$1.00 \times 10^{-4}$</td>
</tr>
<tr>
<td>Minimum absolute increase of $p$ per step</td>
<td>$5.00 \times 10^{-5}$</td>
</tr>
<tr>
<td>Maximum (final) value of $p$</td>
<td>1</td>
</tr>
</tbody>
</table>
The presence of the dependent variable inside an exponential function makes the ODE highly nonlinear. To obtain \( \Phi(x) \) numerically, we performed a first-order Taylor expansion on the exponential function to yield the linearized ODE

\[
\Phi''(x) = \sum_{i=1}^{5} \beta_i [1 + \gamma_i \Phi(x)].
\] (B.4)

We discretized the domain onto a grid and approximated the linearized ODE by finite differences. Following an explicit method, parameter continuation was applied to transition incrementally from the linear to the nonlinear ODE at each time step. After fully recovering the nonlinear problem, the iterations were continued until convergence criteria were reached. To improve stability, convergence was slowed by under-relaxation for all time steps.

To find the effect of anode ORR activity on electrolyte potential, we varied the exchange current density (contained in \( \alpha \) above) for the anode ORR term and repeated the calculation. Otherwise, we used the same proton cell parameters as Reiser et al., as shown in Table B.1 along with numerical parameters. To be consistent with the original model, the oxidant flowed through the cell was air, although in our experimental hydroxide cell setup we use pure oxygen. We did not reparameterize the model for a hydroxide cell; this is a direction for future work, though we expect the results to be qualitatively similar.

### B.2 Python Code

```python
#!/usr/local/bin/python
# Run in Python 2.7.3

import matplotlib
matplotlib.use('Agg') # Plot headless (box I ran this on has no monitor)
import numpy, math, pylab

# Assorted constants
OUTFILE_PRE = 'out'
```

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OUTFILE_EXT = ' .png '  

PLOT_EVERY_N = 1*10**4  

W_I = 1.*10**−1 # Parameter for successive over−relaxation  
P_I = 10**−6 # Initial rate of parameter continuation  
P_GROWTH = 10**−4 # Increase per step (fraction of current value)  
P_MIN_GROWTH = 5*10**−5 # Minimum absolute increase per step  
e = math.e  
N_POINTS = 200 + 1  

H0 = 1.*10**−4 # Grid parameters (L set to 1)  
X_MIN = 0. #  
X_MAX = 0.1 # (cm)  

# Electrochemical constants (see table in Reiser 2005)  
aC = 2.50 * 10**−1  
AC = 6.00 * 10**6  
aH2 = 1.00  
aO2 = 7.50 * 10**−1  
APt = 6.00 * 10**5  
F = 9.65 * 10**4 # My units (C mol−1)  
i0C = 6.06 * 10**−19  
i0H2 = 1.00 * 10**−3  
i0O2 = 1.00 * 10**−9  
k = 1.00 * 10**−1  
L = X_MAX − X_MIN  
LC = 4.00 * 10**−4  
LPt = 4.00 * 10**−4  
nC = 4.00  
nH2 = 2.00  
nO2 = 4.00  
R = 8.31 # My units (J K−1 mol−1)  
T = 6.50 * 10**1 + 273 # C −> K  
tm = 1.50 * 10**1 / 10**4 # um −> cm  
V_Ceq = 5.00 * 10**−1  
V_H2eq = 0.00  
V_ma = V_H2eq
\[ V_{mc} = VH_{2eq} + 0.85 \]

\[ VO_{2eq} = VH_{2eq} + 1.23 \]

\[ \text{HANDICAP} = 10^{**0} \quad \# \text{Multiply Pt's ORR activity by this} \]

\[ \# \text{Originally I was going to use a variably spaced grid but I stayed} \]
\[ \# \text{with a uniform one, so this is more complicated than necessary.} \]

\[ dx = [H_0] \]

\[ \text{tot} = H_0 \]

\[ \text{for} \quad \text{in range}((N_{POINTS}-1) / 2): \quad \# \text{Generate spacings for half the grid} \]
\[ \quad \text{dx.append}(dx[-1] * (1 + dx[-1])) \]
\[ \quad \text{tot} += \text{dx[-1]} \]
\[ \quad \text{upperHalf} = \text{dx} \]
\[ \quad \text{lowerHalf} = \text{list}(\text{dx}) \]
\[ \quad \text{lowerHalf.reverse}() \quad \# \text{Same spacings (symmetrically) for the other half} \]
\[ \quad \text{dx} = \text{lowerHalf} + \text{upperHalf} \]

\[ x = [0.] \]

\[ \text{for} \quad d \quad \text{in} \quad \text{dx}[1:-1]: \quad \# \text{Generate the grid} \]
\[ \quad x.append(x[-1] + d) \]

\[ xRange = x[-1] \quad \# x[0] == 0 \]
\[ x = [el * (X_{MAX} - X_{MIN}) / xRange \quad \text{for} \quad el \quad \text{in} \quad x] \quad \# \text{Scale to physical size} \]

\[ \text{def} \quad \text{step}(y, w, p): \]
\[ \quad \text{DDy} = \text{estimate_{DDy}}(y) \quad \# \text{LHS of } y''(x) = f(y(x)) \]
\[ \quad \text{fy} = \text{get}_{fy}(y, p) \quad \# \text{RHS of same} \]
\[ \quad \text{error} = \text{get}_{error}(\text{DDy}, \text{fy}) \]

\[ yNew = [] \]

\[ \text{for} \quad i \quad \text{in range}(N_{POINTS}): \]
\[ \quad yim1, yip1, him1, hi = \text{get}_{yi}\_hi}(y, dx, i) \]
\[ \quad yi = w * ((him1 * yip1 + hi * yim1) / (him1 + hi)\]
\[ \quad \quad - hi * him1 * fy[i] / 2) + (1-w) * y[i] \]
```python
yNew.append(yi)

return (yNew, error)

def estimate_DDy(y):
    DDy = []

    for i in range(N_POINTS):
        yim1, yip1, him1, hi = get_yi_hi(y, dx, i)
        DDy.append(2 * ((yip1 - y[i]) / hi - (y[i] - yim1) / him1) / (hi + him1))

    return DDy

def get_fy(y, p):
    fy = []

    for i in range(N_POINTS):
        if x[i] < L/2:
            PH2 = 1
        else:
            PH2 = 0

        PO2 = 1 - PH2

        yi = y[i]

        Na = i0H2/nH2 * PH2 * e**((Vma - VH2eq - yi) * aH2*nH2*F/(R*T)) #
        HANDICAP * i0O2/nO2 * PO2 * #
        e**((Vma - VO2eq - yi) * (aO2-1)*nO2*F/(R*T))

        Nc = (e**((Vmc - VO2eq - yi) * aO2*nO2*F/(R*T)) - \ #
            PO2 * e**((Vmc - VO2eq - yi) * (aO2-1)*nO2*F/(R*T)) * i0O2/nO2 * \ #
            i0C*LC*AC/(nC*LPt*APt) * e**((Vmc - Vceq - yi) * aC*nC*F/(R*T)) ~\ #

        # Linearized form of governing equation for parameter continuation
        NaL = i0H2/nH2 * PH2 * (1 + (Vma - VH2eq - yi) * aH2*nH2*F/(R*T)) - \ #
            HANDICAP * i0O2/nO2 * PO2 * (1 + (Vma - VO2eq - yi) * \ #
            (aO2-1)*nO2*F/(R*T))

        NcL = ((1 + (Vmc - VO2eq - yi) * aO2*nO2*F/(R*T)) - \ #
```

\[
PO2 \times \left(1 + \left(Vmc - VO2eq - y_i\right) \times (aO2-1) \times nO2 \times F / (R \times T)\right) \times \\
\times iO2 / nO2 + i0C \times LC \times AC / (nC \times LPt \times APt) \times \\
\left(1 + \left(Vmc - VCeq - y_i\right) \times aC \times nC \times F / (R \times T)\right)
\]

fy.append(\(-LPt \times APt \times (p*(Na + Nc) + (1-p)*(NaL + NcL)) / (k \times tm)\))

return fy

def get_yi_hi(y, dx, i):
    him1 = dx[i-1]
    hi = dx[i]

    if i==0:
        yim1 = \((him1 / hi)*2 \times (y[1] - y[0]) + y[0]\)
    else:
        yim1 = y[i-1]

    if i==N_POINTS-1:
        yip1 = \((hi / him1)*2 \times (y[-2] - y[-1]) + y[-1]\)
    else:
        yip1 = y[i+1]

    return (yim1, yip1, him1, hi)

def get_error(list1, list2):
    sumOfSquares = 0

    for i in range(N_POINTS):
        sumOfSquares += (list1[i] - list2[i])**2

    return sumOfSquares

def plot(x, y, fileName, log=False):
    matplotlib.pyplot.clf()
    matplotlib.pyplot.cla()
    if log:
matplotlib.pyplot.yscale('log')
matplotlib.pyplot.scatter(x, y)
matplotlib.pyplot.plot(x, y)
matplotlib.pyplot.axis([0.0, 0.10, -0.7, 0.9])
pylab.savefig(fileName)

plot(range(len(dx)), dx, 'grid.png', True)  # After defs

dy = (0.1 - 0) / (N_POINTS - 1)
y = [0. + i * dy**2 for i in range(N_POINTS)]

w = W_I
p = P_I
plotCount = 0
errors = []
error = 10 + 1  # Arbitrary large number
while error > 10:
    if plotCount % PLOT_EVERY_N == 0:
        fNumber = str(plotCount)
        while len(fNumber) < len(str(10**7)):
            fNumber = '0' + fNumber
        plot(x, y, OUTFILE_PRE + fNumber + OUTFILE_EXT)
    (y, error) = step(y, w, p)
    plotCount += 1
    if p < 1.:
        p = min(1., p * (1 + PGROWTH), p + P_MIN_GROWTH)

# Export result
f = open(OUTFILE_PRE + '.txt', 'w')
for i in range(len(x)):
    f.write('{' + '.4f}\t{' + '.4f}\n'.format(x[i], y[i]))
    f.close()