

Impedance-Resolved Performance and Durability in Redox Flow Batteries

**A Dissertation Presented for the
Doctor of Philosophy
Degree
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DEDICATION

To my father, Hooshmand, for instilling a curiosity about the world and a love for the sciences.
To my mother, Donna, for teaching me to always care about others.

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ABSTRACT

The realization of redox flow batteries (RFBs) as a grid-scale energy solution depends on improving the performance and lifetime of the technology to decrease the high capital costs. The electrodes are a key component in the RFB; performance enhancement is often achieved through chemical or thermal treatments of commercially available porous carbon materials.

This dissertation uses impedance spectroscopy-based methods to gain insight into performance and durability in RFBs, enabling intelligent cell design. Initial work focused on understanding the impact of improved electrode and membrane properties on system performance. An accelerated stress test was then developed that can be used to screen materials for durability. Given the significant need for advanced diagnostics to understand the changes in performance, subsequent work improved upon the state of the art in impedance spectroscopy for RFBs. This method enabled measurement of finite diffusion resistance under typical laboratory conditions. A previously developed macrohomogeneous porous electrode impedance model was used to interpret impedance data.

With the improved impedance method, the effects of treatment on beginning-of-life performance and durability were elucidated for a series of treatments applied to SGL GFD3 carbon felt. Kinetic deterioration occurred on the negative side and was primarily due to a decrease in the inherent kinetic activity of the surface. The impedance-resolved method identified the excellent electrochemical stability of an ammonia heat treated carbon felt and a long-term cycling experiment conclusively verified this result. The impedance method was also successfully applied to a non-aqueous flow battery chemistry. Finally, a method to passively improve capacity retention was also developed and successfully demonstrated.

The major outcome of this dissertation is the robust methodology for evaluating various aspects of cell design in RFBs, advancing the state of the art for measuring performance and degradation. We demonstrate the broad applicability of a previously developed macrohomogeneous porous electrode model to quantify and resolve ohmic, charge transfer, and finite diffusion processes. Successful application of these methods represents a pathway toward intelligent cell design to optimize performance and lifetime, ultimately improving the viability of RFBs as a grid-scale energy storage solution.

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CHAPTER 1 INTRODUCTION

1.1 Motivation

While fossil energy has fueled the industrialization of the world, it is finite and the predominant source of anthropogenic greenhouse gas emissions. The development of sustainable energy sources, such as wind and solar, is important for reducing the environmental impact of our energy-driven society. Due to the inherent intermittency of wind and solar power, grid-scale storage must be utilized to enable significant penetration of these renewables into the electric grid.^{1,2} In addition to leveling out the intermittency of renewable power generation, energy storage can provide other grid services including: peak shaving, frequency regulation, load shifting, and emergency back-up power.^{1,2}

Several types of energy storage technologies are available, including mechanical, thermal, and electrochemical-based systems. Mechanical systems include pumped hydroelectric, compressed air, and flywheels. Thermal energy storage involves the storage of heat in various media such as molten salts. Electrochemical energy storage devices include batteries, electrolyzers, and electrochemical double-layer capacitors. In addition to power and energy-related capital and operational costs (\$/kW and \$/kWh), performance metrics for energy storage technologies include roundtrip energy efficiency, response time, ramp rate, energy capacity, power capacity, and cycle life, among others.³ The energy storage application dictates which of these metrics is most important.

Similar to traditional enclosed batteries (e.g. lithium-ion, lead-acid), a newer class of open systems known as flow batteries can operate with high roundtrip efficiency and possess a rapid response time and ramp rate. An advantage of flow batteries over other storage systems is

the complete decoupling of system power and energy capacity, allowing for flexible system design. Flow batteries also have the potential for long cycle lifetimes.² These advantages have led to a resurgence in flow battery research in recent years, particularly focused on reduced cost through development of new chemistries and performance enhancement, i.e. increased power and energy density. Although these studies are necessary to achieve commercial viability, they are not sufficient for widespread adoption of flow battery technologies for grid-scale applications. As highlighted by several recent reviews,⁴⁻⁶ further work is needed to understand degradation mechanisms in flow battery devices to ensure the long cycle life demanded for deployment.

To date, only a handful of studies discuss drivers for decreased performance, i.e. reduced round-trip efficiency, energy capacity, or power capacity, etc.⁷⁻¹² These studies provide little mechanistic understanding as to which components change and how these changes affect battery performance. This thesis establishes methods to study the time evolution of flow battery electrode performance and provides evidence-based insight into why battery performance degrades. Application of these methods can guide design of next-generation electrode materials with enhanced stability, improving the cycle life of installed flow battery systems. We apply these methods to analyze the effects of multiple chemical and thermal treatments on electrode performance and beginning-of-life durability. The all-vanadium redox flow battery (VRFB) is the most studied chemistry¹³⁻¹⁵ and is the focus in the majority of this work, though the methods developed herein can be applied to understand electrode degradation with any liquid-phase flow battery chemistry.

1.2 Flow battery overview

1.2.1 Architecture

Flow batteries can be traced to a German patent in 1949, as described in a recent review.¹⁶ NASA continued pioneering a variety of chemistries and designs in the 1970s and the all-vanadium redox flow battery was proposed in the 1980s by researchers at the University of New South Wales in Australia.¹⁷ Combining aspects of fuel cells and traditional enclosed batteries, flow batteries consist of a stack and rechargeable electroactive species dissolved in liquid electrolytes stored in external tanks. The electrolyte solutions often contain a supporting electrolyte such as sulfuric acid to provide sufficient ionic conductivity in the liquid. The electrolyte solutions circulate through the stack shown in Figure 1.1, which consists of repeated unit cells similar in architecture to a fuel cell. Each unit cell consists of two compartments divided by a separator; the separator is electronically insulating but ionically conductive. Within each compartment is a porous conductive electrode material compressed between the separator and a conductive bipolar plate (typically a graphite composite). This plate serves the dual purpose of collecting current and delivering electrolyte into the porous electrode; thus, it is often referred to as a flow field. A channel-land pattern for electrolyte transport is etched into the flow field surface; in a stack configuration, the plate also contains manifolds to distribute electrolyte through all cells in the stack

When electricity is supplied (electrolytic/charge mode), the electroactive specie in the negative electrolyte is reduced at the negative electrode surface, and the specie in the positive electrolyte is oxidized at the positive electrode surface. When electricity is required (galvanostatic/discharge mode), the reverse reactions occur. These reactions are shown for a

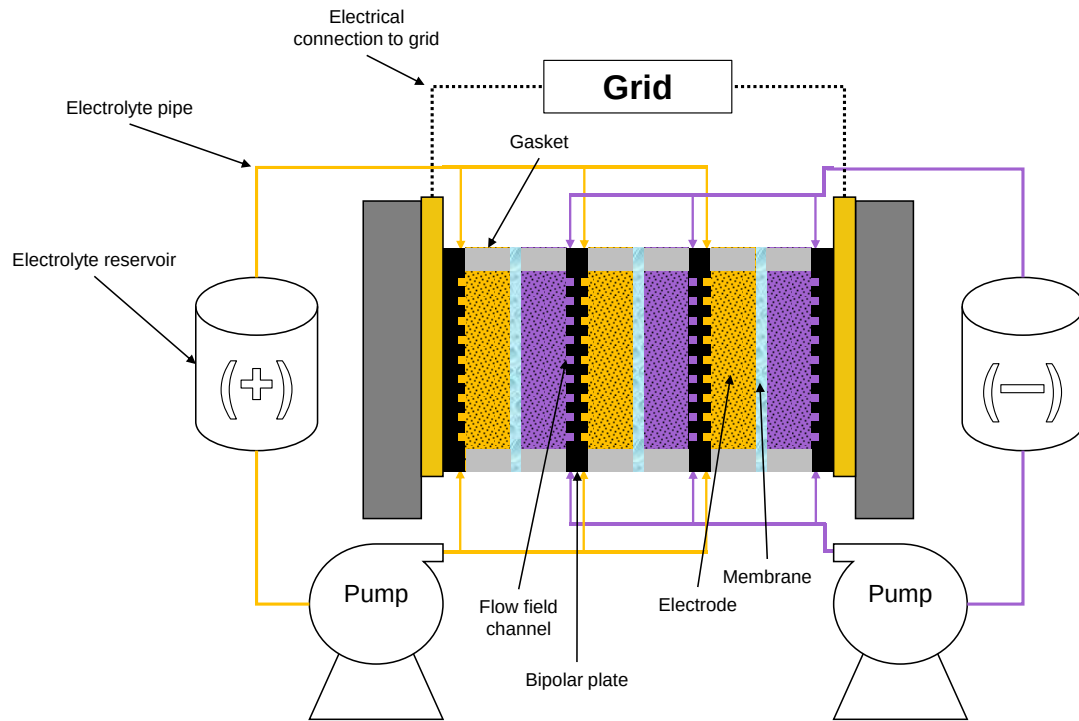
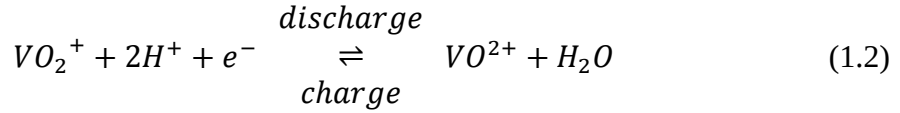
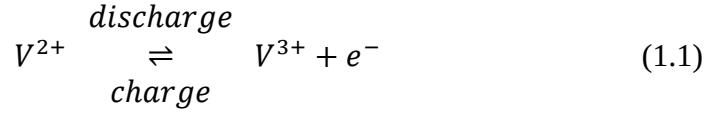


Figure 1.1. Flow battery stack schematic with labeled components.

VRFB in Eqns. 1.1 and 1.2. Ionic current flows through the separator for charge conservation in the liquid electrolytes.



1.2.2 Advantages

As a result of the tank-reactor structure, the energy capacity (determined by tank size) and power capacity (determined by stack size) are completely decoupled. This decoupling allows for a flexible design strategy that can satisfy the requirements of a variety of energy storage applications. Further, the modular nature means that the power and energy of an installed system can be reconfigured independently. For example, consider a facility that is initially designed to provide 10 MW power output and 10 MWh of energy storage. If the initial design requirement of 10 MW changes, but 10 MWh is still a sufficient total energy capacity, the facility could add (or reutilize elsewhere) stack modules to accommodate the new power requirement without purchasing additional energy storage material (e.g. vanadium). In contrast, if a lithium-ion or lead-acid energy storage facility required an increase in power output, additional battery packs would be needed, forcing the expense of unnecessary electroactive material (e.g. lithium, lead).

The cycle life of enclosed (non-flow) batteries that undergo solid-phase electrode reactions (e.g. lithium-ion, lead-acid, etc.) is limited by capacity fade, which can occur as a result of several complex processes.¹⁸⁻²¹ Capacity fade is generally irreversible and ultimately decreases the charge/discharge capability of the energy storage system. One fade mechanism in

solid-intercalation batteries is related to mechanical stress. The repeated expansion and contraction of the intercalation material can cause small portions of the electrode to lose electrical connection with the current collector. Solid electrolyte interface (commonly referred to as SEI) formation can also occur, which increases the internal resistance of batteries and ultimately limits charge/discharge performance.

In flow batteries, these particular modes of capacity fade are not present in any significant quantities, because the redox reactions involve no phase transition of the redox active materials. Although flow batteries do not suffer from the same capacity fade modes present in solid-phase electrode materials, other fade mechanisms do occur. For example, crossover is the movement of electroactive species across the membrane. In the short term, crossover causes self-discharge, lowering the coulombic efficiency. In the long-term, net crossover of electroactive species to one side of the battery causes capacity fade. Because the electrolyte is easily removable from the stack, crossover-induced capacity fade can be reversed in some cases. Capacity loss due to side reactions such as hydrogen or oxygen evolution or precipitation of vanadium can also occur. The electrolyte can be reconditioned chemically or electrochemically to reverse the effects of the side reactions and precipitates can be re-dissolved. For these reasons, flow batteries may have the long cycle lifetime desirable for long-term grid operation.

Despite the oft-repeated claim of potentially long-term cycle life, few studies have specifically examined flow battery performance as a function of time. Electrode and membrane degradation may occur, contributing to both capacity fade and decreased energy efficiency. These processes are virtually undocumented in the literature and the reversibility of these processes is unexplored.

The motivation of this work is to provide phenomenological understanding of electrode degradation in flow batteries and highlight its impact on capacity fade and decreased energy efficiency. A protocol is presented for accelerated degradation, which will be useful for the rapid screening of new materials. An impedance-based method to diagnose electrode degradation in situ is also demonstrated in this work.

1.2.3 Flow battery performance metrics

In the laboratory, flow battery testing is typically carried out via cycling experiments. The electrolyte is charged at a constant current until a pre-defined upper voltage cut-off limit is reached; then, the electrolyte is discharged at a constant current until the lower voltage cut-off limit is reached. While this mode of testing is not an accurate representation of a grid-connected duty cycle, it provides common ground for laboratory-scale testing. The metrics typically used to compare flow battery performance are:

- coulombic efficiency
- voltage efficiency
- electrochemical energy efficiency
- electrolyte utilization.

Energy density and power density are also used as metrics of comparison. The efficiencies for one cycle are defined as

$$\text{coulombic efficiency} = \frac{\int_0^{t_d} I_d dt}{\int_0^{t_c} I_c dt} \quad (1.3)$$

$$\text{voltage efficiency} = \frac{\int_0^{t_d} V_d dt}{\int_0^{t_c} V_c dt} \quad (1.4)$$

$$\text{electrochemical energy eff.} = \text{coulombic eff.} \times \text{voltage eff.} \quad (1.5)$$

where I and V refer to the current and voltage, respectively, and the subscripts refer to charge and discharge.

The operating voltage is determined by the open circuit or equilibrium voltage, E_{oc} , and the overpotentials

$$V_c = E_{oc} + \eta_c \quad (1.6)$$

$$V_d = E_{oc} - \eta_d \quad (1.7)$$

where V_c and V_d are the operating voltages during charge and discharge, respectively, and η_c and η_d are the overpotentials during charge and discharge. The overpotential is the energetic penalty that is paid to drive current in the device; a higher current requires a higher overpotential. When the overpotential for a given current is reduced, the operating efficiency increases and a higher power density can be achieved. A detailed discussion regarding the origins of various forms of overpotential is included in Section 1.3.3.

Electrolyte utilization refers to the capacity discharged from the electrolyte during a charge/discharge cycle divided by the total theoretical amount of charge that could be stored in the electroactive material. For example, for 50 mL of a 1 molar vanadium solution, the amount of charge that can be theoretically stored is 0.05 moles of electrons or 4,824 coulombs. If 2,412 coulombs are discharged during cycling, the electrolyte utilization is 50%. The pre-defined voltage cut-offs limit electrolyte utilization. The voltage cut-offs during charge and discharge are chosen to minimize side reactions such as hydrogen evolution or carbon corrosion in aqueous systems like VRFBs and to prevent damage to the battery components. The operating overpotential also limits electrolyte utilization; with high overpotentials, the charge and discharge cut-off voltages will be reached lower and higher state of charge (SoC), respectively.

Electrolyte utilization is a particularly important metric when considering electrolyte cost, because low utilization requires the use of excess quantities of electroactive material.

Performance degradation refers to an undesirable change in one or more of the above metrics as a function of time. The primary concerns are with decreased energy efficiency and capacity fade, which is a decrease in electrolyte utilization. Mechanisms of performance degradation are discussed in Section 1.3.4.

1.3 Literature review

Several flow battery chemistries exist; flow batteries are classified by the solvent (aqueous vs. non-aqueous) and the electroactive material (metal, organic, inorganic non-metal).^{1,2,5,16,22,23} Various combinations of solvent and electroactive material are possible. In addition, hybrid systems in which at least one of the redox couples undergoes a phase change are known; these hybrid systems are not discussed here. The unit cell itself described in Section 1.2.1 is nearly independent of the particular chemistry, though the specific electrode and separator materials are chosen with chemical compatibility and functionality for the particular electrolyte system. In the following sections, developments in the three main thrusts of flow battery research will be discussed. The first two sections briefly discuss the development of new chemistries and the enhancement of energy density in the all-vanadium system. The third section will discuss stack performance optimization efforts, followed by a summary of the available VRFB degradation literature.

1.3.1 Chemistries

Vanadium is a large portion of the capital cost of VRFBs²⁴ and may limit widespread commercial implementation of the all-vanadium chemistry⁵ unless commodity prices decrease

appreciably. However, it remains the predominant chemistry in flow battery research. Other aqueous metal-based chemistries face significant challenges including low operating voltage (resulting in low efficiency), irreversible cross-contamination due to crossover, and poor kinetics.^{22,23} Thus, research for new chemistries is ongoing in an effort to reduce the cost and improve the performance of flow batteries. Recently, much interest has been placed in the development of organic molecules for both aqueous and non-aqueous solvents,^{5,15,22,23} with some lab-scale demonstrations.^{25–27} Design guidelines for both aqueous and non-aqueous chemistries have been presented, incorporating economic considerations.²⁸

Some of the expected benefits specific to organic molecules are rapid kinetics relative to vanadium and other metal-based systems, decreased electroactive material cost relative to vanadium, and the potential for inexpensive microporous separators to replace expensive ion exchange membranes as the size of organic molecules may preclude crossover altogether. A disadvantage for organic molecules in both aqueous and non-aqueous solvents is a lower diffusion coefficient if the tailored organic molecules are larger than vanadium or other metal ions. Non-aqueous solvents require organic solvents, which possess much lower conductivities than aqueous solutions; the cost of organic solvents is also high.²⁸

1.3.2 Energy density

Several studies have made efforts to improve the solubility of vanadium species in the electrolyte in order to widen the operating temperature window and increase the energy density of the electrolyte solutions. Additives including hydrochloric acid²⁹ and a variety of other compounds^{30–33} have been shown to improve solubility of vanadium from ~1.5–2 M to 3 M; in these studies, some of the additives were observed to have the secondary benefit of improving

the vanadium redox reaction kinetics. Though increased energy density and a wider temperature window may reduce the size and cost of electrolyte storage tanks and decrease the need for temperature control, the net benefits are unclear. Water is a low-cost solvent; thus, high solubility is not as imperative as it is with high-cost non-aqueous solvents. High energy density is a major requirement for mobile applications such as transportation and electronic devices, but is not necessary for stationary energy storage. Additionally, the presence of chloride may lead to the generation of chlorine gas.³⁴

1.3.3 Stack optimization

Optimization of components within the stack ultimately results in either reduced overpotential at a fixed current or increased current at a fixed overpotential. In the former case, the energy efficiency and electrolyte utilization increase. In the latter case, the power density of the stack rises. With these improvements, capital and operating cost reductions can be achieved by shrinking the stack and/or decreasing the amount of electroactive material required for a fixed amount of energy storage. In the following sections, the term “reduced overpotential” implies that the overpotential at a fixed cell current has decreased. Roundtrip energy efficiency in VRFBs is typically around 70-80%, though the operating current density to achieve this efficiency varies from <50 to >200 mA/cm².

The sources of overpotential in electrochemical systems are typically attributed to charge transfer/activation, concentration/mass transport, and ohmic processes. The electrode and reactants determine the activation polarization. A combination of the electrode and flow field design largely determines the concentration polarization. Ohmic polarization is a reality of any

electrochemical device. In the following sections, we review the sources of overpotential, pressure drop, and crossover with these components in mind.

The flowchart shown in Figure 1.2 graphically illustrates the dependency of overall battery performance on each component. This flowchart shows only first-order effects and is not comprehensive. The chart assumes that the temperature, electrolyte chemistry (i.e. electroactive species, electroactive species concentration, supporting electrolyte, and solvent), operating current, and flow rate are all fixed a priori for simplicity. In reality, temperature and electrolyte chemistry affect the dynamic physical properties of the solution (e.g. conductivity, viscosity), as well as fundamental kinetic and transport processes; thus, temperature and electrolyte chemistry will have an impact on all three sources of overpotential, as well as pressure drop and crossover in real systems. The operating current affects all three sources of overpotential as well as crossover. Flow rate primarily affects concentration polarization and pressure drop.

Activation/charge transfer polarization

Activation overpotential in electrochemical systems is mathematically described by the Butler-Volmer equation of electrochemical kinetics. The Butler-Volmer equation contains a parameter known as the exchange current, i_0 , which is a measure of kinetic facility of a particular redox system with respect to a given electrode material. A higher exchange current is desirable as it reduces the activation overpotential in a cell. The exchange current is defined as

$$i_0 = F A k_0 c_O^\alpha c_R^{1-\alpha} \quad (1.8)$$

where F is the Faraday constant, A is the electrochemically active surface area, k_0 is the kinetic rate constant, c_O and c_R refer to the concentrations of the oxidized and reduced forms of the electroactive species, respectively, and α is the transfer coefficient. The solution composition determines the concentrations; generally, higher concentration decreases activation overpotential.

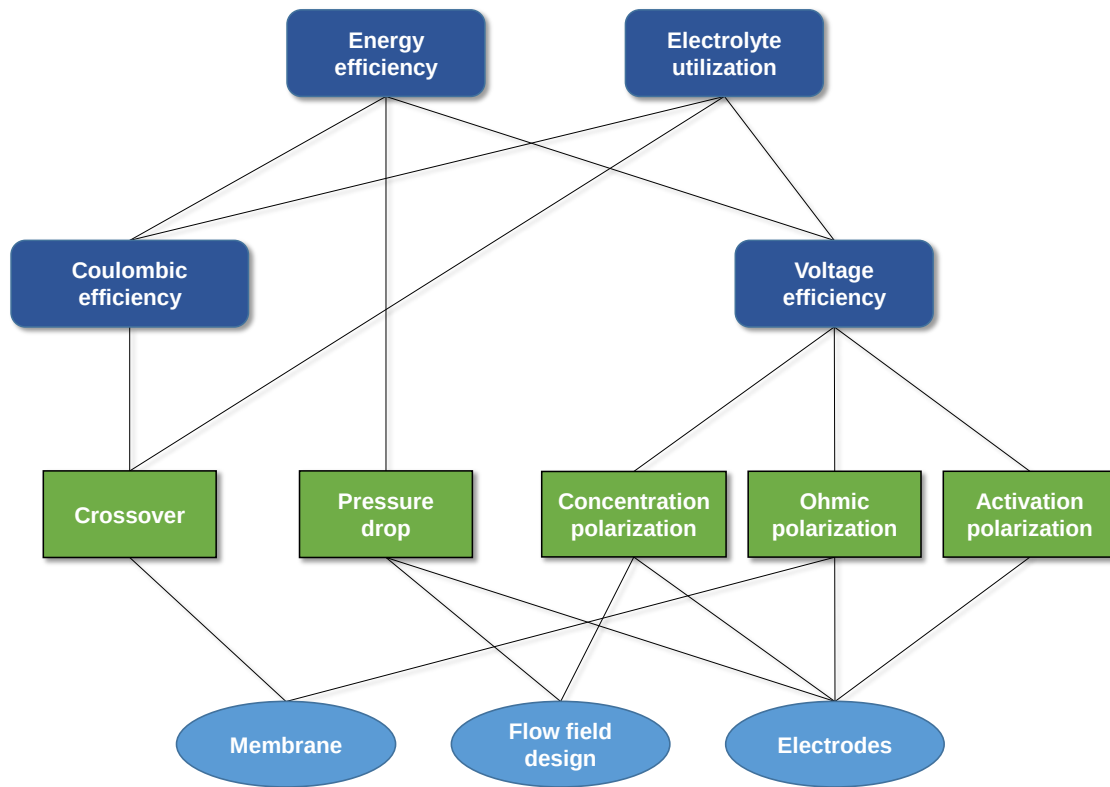


Figure 1.2. Flow battery performance dependence on components.

The rate constant is determined by the surface chemistry of the electrode material and is a measure of the inherent catalytic activity of the electrode material with respect to the electrode reaction of interest. The rate constant is therefore dependent on both the electrode material and the electrolyte chemistry. An ideal electrode material has a high surface area and good catalytic activity toward the redox reactions in order to maximize exchange current and minimize activation overpotential.

In VRFBs, virtually all electrodes are porous carbon materials, using the carbon surface itself as the reaction site for the redox reactions. Rate constants can vary several orders of magnitude (10^{-3} to 10^{-6} cm/s) depending on the carbon material and whether the V^{2+}/V^{3+} or VO^{2+}/VO_2^{+} reaction is considered; conflicting results have been shown as to whether the negative or positive electrode reaction is faster.³⁵ More recent studies seem to indicate that the negative electrode is more sluggish, with the exchange current for the same electrode material being measured as over forty-fold lower³⁶. Several studies report on the creation or modification of electrodes with the use of carbon nanotubes and graphene-based electrode materials, sometimes simultaneously.^{37–45} Other studies have doped carbon electrode surfaces with metal-based catalysts to improve the reaction kinetics.^{40,46–49} Another common approach to improving electrode kinetics has focused on improving the specific activity of the carbon electrode surface by modification through chemical, thermal, microwave, plasma, or other treatments.^{38,39,43,50–59} The overwhelming conclusion reached in the literature is that these treatments add functionalities to the electrode surface, most often in the form of oxygen-containing groups and sometimes nitrogen-containing groups. It is hypothesized that these functional groups provide increased catalytic activity for the vanadium redox reactions, which improves cell performance by

reducing activation overpotential. These studies often fail to consider that functional groups may also enhance wettability, which can increase the electrochemically active surface area. The treatment may also increase the surface area of the material through morphological changes. The effects of surface area must be decoupled from the effects of the functional groups in order to conclusively state that the functional groups themselves provide more activity.^{35,42,60–62} With these considerations, one study has suggested that oxygen-containing functional groups improve kinetics on the negative side while hampering kinetics on the positive side.³⁵

Concentration polarization

Concentration overpotential occurs when there is a difference in electroactive species concentrations between the bulk liquid electrolyte and the electrode surface. We assume that transport can be described by a Nernstian boundary layer in the electrode. Of course, the hydrodynamics may vary throughout the electrode, resulting in non-uniform boundary layers. Nonetheless, we consider an averaged boundary layer thickness. This description of transport implies that a linear concentration gradient is established between the electrode surface and the bulk electrolyte, which has a uniform concentration c_{bulk} . The concentration polarization can be described by Eqns 1.9 and 1.10:

$$\eta_{concentration} = \frac{RT}{nF} \ln \left(1 - \frac{i}{i_{lim}} \right) \quad (1.9)$$

$$i_{lim} = nFD \frac{c_{bulk}}{\delta} \quad (1.10)$$

where i is the operating current, i_{lim} is the limiting current (the maximum current that the cell can provide), and δ is the boundary layer thickness. An increase in the limiting current results in reduced concentration overpotential with a fixed operating current i .

The limiting current can be raised by increasing the bulk concentration or diffusion coefficient. The bulk concentration is limited by the solubility of the electroactive species. The diffusion coefficient is dependent on the mobility of the electroactive species in the electrolyte solution. This mobility is a function of temperature and solution viscosity. These parameters are generally fixed when the electrolyte composition is determined.

Alternatively, the limiting current can also be raised by decreasing the boundary layer thickness, which is controlled by the hydrodynamics in the electrode. The hydrodynamics are controlled by the flow rate, the electrode morphology, and the flow field design. A higher flow rate will result in a higher electrode velocity and decreased boundary layer thickness. Electrode morphology can be described by the effective porosity and tortuosity through the porous electrode, though the geometry and macroscopic ordering of the fibers themselves are also relevant. These parameters govern how fluid flows throughout the porous electrode.

Several studies detail the mechanisms of forced convection with different flow field designs.^{63–67} The conclusions drawn regarding “superiority of flow field” are highly dependent on the electrode material properties, particularly hydraulic permeability and thickness.⁶³ An excellent computational study has investigated in detail the effects of electrode material properties and interdigitated flow field design parameters on the performance of a bromine electrode.⁶⁸ Overall, when one considers concentration polarization, the combination of the electrode material and flow field design are important; neither stands on its own as the determining factor. In addition to effects on concentration polarization, the flow rate and hydrodynamics in the cell determine the pressure drop, which determines parasitic pumping losses and reduces overall energy efficiency of a flow battery.

The concentration gradient is also dependent on the local current density relative to the limiting current density. In this context, the current density refers not to the geometric current density (which is the projected 2D cell area), but to the current density at a unit element of electrode surface. A high electrode surface area decreases the local current density, which will reduce concentration polarization, provided that the boundary layer has not changed.

Ohmic polarization

Ohmic resistance is the sum of resistances due to the separator, electrode, liquid electrolyte, and electronic contact resistance. In VRFBs, the separator is typically an ion exchange membrane that allows conduction of ionic species in the electrolyte while preventing the transport of vanadium ions. The membrane resistance is proportional to thickness and inversely proportional to ionic conductivity. The electronic conductivity and thickness of the electrode play a role, as well as the ionic conductivity of the liquid electrolyte solutions. The total resistance through the thickness of the electrode/electrolyte domain can be calculated according to Sun and co-workers⁶⁹ and is sometimes called the distributed resistance⁷⁰, as it is a parallel combination of the ionic and electronic resistances in the electrode domain.⁶⁹ A discussion of the importance of electrode thickness and conductivity is included in Chapter 5. Electronic contact resistance is related to imperfect contact between the electrode material and flow field plate and is rather small.⁶⁴ The membrane is usually the largest source of ohmic resistance in VRFBs.⁷¹ The most commonly used membrane material is Nafion due to its chemical stability and commercial availability; however, it is a significant portion of the stack cost.²⁴ Area specific resistance is typically in the range of 200 to 500 mΩ·cm².

Crossover

In addition to being the largest source of ohmic resistance, the membrane allows undesirable crossover of vanadium species through the membrane, resulting in self-discharge and a decrease in coulombic efficiency. Ultimately, capacity fade occurs if there is a bias in the direction of crossover from one side of the battery to the other. Many consider the selectivity to be an important design parameter, which is defined as the ratio of the membrane conductivity to vanadium diffusivity. It should be noted that crossover can occur as a result of diffusion, convection, and migration across the membrane;^{72,73} the sum of these transport mechanisms is of more importance than just diffusion when considering crossover. It is experimentally difficult to measure the individual contributions of these three phenomena and thus most studies have focused on reducing diffusion-based crossover. Several reports have shown progress toward improved selectivity through modification of Nafion membranes.^{74–79} Others have synthesized other types of polymeric membranes in an effort to reduce cost.^{80–85} Coulombic efficiencies of 95-98% are typical of VRFBs with ion exchange membranes.

1.3.4 Degradation

As stated in the previous sections, flow battery performance degradation refers to a decline in one or more performance metrics. Any detrimental evolution in component properties will lead to performance loss. In Section 1.3.3, a systematic discussion of how electrodes, membranes, and flow fields influence the processes that determine energy efficiency and electrolyte utilization was presented. Energy efficiency can decline when any source of overpotential increases or if the coulombic efficiency changes. Capacity fade will also occur when any source of overpotential increases or if there is a net-crossover-induced imbalance in the electroactive species between the positive and negative sides. It is noted that operating

parameters such as temperature and electrolyte chemistry can play a role in the rate of degradation of the components.

Although much research has focused on cell and electrolyte optimization, there is a relative paucity of existing literature that addresses durability. The remainder of this section discusses some possible modes of degradation for each component and reviews published durability/degradation-related studies.

Electrodes

Electrode surface chemistry, surface area, and morphology may change with usage in the battery, affecting various overpotentials and ultimately both energy efficiency and capacity fade. Clogging of the electrode due to silicon in the electrolyte has also been observed, though it was mitigated by pre-filtering the electrolyte solutions.⁸⁶

In one study, overcharge with polyacrylonitrile (PAN) and rayon fiber-based carbon felt was investigated.¹¹ In this work, the total cell resistance (i.e. the sum of activation, mass transport, and ohmic resistances) and electrical resistivity of the felt material were measured before and after overcharge. On the negative side of the battery, overcharge had minor effects on the electrical resistivity; on the positive side of the battery, moderate increases in the electrical resistivity of the felt were observed with additional increases observed in the total cell resistance. The authors speculated with no evidence that the electrochemical activity of the electrode surface decreased. They also studied the surface chemistry of the felt materials, which showed dramatic increases in oxygen functional groups in some cases.

Carbon felt used as the positive electrode in a standard cycling test was characterized with X-ray micro-tomography to analyze changes in the microstructure.⁸ The authors found that a combination of fiber agglomeration and carbon oxidation resulted in a ~37% decrease in

surface area and suggested that this decrease in surface area could contribute to degraded cell performance.

Observations of energy efficiency decline and capacity fade were presented along with a proposed method to rehabilitate the energy efficiency in another work.⁹ The internal cell resistance increased by over 60% after 100 hours of cycling; accordingly, the energy efficiency dropped by over 10%. The authors speculated that a loss of oxygen functional groups on the negative electrode resulted in reduced electrode activity and thus increased charge transfer resistance. They hypothesized that reversing the battery polarity for a short period of time would reactivate the negative electrode surface. Their method was successful in reducing the internal cell resistance to its initial value. However, the energy efficiency did not return to its initial value; the authors suggested that electrolyte reconditioning was also necessary. It is unclear if the polarity reversal method is a viable strategy for long-term operation.

So-called passivation of the negative electrode, defined as a decrease in the effective kinetics, was observed in another study as well.¹² In that study, the kinetics in an ex situ three-electrode cell were found to decline on both the positive and negative side as a function of time and usage with four different carbon materials. The authors hypothesized without evidence that on the negative side of the battery, usage resulted in a decrease in oxygen functional groups that were beneficial for V^{2+}/V^{3+} kinetics. Electrodes that had been treated anodically (oxidized) had V^{2+}/V^{3+} rate constants up to 25 times higher than those treated cathodically (reduced). Similarly, they speculated that on the positive side, usage resulted in an increase in oxygen functional groups that were detrimental to the VO^{2+}/VO_2^+ kinetics. Here, anodically treated electrode rate

constants for the or $\text{VO}^{2+}/\text{VO}_2^+$ reaction were up to 10 times lower than cathodically treated electrodes.

Another recently published study looked at the evolution in electrochemical impedance spectra over the course of a cycling experiment⁸⁷. The authors concluded that the charge transfer resistance increased significantly on the negative side, while it was stable on the positive side. The decreased kinetic performance was attributed to a “peeling” of the electrode surface from the bulk fiber, resulting in a loss of surface area. It is noted here that the electrochemical impedance spectroscopy (EIS) measurements were carried out at ~0 and 100% SoC in some cases; the sensitivity of the exchange current at either extreme in SoC means that the charge transfer resistance will also be sensitive to slight variations in concentration. Unless the SoCs were reproduced extremely accurately, the impedance results at 0 and 100% SoC are compromised. Further, EIS measurements taken at the beginning or end of charge/discharge in a cycle are also influenced by changes in electrolyte composition as a result of crossover. Thus, the results in this work may be qualitatively correct, but quantitatively inaccurate. Post-mortem X-ray photoelectron spectroscopy (XPS) analysis showed that the negative electrode was more heavily oxidized after usage in the battery.

Overall, these studies confirm that the positive electrode undergoes changes in its surface chemistry and morphology; noticeably, the negative electrode surface chemistry was examined in only one study. Decreased energy efficiency was attributed to higher internal cell resistance. However, these studies did not decouple the internal cell resistance into its charge transfer, mass transport, and ohmic contributions; thus, a link between higher internal resistance and decreased electrode activity is speculative at best at this point in time. Only one study attempted to use EIS

to examine changes in charge transfer resistance over time; however, the use of 0 and 100% SoC solutions may result in large inaccuracies in the measured charge transfer resistance if the SoC was not very accurately controlled. Much more remains to be studied in order to truly understand if, how, and why the electrode performance degrades. Standard, well-controlled methods to evaluate electrode performance evolution would be very beneficial for the field.

Membrane

The harsh environment of the flow battery may lead to degradation of membrane materials. Multiple types of polymer membranes fell apart after exposure to the VO_2^+ in the positive electrolyte.^{80,88,89} Beyond total membrane failure, changes in the material properties such as conductivity and vanadium permeability can also occur as a function of usage in the battery, affecting ohmic resistance and crossover. One study found that the vanadyl cation fouls Nafion membranes;⁹⁰ another concluded that Nafion conductivity and vanadium permeability converge to a stable value after cycling in the battery.⁹¹ Much work remains to be done in this area.

Electrolyte composition

Changes in the vanadium concentrations on either side of the battery can occur over time due to crossover or side reactions. Capacity fade results when the total vanadium on one side changes relative to the total vanadium on the other, or when a valence mismatch occurs between the two sides, e.g. 50% SoC on the negative side and 100% SoC on the positive.

In a comprehensive experimental study of crossover-induced capacity fade, the vanadium concentration in each half-cell was periodically measured throughout cycling.⁷ A net crossover of vanadium from the negative to the positive side was observed, with initial concentrations of 1.7 molar vanadium on both sides resulting in finally reaching ~2.0 and ~1.3 molar

concentrations on the positive and negative side, respectively. It was noted that when either V^{2+} or V^{3+} ions cross to the positive side, the resulting self-discharge reaction converts VO_2^+ to VO^{2+} . As a result, the SoC of the positive side was always less than that of the negative side. Thus, the positive electrolyte limited discharge, while the negative electrode limited charge. A portion of the positive electrolyte was moved to the negative electrolyte periodically to restore capacity. This partial rebalancing was successful in recovering most of the initial capacity. The energy efficiency only declined $\sim 1\%$, suggesting that crossover-induced capacity fade did not significantly contribute to a loss of energy efficiency. Other work suggested using asymmetric charge and discharge currents to reduce the net imbalance in vanadium crossover.⁹²

Hydrogen evolution in the negative electrode can occur when electrons are supplied by the conversion of V^{2+} to V^{3+} ions. This parasitic loss can decrease the SoC of the negative electrolyte, while the positive side remains unchanged. This ultimately results in SoC imbalance and capacity fade. The rate of hydrogen evolution is dependent on the electrode surface chemistry and surface area⁹³, in addition to the voltage limits during cycling.

Secondary rebalancing cells and chemical reducing agents can be used to offset hydrogen evolution. Strategies to mitigate crossover-induced capacity fade include rebalancing operations or altering the charge/discharge currents. Electrolyte rebalancing was demonstrated successfully, but is still a form of maintenance that requires periodic attention. Because the flow battery must respond to grid conditions, altered charge/discharge currents may not be a viable strategy. Devising other methods to suppress or mitigate capacity fade with reduced maintenance requirements would be a significant contribution to the field.

Graphite materials

A few studies address corrosion of graphite in VRFBs. Two of these studies from the same group polarized the positive electrode until gas was evolved.^{94,95} In the first study, the authors observed that oxygen functionalities and noticeable defects were introduced on the graphite as a result of the high voltage. In the second study, the gases formed were studied with on-line mass spectrometry. Carbon dioxide was the first gas to appear with increasing potential, followed by carbon monoxide, and then oxygen. At extremely high voltage, oxygen was the most abundant gas evolved, followed by carbon dioxide, and then carbon monoxide. In another study, corrosion of a graphite current collector was observed in a stack as a result of shunt currents. Corrosion was mitigated by using an o-ring for electrical isolation between the electrolyte solution and the graphite current collector to minimize shunt currents.¹⁰ In all three of these studies, bulk graphite was the material of interest. Graphite is typically used as a bipolar plate; however, the primary surface for the electrochemical reactions in the flow battery is a porous carbon electrode, which is based on carbon fiber materials and is not prepared from bulk graphite. Therefore, though the durability of graphite bipolar plates is important in stack design, the applicability of these studies to understand laboratory-scale performance losses over time is limited if one stays within safe voltage limits.

Outlook and motivation

Understanding of degradation in VRFBs and flow batteries in general is limited. Crossover-induced capacity fade is reasonably well understood; however, other factors that may contribute to diminished capacity have not been examined experimentally. Specifically, any increase in cell overpotential should lead to some capacity fade, but experimental observations of this phenomenon are not presented in the literature. This particular mode of capacity fade may

become increasingly important as high-performance systems with high current density operation are developed. Electrochemical characterization of performance degradation has been limited to the overall observations of diminished energy efficiency and an increase in the total internal cell resistance. These observations are symptomatic of component degradation, but do not ultimately identify which components are degrading. Ex situ electrode characterization has shown that the electrode surface and morphological properties change, but definitive links to performance loss have not been demonstrated.

This thesis focuses on measurement and diagnosis of degradation in electrode materials utilizing electrochemical characterization and post-mortem materials analysis. The particular materials of interest were SGL GFD3 carbon felt and SGL 10AA carbon paper subjected to a multitude of pretreatments. We develop protocols to resolve changes in the ohmic, activation, and concentration polarizations as a function of time; these experiments yield insight into degradation phenomena. An accelerated degradation method is also developed in order to provide a more rapid screening tool than standard cycling experiments. We also present a new concept to mitigate crossover-induced capacity fade. Aspects of membrane and bipolar plate durability were not considered, nor were changes in electrolyte composition as a result of side reactions considered. Though these are important for commercial implementation, they were beyond the scope of this work.

1.4 Method of approach

Most electrochemical characterization of flow batteries is performed by observation of voltaic efficiency combined with ex situ methods; cyclic voltammetry (CV) experiments are most prevalent. CV is an electrochemical technique in which a triangular voltage wave is applied

to an electrode in a static electrolyte solution. The resulting current vs. voltage voltammograms can be interpreted to find rate constants and diffusion coefficients for the electrode reactions.⁹⁶ The rotating disc electrode (RDE) experiment is another ex situ technique in which the current response to an applied voltage is measured. In RDE experiments, the working electrode is rotated to control mass transport boundary conditions. Polarization curves are another type of polarization experiment where current is measured in response to an applied steady voltage or vice versa. Information regarding kinetics, ohmic, and mass transport can be interpreted. Polarization curves are the primary electrochemical diagnostic tool for fuel cells⁹⁷ and have been applied to flow batteries as well.⁹⁸ Of the measurements discussed in this paragraph, polarization curves provide the information most relevant to predicting cell performance.

Standard cycling experiments were used in this work to evaluate overall cell performance. Periodic electrolyte remixing was used at times to reverse the effects of crossover. In addition to cycling experiments, we developed an alternative test bed for accelerated performance degradation. This method is described in detail in Chapter 4. Polarization curves were employed before, during, and after both cycling and accelerated degradation tests. These experiments were carried out with a solution separate from the cycling solution to ensure the electrolyte composition was not affected by crossover, etc. Single-pass experiments were useful in ensuring a constant SoC was maintained at the cell inlet; sometimes the curves were taken with recirculation.

Though polarization curves do provide some resolution of kinetic, transport, and ohmic processes, these overpotentials are present over the entire range of current density, preventing complete decoupling of the phenomena. Kinetic and transport-related parameters derived from

CV and RDE rely on mathematical relationships that were derived for planar electrodes; these are not applicable with porous electrodes.^{42,62} EIS was shown to be a useful tool for examining the performance of an electrode.^{69,99} In that work, the impedance spectra were obtained in conjunction with a polarization curve. The charge transfer, finite diffusion, and ohmic resistances were resolved and integrated to give the activation, concentration, and ohmic polarizations at each current density,⁶⁹ which provided detail into how increasing the electrode thickness and operational flow rate affected the overpotentials individually. A mathematical model based on macrohomogeneous porous electrode theory was also applied; the model was able to fit the open circuit impedance spectra quite accurately.⁶⁹ A few other studies used EIS to quantify the charge transfer resistance and electrochemically active surface area, from which the rate constant could be derived.^{35,42,62} These reports used simple equivalent circuit modeling instead of a model based on physical parameters. Equivalent circuit modeling is only valid when the porous electrode response frequency range does not significantly overlap with the charge transfer feature; if the exchange current is high, the exchange current and kinetic rate constant are not easily recovered.¹⁰⁰

This thesis relies heavily upon EIS analysis to diagnose changes in cell performance. Special care must be taken to ensure steady state operation for EIS during the course of the measurement, which can run for several minutes to sweep the relevant frequency range. Such steady states are difficult to achieve in a full cell because crossover and the passage of current alter electrolyte composition. Thus, EIS was carried out in a symmetric cell where only one electrolyte is circulated through both sides of the cell to maintain a constant electrolyte

composition.^{36,69,101} A detailed discussion of the symmetric cell is included in Chapter 5. In order to interpret our EIS data, we use the model developed by Sun, Delnick, and coworkers.⁶⁹

XPS and Raman spectroscopy were the primary methods used to characterize the electrode surface before and after service in the battery.

A variety of chemical and thermal pre-treatments were performed on the electrode materials to induce changes in electrode performance. Thermal treatments were carried out in a tube furnace. Temperature, treatment gas, and time of treatment were varied. Chemical treatments included simple acid soaks as well as elevated temperature acid treatments in a sealed autoclave reactor.

1.5 Chapter preview

In Chapter 2, heat treatment of SGL10AA electrode materials to improve performance is discussed. Polarization curve analysis and cycling experiments were used to demonstrate the performance enhancement with heat treatment. Further cell optimization efforts were carried out in Chapter 3, where membranes developed at Sandia National Laboratory were also characterized by polarization curve and cycling analysis.

Using the optimized electrodes identified in Chapter 2, we began investigations into electrode performance loss in Chapter 4. We developed an accelerated degradation protocol and compared the results with a standard cycling experiment. Post-mortem electrode characterization with XPS was also carried out.

EIS is a useful tool for understanding why cell performance degrades. In Chapter 5, we improve upon the prior art⁶⁹ by altering the experimental set-up to greatly decrease the required time to obtain useful impedance data over the entire frequency range. We used EIS to explain the

impacts of electrolyte composition, electrode material (SGL10AA paper vs. SGL GFD3 felt, and flow field design on cell performance. The EIS method developed in Chapter 5 was then extended in Chapter 6 to diagnose the time evolution of performance in treated SGL GFD3 electrodes in a symmetric cell configuration. We investigated beginning-of-life performance degradation for these electrodes deployed in both the positive and negative electrode with the use of EIS to study changes in the electrochemical parameters. These changes are correlated with changes in electrode surface chemistry, obtained through XPS and Raman spectroscopy. Chapter 7 similarly investigates performance loss in treated 10AA electrodes, though only the negative electrode was analyzed, and materials characterizations were not carried out. The flexibility of the EIS method developed in Chapter 5 is shown in Chapter 8 by applying it to a non-aqueous system.

In Chapter 9, high-current cycling results are shown for an electrode that exhibited good beginning-of-life durability from Chapter 6. A method is also proposed to reduce crossover-induced capacity fade and demonstrate its efficacy.

CHAPTER 2
HIGH PERFORMANCE ELECTRODES IN VANADIUM REDOX FLOW BATTERIES
THROUGH OXYGEN-ENRICHED THERMAL ACTIVATION

Abstract

This chapter is revised based on the published paper with permission from Elsevier:⁶¹

Alan M. Pezeshki, Jason T. Clement, Gabriel M. Veith, Thomas A. Zawodzinski, and Matthew M. Mench. “High performance electrodes in vanadium redox flow batteries through oxygen-enriched thermal activation.” *Journal of Power Sources* 294 (2015): 333-338. [http://dx.doi.org/10.1016/j.jpowsour.2015.05.118]

My primary contributions to this work were the collection, reduction, and interpretation of data as well as composition of the manuscript. Clement assisted in heat treatments and collection of electrochemical data. Veith collected XPS data.

2.1 Introduction

As described in Section 1.3.3, stack optimization is one avenue by which to reduce capital costs. Recent studies have focused on improving electrode and membrane performance to increase power density and therefore decrease stack-associated costs.^{2,14,102–104} These advancements also improve efficiency, which reduces electrolyte cost since more energy can be extracted per charged vanadium ion.

Electrode kinetic overpotential is a function of electrode surface area and surface chemistry.^{96,105} Many studies have attempted to modify carbon or graphite felt surface chemistry through chemical^{57,106,107} and thermal treatments.^{40,54,107} In these investigations, increased activity of the electrode surface is generally attributed to enhanced oxygen content on the surface. However, the connection between oxygen content and electrode activity has not been conclusively verified.

Thermal treatments on graphite felts were first pioneered in VRFB systems by Sun and Skvlas-Kazacos.⁵⁴ In this chapter, carbon paper electrodes were thermally treated under varied oxygen concentrations and then used in the high power density no-gap architecture.¹⁰⁴ This

chapter demonstrates performance gains and associated system-level benefits that can be achieved by using enhanced carbon paper electrodes in a favorable architecture. The use of an enriched oxygen environment during treatment decreases the amount of time required for heat treatment, resulting in energy and cost savings during processing. Initial characterization results indicate that the large increase in the surface area was responsible for the enhanced kinetic performance, rather than the addition of oxygen functionalities, as previous authors have suggested.^{40,54,57,106,107} This implies that electrode modification studies must account for the change in surface area to complement analysis of the surface chemistry when attempting to explain any apparent change in electrode kinetics.

2.2 Experimental methods

2.2.1 Electrode preparation

Untreated SGL10AA carbon paper (SGL Group) was used as the baseline electrode material. Nine sets of the 10AA electrodes were heat treated in a tube furnace at 400 °C with oxygen concentrations of 0% (nitrogen), 21% (air), and 42% (enriched) balanced by nitrogen (Airgas) for 15, 30, and 45 hours for each oxygen concentration. Prior to heat treatment, the electrodes were purged in the furnace with the treatment gas for two hours. Selected electrodes were characterized to determine oxygen content, surface area, and wetted surface area with a PHI 3056 X-ray photoelectron spectrometer with an Al K α X-ray source (1486.6 eV) at 350 W, an Autosorb-iQ surface area analyzer (BET method), and electrochemical impedance spectroscopy, respectively.⁹³ Mass loss was determined by weighing samples before and after heat treatment.

2.2.2 Cell architecture

Single-cell flow batteries with 5 cm² of geometric active area were constructed with a serpentine flow field using the no-gap architecture.¹⁰⁴ Three layers of carbon paper compressed to ca. 70% of their original thickness were used in both sides of the cell. A Nafion 117 membrane (DuPont) was utilized to maximize coulombic efficiency. For all testing, a flow rate of 90 mL min⁻¹ was provided by a dual-channel peristaltic pump (Cole-Parmer). Cell temperature was maintained at 30 °C.

2.2.3 Electrolyte solution

Electrolyte solutions consisting of 1 M vanadium ions in 5 M sulfuric acid were prepared from vanadium (IV) sulfate oxide hydrate (Alfa Aesar, 99.9%) and sulfuric acid (Alfa Aesar, ACS grade) in deionized water. Initial charging was performed with 100 mL catholyte and 50 mL anolyte. Upon reaching ca. 100% SoC, one half of the catholyte solution was discarded to obtain a 1:1 ratio of charged catholyte and anolyte solutions. A nitrogen purge (Airgas, UHP) was used over both tanks of electrolyte to prevent oxidation of the vanadium species.

2.2.4 Electrochemical characterization

Polarization curves were obtained with alternating 30 second galvanostatic discharge and open circuit steps with no recharge, resulting in a continuous decrease in SoC over the course of the curve. High-frequency resistance (HFR) measurements were taken during discharge steps to *iR*-correct the polarization curves. Two cycles at both 100 mA cm⁻² and 200 mA cm⁻² were carried out with the same electrolyte solution used for the polarization curves. Cutoff voltages of 1.7 and 0.6 V were used upon charge and discharge, respectively. HFR measurements were also taken during cycling and used to *iR*-correct the charge and discharge profiles. Electrochemical

measurement and control and temperature control were carried out with a Scribner Associates 857 Redox Test System potentiostat.

2.3 Results and discussion

2.3.1 Polarization curves

With the passage of current, electrochemical systems deviate from their thermodynamic cell potential due to activation/kinetic, ohmic, and concentration polarizations. Polarization curves are a useful tool for resolving these sources of overpotential.⁹⁷ In this work, polarization curves were *iR*-corrected to remove the ohmic losses from the membrane, leaving ohmic losses in the liquid electrolyte and activation and concentration polarizations. While these contributors to polarization appear over all current densities, the activation overpotential dominates at lower current densities.⁹⁸ Given that there was no significant difference between polarization curves with and without recharge between discharge steps for low current densities (0 – 0.5 A cm⁻²), the concentration polarization is negligible in the low current density regime. Ohmic losses in the liquid electrolyte were assumed to be similar between different cell builds and are not discussed in the remainder of this work.

Treatment in nitrogen (0% oxygen) provides a moderate improvement in cell performance, while treatments in air (21% oxygen) and enriched (42%) oxygen provide a more marked improvement, as shown by the *iR*-corrected curves with the 15 hour treated electrodes in Figure 2.1(a). Similar trends were observed for both 30 and 45 hour treated carbon papers. Figure 2.1(b) shows the difference in *iR*-corrected voltage between each of the treated and untreated electrodes. The air and enriched oxygen treatments resulted in improvements of 100 mV over untreated carbon paper at a current density of 100 mA cm⁻² that asymptote to 140 mV

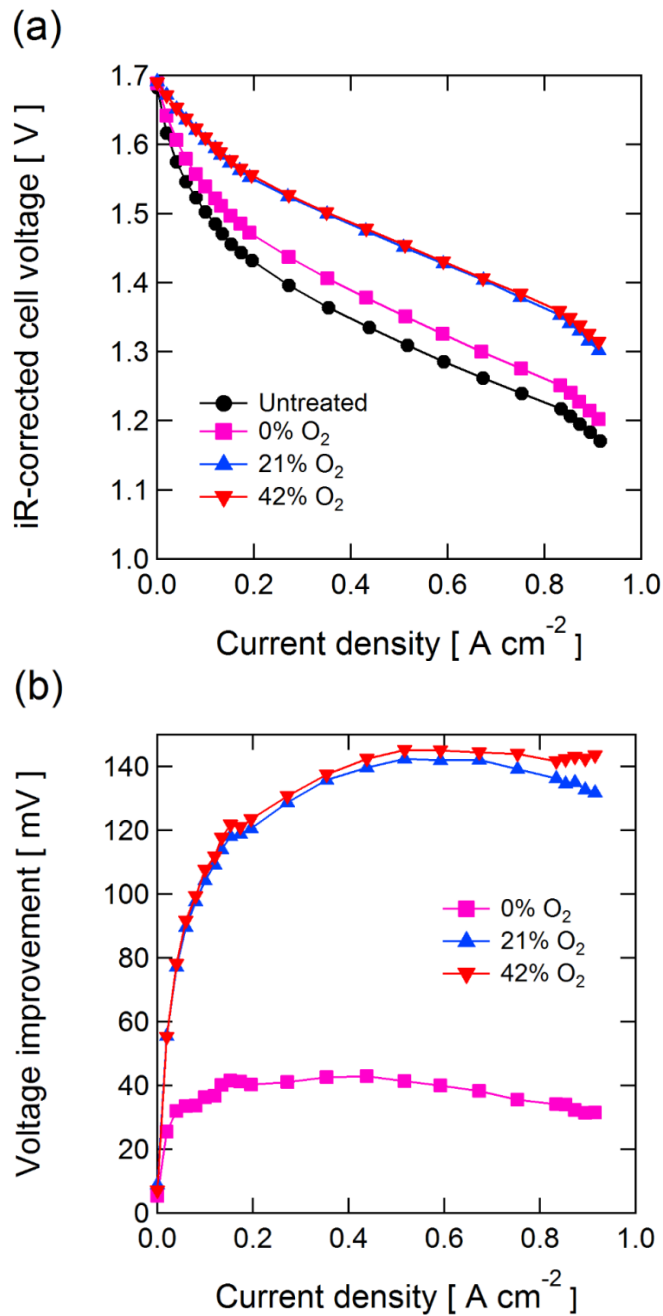


Figure 2.1. (a) iR-corrected polarization curves for untreated carbon paper and those treated for 15 hours in 0%, 21%, and 42% oxygen environments and (b) iR-corrected voltage improvement of each heat treatment relative to untreated carbon paper.

at 0.5 A cm^{-2} . The pure nitrogen treatment showed a more modest boost of 40 mV that does not increase with current density beyond 40 mA cm^{-2} . Sharp gains in the low current density region of the polarization curve ($0 - 0.5 \text{ A cm}^{-2}$) with gains that level off at higher current densities ($> 0.5 \text{ A cm}^{-2}$) indicate an improvement in the kinetic performance of the vanadium redox reactions on the electrode surface.

2.3.2 Electrode characterization

Both surface area and chemistry have an impact on reaction rates. The surface chemistry, probed with XPS, showed a small increase in oxygen content on the electrode, from 1% untreated to 2% with the enriched oxygen treated electrode. This change is much smaller than the increase from 4% to 20% observed by Sun and Skyllas-Kazacos on heat treated carbon felt;⁵⁴ however, carbon paper is a different material than felt and may be less susceptible to oxygen functionalization. The BET surface area of the 42% oxygen treated material was $21.0 \text{ m}^2 \text{ g}^{-1}$, a significant gain over the $1.0 \text{ m}^2 \text{ g}^{-1}$ for the untreated material.⁹³ This increase in surface area is likely a roughening of the carbon fiber surface that is not visible by SEM; Lee and Kang confirmed by atomic force microscopy that heat treating PAN-based carbon fibers introduces micropores in the carbon fiber structure.¹⁰⁸ Because BET surface area measurements may be limited by the ability of nitrogen physisorption to probe extremely small pores,¹⁰⁹ the double-layer capacitance was also measured and used to estimate the surface area. This method provides a more accurate measure of the electrochemically active wetted surface area. The capacitance measured by electrochemical impedance spectroscopy indicated the wetted surface area increased from $0.24 \text{ m}^2 \text{ g}^{-1}$ untreated⁹³ to $39.10 \text{ m}^2 \text{ g}^{-1}$ for the air treated electrode and to $51.22 \text{ m}^2 \text{ g}^{-1}$ for the enriched oxygen treated electrode, a 200-fold increase in the surface area. It is

noted that the enriched oxygen treated electrode also showed a large increase in hydrophilicity, which may also contribute to the increase in the wetted surface area. Droplets of battery electrolyte were completely absorbed by the electrode, in contrast with the 132° contact angle observed with the untreated electrodes;¹¹⁰ this increase in hydrophilicity compares similarly to electrodes treated by electrochemical methods.¹¹¹ A simplified calculation based on the Butler-Volmer equation shows that a 200-fold increase in surface area can explain the reduced overpotential observed with the treated electrodes. Assuming Tafel behavior for a one electron process, activation overpotential is given by

$$\eta = \frac{RT}{F} \ln \frac{i}{i_0} \quad (2.1)$$

If it is assumed that the nature of the carbon surface remains the same, the exchange current density, i_0 , is constant. The change in overpotential as a result of heat treatment is then

$$\eta_{HT} - \eta_v = \frac{RT}{F} \left(\ln \frac{i_{HT}}{i_0} - \ln \frac{i_v}{i_0} \right) = \frac{RT}{F} \ln \frac{i_{HT}}{i_v} \quad (2.2)$$

where the subscripts refer to heat treated (HT) and untreated (U) carbon paper. With an assumed 200-fold increase in surface area, the ratio i_{HT}/i_v is equal to 1/200 because the effective current density on the heat treated electrode is reduced by a factor of 200. At

30 °C, the difference in activation overpotentials, $\eta_{HT} - \eta_v$, is ca. -138 mV. While changing the surface area by a factor of 200 may mean that the electrode behavior cannot be described simply by Tafel kinetics, this calculation is reasonable for order of magnitude estimates. Additionally, heat treatment may induce some changes in the surface properties of the carbon fibers, including the addition of oxygen functional groups, which can affect the exchange current density.

However, any effect is expected to be relatively minor in comparison with the 200-fold increase

in surface area, which alone can account for the observed electrode overpotential change of 140 mV.

Because a large increase in surface area is observed with small changes in the oxygen content on the electrode surface, it is concluded that an increase in the surface area, not an increase in the oxygen content, is predominantly responsible for the enhanced kinetic performance. This observation is a departure from other studies in which enhanced kinetics on treated electrode surfaces are attributed to oxygen functional groups,^{40,54,57,106,107} but agrees with the findings of Melke et al.⁶⁰ This disparity suggests that the various treatments may have different mechanisms by which they affect the reaction kinetics for carbon felts as compared to carbon papers. Furthermore, this result shows that XPS and other similar techniques that measure changes in the surface chemistry are not sufficient to explain the performance enhancements induced by electrode treatments. The electrochemically wetted surface area is an important factor that must also be considered.

The 400 °C heat treatment in oxygen environments resulted in slight mass loss in the carbon material, up to 7.7% for treatment in enriched oxygen for 45 hours. The rate of mass loss was roughly proportional to the amount of oxygen present in the treatment gas and appeared to be linear with respect to time, based on the three time points tested. Nitrogen, air, and enriched oxygen treatments resulted in negligible, 0.10% per hour, and 0.17% per hour mass loss, respectively.

Although the enriched oxygen treatment resulted in a higher wetted surface area than the air treatment, as described above, the electrochemical performance was similar. This suggests that additional kinetic improvements cannot be achieved by further increasing the surface area;

there is a maximal surface area that can be utilized. Because a higher oxygen content in the treatment environment results in a higher surface area for the same treatment time, it is possible to reduce treatment time while achieving sufficient surface area by using a higher concentration of oxygen during heat treatment.

2.3.3 Cycling

Charge/discharge profiles for cycling at 200 mA cm^{-2} are shown in Figure 2.2(a). It is noted that the SoC is not the same at the beginning of each discharge profile as a result of differing depths of charge, described in detail later in this section. The improved kinetic performance decreased the charging voltage and increased the discharging voltage, resulting in increased cycling efficiency. Shown in Figure 2.2 (b) is a graphical representation of losses associated with kinetic, ohmic, and mass transport polarization for the enriched oxygen treated electrode cycled at 200 mA cm^{-2} .

The ohmic loss is found by iR -correction of the charge and discharge profiles with the HFR measurements obtained during cycling. The mass transport loss is estimated as the ‘tail’ region during discharge, and is estimated as the deviation from pseudo-linearity present over the majority of the discharge profile. The charge profile remains quasi linear, indicating little mass transport loss during charging. The remaining losses are attributed to kinetic polarization. Integration of these curves yields the discharge and charge energies and the energy lost to ohmic and mass transport processes:

$$\text{charge energy} = \int V_c I_c dt \quad (2.3)$$

$$\text{discharge energy} = \int V_d I_d dt \quad (2.4)$$

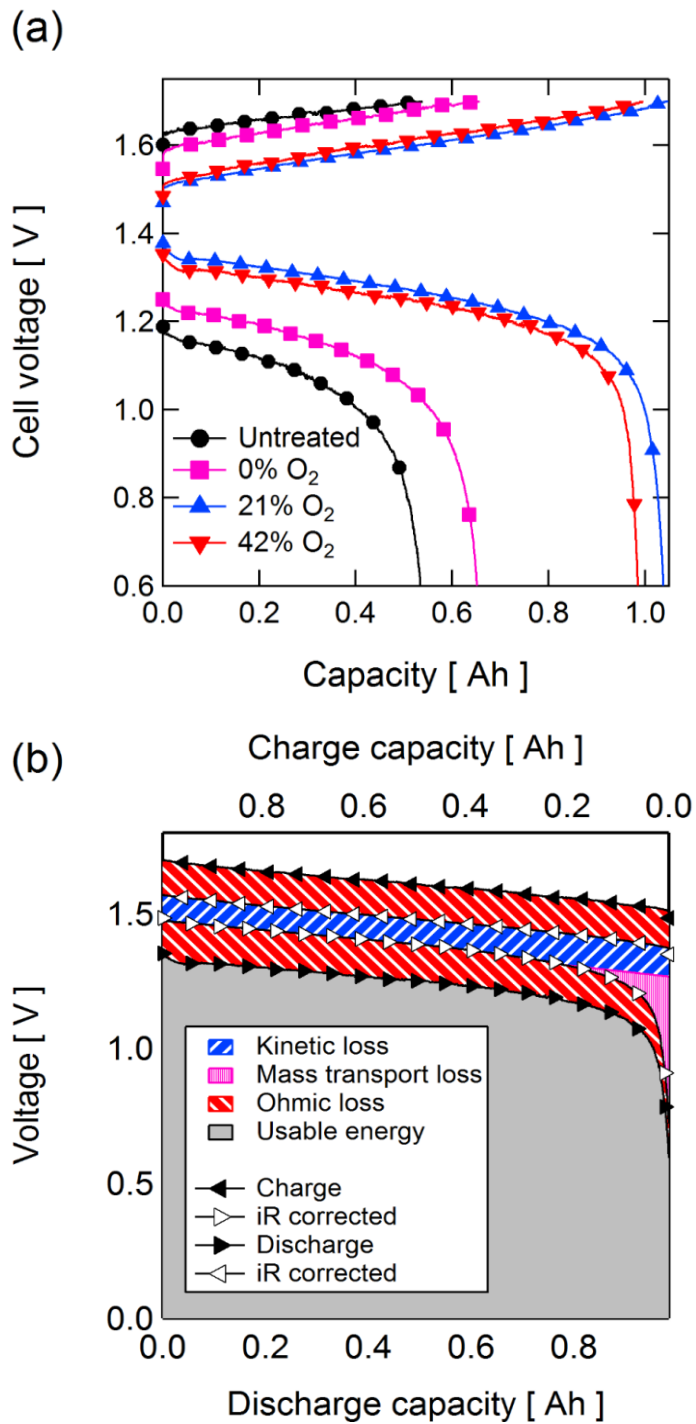


Figure 2.2. Charge/discharge profiles obtained at 200 mA cm⁻² for (a) untreated and 15 hour treated samples and (b) 15 hour enriched oxygen treated electrode with breakdown of losses from kinetic, ohmic, and mass transport polarization.

$$\text{ohmic energy loss} = \int (V_c - V_{c,iR \text{ corrected}}) I_c dt + \int (V_{d,iR \text{ corrected}} - V_d) I_d dt \quad (2.5)$$

$$\text{mass transport energy loss} = \int (V_{d,linear \text{ extrapolation}} - V_{d,iR \text{ corrected}}) I_d dt \quad (2.6)$$

$$\text{coulombic efficiency (CE)} = \frac{\int I_d dt}{\int I_c dt} \quad (2.7)$$

$$\text{kinetic loss} = \text{charge energy} \times \text{CE} - \text{discharge energy} - (\text{ohmic} + \text{mass transport energy loss}) \quad (2.8)$$

where I and V refer to the current and voltage, and the subscripts “c” and “d” refer to charge and discharge, respectively. The linear extrapolation used to calculate the mass transport loss is shown in Figure 2.2(b). The coulombic energy loss is primarily due to crossover of vanadium ions through the membrane and was ca. 1% for all experiments run, i.e., the coulombic efficiency was ca. 99%.

A summary of these kinetic, ohmic, and mass transport losses as a fraction of the total charge energy is shown in Figure 2.3(a) for electrodes cycled at 200 mA cm⁻². Kinetic losses were reduced from 20% of the total energy for untreated to 6.0% of the total energy with the enriched oxygen treatment. At 100 mA cm⁻², kinetic losses were reduced from 12.5% (untreated) to 3.2% (enriched oxygen treated). The average cell areal specific resistance, taken as the product of the geometric active area and HFR, was measured to be 673.8 ± 45 mΩ cm² and resulted in ohmic losses of 14.5–16.5% at 200 mA cm⁻² and 7.6–8.7% at 100 mA cm⁻². The difference in ohmic losses can be attributed to variation between cell builds. The mass transport loss was estimated as 1.9% at 200 mA cm⁻² for the untreated electrodes; the enriched

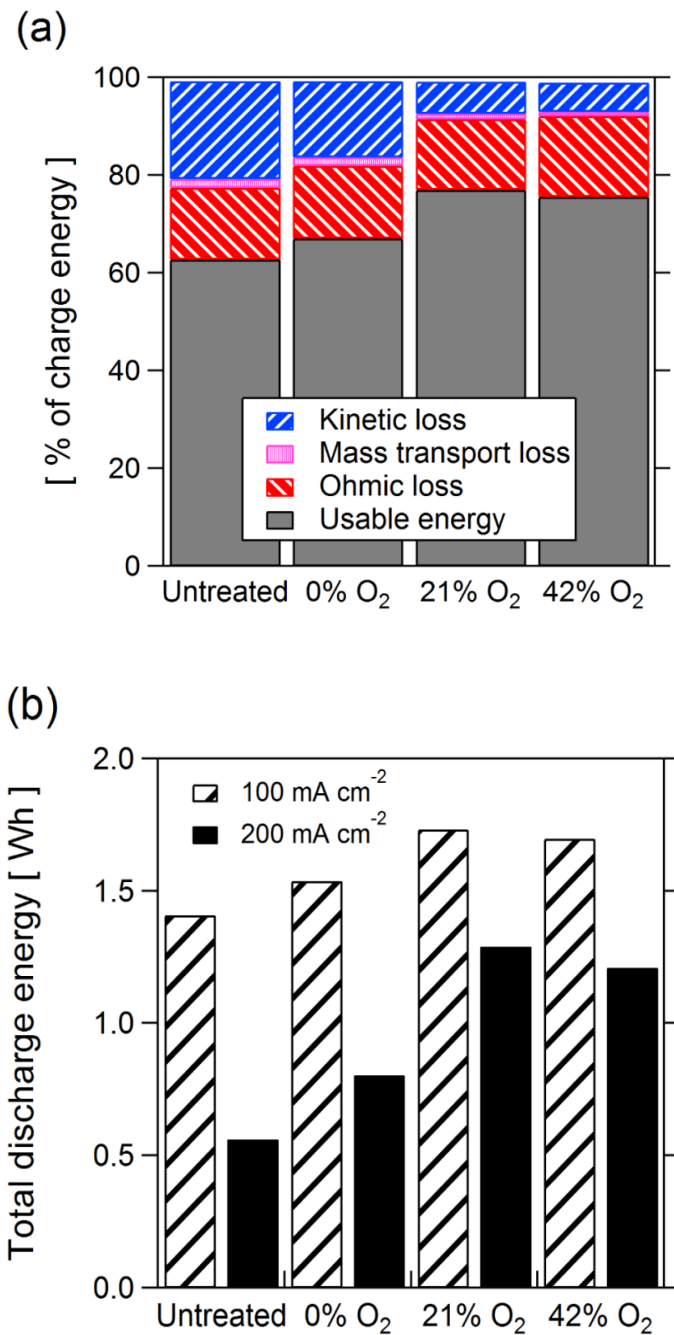


Figure 2.3. Summary of cycling for untreated and 15 hour treated samples: (a) usable energy and kinetic and ohmic losses at 200 mA cm⁻² and (b) total discharged energy at 100 mA cm⁻² and 200 mA cm⁻².

oxygen treated electrodes had a transport loss of 0.9%. At 100 mA cm^{-2} , the mass transport losses were 1.1% (untreated) and 0.6% (enriched oxygen). Since Figure 2.1(a) shows that the concentration polarization was similar with all electrodes, this difference in mass transport loss is not a result of improved transport behavior for treated electrodes. Rather, the apparent mass transport difference is attributed to the fact that the raw electrode has a much smaller charge/discharge window, and therefore a larger portion of the charge/discharge curve resides in the mass transport-affected region. Overall, the energy efficiency (non iR -corrected) at 200 mA cm^{-2} was increased from 63% to 76% and from 77% to 86% at 100 mA cm^{-2} . This is a significant improvement, especially at these relatively high current densities. It should be noted that, while the energy efficiency could be further improved by selection of a thinner membrane to reduce ohmic losses, the kinetic overpotential in the electrodes was the focus of this study.

In addition to the increased efficiency, treated electrodes enable a deeper charge and discharge window because a lower kinetic overpotential means that a higher SoC can be reached upon charging with the same cutoff voltage. The discharge capacity at 200 mA cm^{-2} was increased from 0.5 Ah for untreated electrodes to 1 Ah with oxygen treated electrodes, which represents an increase from 37% to 74% in the range of SoC that is swept during cycling. The energy discharged was increased from 0.56 Wh (untreated) to 1.21 Wh (enriched oxygen), shown in Figure 2.3(b). At 100 mA cm^{-2} , gains were less pronounced but still significant, improving the discharge energy from 1.41 Wh (untreated) to 1.70 Wh (enriched oxygen). These results illustrate an important concept: using high performance electrodes can not only reduce stack costs, but also reduce vanadium costs associated with storing a given quantity of energy, especially at higher current densities. Because a larger SoC window is used and higher discharge

voltages are achieved, more vanadium is accessible, and the total amount of energy per vanadium is also increased. These results show that the electrolyte cost to store a fixed amount of energy could be cut by 50% for a cell operating at 200 mA cm^{-2} or 17% at 100 mA cm^{-2} . Given that the electrolyte is ca. 40% of the total system capital cost,²⁴ the reduction in vanadium use could be on the order of 5–20% of the total system cost. It should be noted that further increases in the SoC window are possible with advanced design and materials that are the focus of other studies in our laboratory.

2.4 Conclusions

A high performance carbon paper electrode was developed by heat treating a standard carbon paper in partial oxygen environments. The oxygen concentration of the treatment gas affected the rate of oxidation as well as the final surface area of the treated material. The heat treatment resulted in large surface area enhancements, which explain the reduced activation overpotentials on the order of 140 mV as measured by polarization curves. The increase in surface area, not a change in surface chemistry, can account for the decrease in overpotential. Translated to cycling experiments, heat treating electrodes in an oxygen environment increased energy efficiency from 63% to 76% and more than doubled the usable capacity at a high current density of 200 mA cm^{-2} . Doubling the usable capacity represents an opportunity to decrease system cost by up to 20% by reducing the amount of vanadium necessary to store a given amount of energy.

CHAPTER 3
FULL CELL STUDY OF DIELS ALDER POLY(PHENYLENE) ANION AND CATION
EXCHANGE MEMBRANES IN VANADIUM REDOX FLOW BATTERIES

Abstract

This chapter is revised based on the published paper with permission:¹¹²

Alan M. Pezeshki, Zhijiang Tang, Cy Fujimoto, Che-Nan Sun, Matthew M. Mench, and Thomas A. Zawodzinski: “Full cell study of Diels Alder poly(phenylene) anion and cation exchange membranes in vanadium redox flow batteries.” *Journal of the Electrochemical Society* 163 (2016): A5154-A5162. [<http://dx.doi.org/10.1149/2.0201601jes>] Copyright 2003, The Electrochemical Society.

My primary contributions to this work were the collection, reduction, and interpretation of data as well as composition of the manuscript. Tang contributed to composition of the manuscript. Fujimoto synthesized the membranes. Sun assisted in experimental design. Zawodzinski assisted in interpretation of electrochemical data.

3.1 Introduction

As described in Chapter 1, one of the key components in VRFBs is the membrane. As the separator between the positive and negative sides, the membrane is responsible for limiting undesired crossover of vanadium species and water while enabling ion conduction. The membrane's ability to restrict crossover is the key factor in cell coulombic efficiency and is important in slowing capacity fade. The conductivity determines the ohmic drop in the membrane, which is the major source of ohmic resistance in the battery and therefore plays a key role in determining voltage loss.¹¹³ Thus, it is desirable to engineer membranes that have a high selectivity, i.e., low vanadium permeability with high conductivity for charge carrying ions, predominantly protons or bisulfate. Commonly used membrane materials in the laboratory consist of perfluorinated polymers that provide chemical-mechanical stability, with polar side chains to provide ion conduction pathways; however, materials such as Nafion are relatively

expensive and exhibit poor selectivity. Modified Nafion membranes can provide improved selectivity,^{77,114} but are still based on the expensive Nafion material.

Several studies have investigated alternative hydrocarbon backbone polymers as a means to decrease cost and improve selectivity.¹¹⁵ Proton exchange membranes in the form of sulfonated aromatic polymers have received the most attention^{1,81,84,85,116,117} due to the relative ease of preparation and promising VRFB performance. However, issues of low membrane cyclic lifetimes have been reported and suggest membrane oxidation through the VO_2^+ ion.¹¹⁸ Therefore, anion exchange membranes (AEM) have been presented as an attractive option because vanadium permeation is expected to be limited by the Donnan potential generated by the positively charged functional groups, which would not only reduce vanadium crossover, but also hinder VO_2^+ from entering the membrane pores and thus should improve membrane lifetime.¹⁰³

From studies of direct methanol fuel cells (DMFC), which also suffer liquid phase crossover issues, it is known that increasing the ion exchange capacity (IEC) can improve membrane conductivity, with the tradeoff of increased rates of crossover.¹¹⁹ IEC is a measure of the fixed charge functional groups within the polymer membrane; a higher IEC corresponds to a greater amount of fixed charged moieties. An increase in IEC typically results in increased water uptake due to the attraction between water molecules and the polar groups in the charged functional groups within the membrane. Increased water uptake increases membrane conductivity as more pathways are present for proton conduction that occurs within the bulk water within the membrane. It is noted that the conduction mechanism is predominantly due to protons through bulk water (the Grotthus mechanism) when the membrane exists in a highly hydrated state, as it does when surrounded by liquid phase water/acid solution in the VRFB. We

note that a secondary conduction mechanism whereby ions move by a hopping mechanism along the charged functionalities may also be present; an increase in IEC can improve this secondary conduction mechanism. Understanding how IEC affects performance, as well as membrane transport properties on a more fundamental level, is important in continued development and optimization of high performance membranes. In addition to IEC's effects on conductivity and crossover, membrane durability and IEC are inversely related.⁸⁸ Therefore, it is desirable to minimize IEC while still achieving acceptable system performance.

In this chapter, we report the results of cell testing with quaternary ammonium functionalized and sulfonated Diels Alder poly(phenylene) membranes (QDAPP and SDAPP, respectively) with systematically varied IEC. QDAPP is an AEM with its positively charged quaternary ammonium functional groups tethered on aryl side chains; SDAPP is a cation exchange membrane (CEM) with its negatively charged sulfonic acid functionalized aryl side chains, as shown in Figure 3.1. Data on some of the properties of these membranes was previously reported^{88,120} in two papers from our team. In that work, the membrane properties were compared to those of Nafion under similar conditions. Estimates of the extent of hydration, the conductivity, and the permeability of membranes were presented in varying degrees of detail. Also, the morphology of SDAPP and Nafion were compared.

This work affords a unique opportunity for comparison of closely related cation- and anion-exchange membranes. The focus is on the behavior of these materials in cells. Polarization curves were obtained to demonstrate the cell voltage as a function of current density, as VRFBs used for grid-scale energy storage are not typically subjected to constant-current charging and discharging as in the laboratory; charge and discharge currents are dependent on dynamic grid

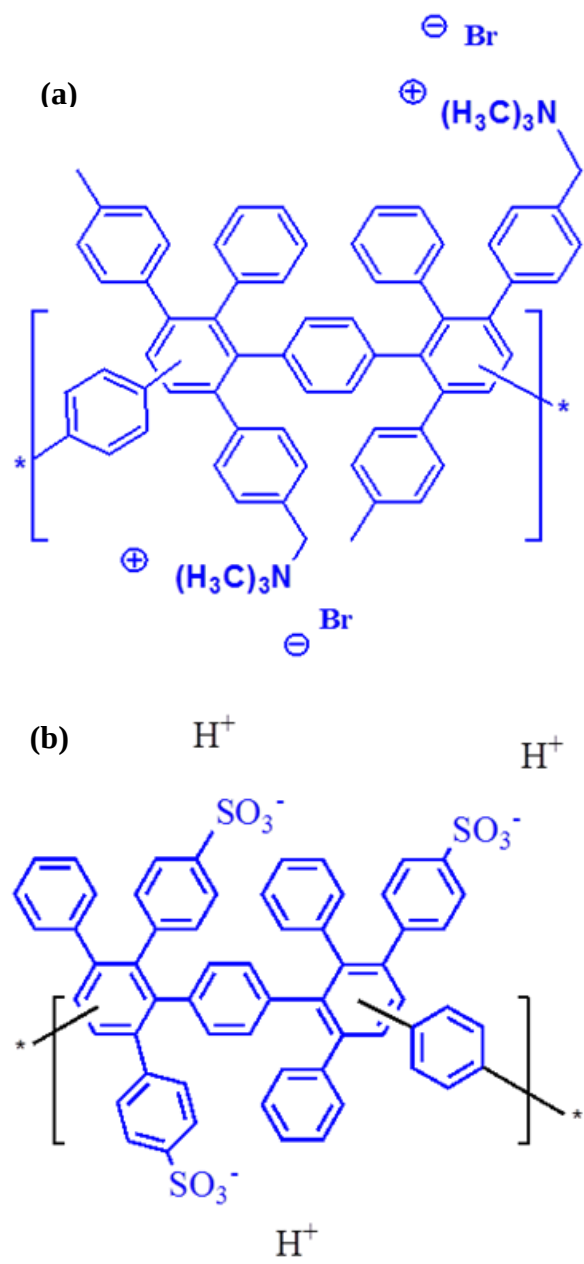


Figure 3.1. Membrane structures synthesized in this work: (a) QDAPP and (b) SDAPP.

conditions, and therefore must be able to operate over a range of currents. Polarization curves are also a commonly used tool for resolving activation, ohmic, and concentration polarizations in electrochemical devices in order to understand the origin of losses and identify performance-limiting factors;^{97,98} such information is not readily available from the cycling experiments typical of VRFB studies. Open circuit voltage (OCV) decay measurements were used to compare the relative vanadium permeability of the different membranes. Cycling at a current density of 200 mA/cm² was also carried out to evaluate energy efficiency, coulombic efficiency, and voltage efficiency.

3.2 Experimental

Membranes were characterized by ex situ measurements as well as full cell testing including polarization curves, open circuit voltage decay, and cycling. The SDAPP and QDAPP membranes used in this work were synthesized and fabricated at Sandia National Laboratory, following the method in our previous work.^{121,122} The IEC of each membrane was determined by the back-titration method.^{121,122} The IECs of SDAPP membranes were measured as 1.4, 1.8 and 2.2; the measured IECs for QDAPP membranes were 0.4, 0.8 and 1.2. The membranes are named after their IEC to ease further discussion. The synthesized membranes were kept in DI water (18 M Ω cm) at ambient temperature until use. Nafion 117 and 211 membranes (Ion Power) were used as received.

Membrane conductivity was previously reported by our group in References 88 and 120; the conductivity data in Table 3.1 is a reproduction of these data sets. Conductivity was measured after equilibration in 5 M H₂SO₄ solution for over 24 hours to mimic behavior in battery electrolyte. The membrane conductivity was measured with a four probe conductivity

cell in a protocol described elsewhere.¹²³ Thicknesses of membrane samples were taken by a Mitutoyo 369-350 digital micrometer after soaking in DI water.

Table 3.1. The properties of SDAPP and QDAPP membranes with different sulfonation or quaternization stoichiometry. Thicknesses were measured after soaking in DI water; conductivities were measured in 5 M sulfuric acid solution.

Polymer	Membrane	IEC (meq/g)	Thickness (μm)	Conductivity (mS/cm)	ASR ($\Omega \text{ cm}^2$)
SDAPP	1	1.4	47.0 $\pm$ 6.0	19.8 $\pm$ 3.3	0.237
	2	1.8	40.7 $\pm$ 7.3	61.1 $\pm$ 4.7	0.067
	3	2.2	49.7 $\pm$ 2.7	107.3 $\pm$ 31.8	0.046
QDAPP	1	0.4	59.7 $\pm$ 6.3	30.0 $\pm$ 9.3	0.199
	2	0.8	53.7 $\pm$ 3.7	96.8 $\pm$ 10.7	0.055
	3	1.2	54.0 $\pm$ 8.0	87.8 $\pm$ 6.2	0.062
Nafion	117	0.91	198.7 $\pm$ 6.3	73.1 $\pm$ 0.7	0.272
	211	0.91	28.7 $\pm$ 6.3	125.0 $\pm$ 3.1	0.023

3.2.1 Electrolyte solution preparation

Vanadium electrolyte solutions of 1.7 M vanadium with 5 M total sulfate were prepared from vanadyl sulfate (99.9%, Alfa Aesar) and sulfuric acid (96%, Alfa Aesar) dissolved in DI water. A flow cell with a 25 cm² geometric active area and one layer of SGL 10AA carbon paper on each side of the battery separated by two layers of Nafion 117 was used to carry out bulk charging and discharging of solution. Two layers of membrane were used to minimize crossover of vanadium species. Initial charging of the solution was carried out at a constant cell voltage of 1.8 V with a 2:1 ratio of catholyte to anolyte volumes. Charging was terminated when the current density in the charging cell decreased to 10 mA/cm², where an SoC of 100% was assumed. Upon

completion of charging, one half of the catholyte solution was discarded to obtain a 1:1 catholyte:anolyte ratio.

3.2.2 Cell architecture

Battery testing was carried out in a zero-gap architecture 5 cm² cell with single channel serpentine flow fields.¹⁰⁴ CP-ESA carbon paper (supplied by SGL carbon) was used as the electrode material on both sides of the battery. The carbon paper, originally 370 µm thick, was compressed to ca. 65% of its original thickness. Membranes were removed from DI water and blotted dry before assembly. All experiments were carried out in a temperature chamber controlled at 30 °C. An ultra-high purity nitrogen purge in the electrolyte storage tanks was used to prevent oxidation of the vanadium species. During polarization curves and cycling experiments, a flow rate of 90 mL/min was provided by a dual-channel peristaltic pump (Cole Parmer). Electrochemical measurement and control was performed with a Bio-Logic VSP potentiostat with a 20 A booster.

3.2.3 Polarization curves

A single-pass flow configuration was used, in which solutions were pumped from one tank, through the cell and into a separate tank, i.e. there was no recirculation. In this manner, constant SoC conditions were maintained in the electrolyte solution at the cell inlet. Curves were obtained with 440 mL of solution at 100% SoC and 50% SoC. The 50% SoC solution was obtained by discharging 100% SoC solution in a separate cell held at 0.9 V until one half of the coulombs were discharged.

Potential steps in increments of -0.1 V with a superimposed AC signal with a 10 mV amplitude were carried out to obtain the polarization curves. The cell resistance was taken as the

high-frequency intercept of the impedance spectra with the real axis and was used to iR -correct the curves. The area specific resistance (ASR) was calculated by multiplying the HFR by the cell cross-sectional area.

3.2.4 OCV decay

The OCV decay was monitored to obtain a qualitative comparison of vanadium ion permeation across each membrane. OCV decay was measured after 100% SoC solution was pumped into the cell and then statically held in the cell.

3.2.5 Cycling

Cycling was carried out at a constant current density of 200 mA/cm², with cutoff voltages at 1.2 and 1.65 V. HFR measurements during cycling were carried out with a superimposed 10 mV AC signal on a DC potential of 1.2 and 1.65 V at the end of discharge and charge, respectively. 50 mL of solution was used on both the positive and negative sides of the battery. Efficiencies were calculated by the following equations:

$$\text{coulombic efficiency} = \frac{\text{discharge capacity}}{\text{charge capacity}} \quad (3.1)$$

$$\text{voltage efficiency} = \frac{\text{average discharge voltage}}{\text{average charge voltage}} \quad (3.2)$$

$$\text{energy efficiency} = \text{coulombic efficiency} \times \text{voltage efficiency} \quad (3.3)$$

3.3 Results and discussion

3.3.1 Membrane properties

In Table 3.1, synthesized SDAPP and QDAPP membrane properties are presented. The IEC ranges of SDAPP (1.4 – 2.2 meq/g) and QDAPP (0.4 – 1.2 meq/g) were chosen to provide similar water uptake and conductivity values, as VRFB performance is directly related to these transport parameters. The thickness of DI water-soaked SDAPP and QDAPP membranes used in

cell testing varied from 41 to 50 μm for SDAPP and 54 to 60 μm for QDAPP. Because these thicknesses are relatively close to each other within each membrane family, any difference in membrane properties is attributed to the varying IEC and not thickness. The ASR included in the table is calculated by dividing the membrane thickness by the conductivity. SDAPP 1.8 and 2.2 and QDAPP 0.8 and 1.2 obtained conductivities between 61 and 107 mS/cm, comparing favorably with the 73 mS/cm of Nafion in the 5 M H_2SO_4 electrolyte environment. The conductivity of SDAPP follows the expected trend, with conductivity increasing from 19.8 mS/cm at 1.4 meq/g to 61.1 mS/cm at 1.8 meq/g and 107.3 mS/cm at 2.2 meq/g. However, the QDAPP samples displayed differing behavior, with conductivity increasing from 30 to 96.8 mS/cm with an increase in IEC from 0.4 to 0.8 meq/g followed by a slight drop in conductivity from 96.8 to 87.8 mS/cm with an additional increase in IEC from 0.8 to 1.2 meq/g. Superficially, this anomaly could be attributed to a dilution effect, described in detail by Kim and Pivovar¹²⁴: as the IEC increases, water uptake increases. Beyond a certain point (the percolation threshold), additional water uptake can decrease the concentration of the charged functional groups, which can result in reduced conductivity. However, attributing the observed phenomenon to the dilution effect is speculative at this point. The behavior of the membrane immersed in sulfuric acid is significantly more complex than that of membranes in deionized water since additional charge carriers (sulfuric acid components) beyond those contributed by the fixed sites are present in the former case. This would seem likely to mitigate any dilution effects.

In QDAPP, the observed conductivities in sulfuric acid solution were similar to those obtained with SDAPP and Nafion, in spite of the fact that anion mobility in AEMs is typically lower than proton mobility in CEMs.^{125,126} While AEMs can be effective at blocking cation

permeation at low concentration, uptake of acid (water) can occur in the high acid concentration environment.^{127,128} Our results point to a major role for imbibed acid in the membranes exposed to concentrated sulfuric acid. In the presence of excess acid, it is possible that the protons carry substantial charge in the AEM, while anions do not exhibit similar behavior in the PEM. Keep in mind that at high hydration levels typical of the conditions used here, transport occurs through the bulk of solution in any pores, with little direct involvement from the side chains. The data in this and other studies clearly suggest a more complex transport process. Of course, this conclusion is primarily associated with membranes equilibrated with pure water and therefore must be regarded as tentative. Another consequence of this assertion (that both species are mobile) is that transport of acid or salts takes place under conditions in which electroneutrality is maintained locally within the membrane.

3.3.2 Polarization curves

The cell voltage, *iR*-free cell voltage, and ASR obtained during polarization curves at 50% SoC and 100% SoC for QDAPP and SDAPP are shown in Figure 3.2 and Figure 3.3, respectively, with Nafion included for reference. *iR*-free polarization curves represent a combination of activation and concentration polarizations, which are primarily attributed to the electrode kinetics and mass transport through the electrode induced by the flow field, respectively. As seen in Figure 3.2(a,b) and Figure 3.3(a,b), at current densities below 1000 mA/cm², the *iR*-free cell voltage is essentially the same between membranes and membrane types, indicating consistent electrode behavior between different cells. At current densities above 1000 mA/cm² in Figure 3.2, the *iR*-free cell voltage curves for SDAPP and QDAPP diverge from

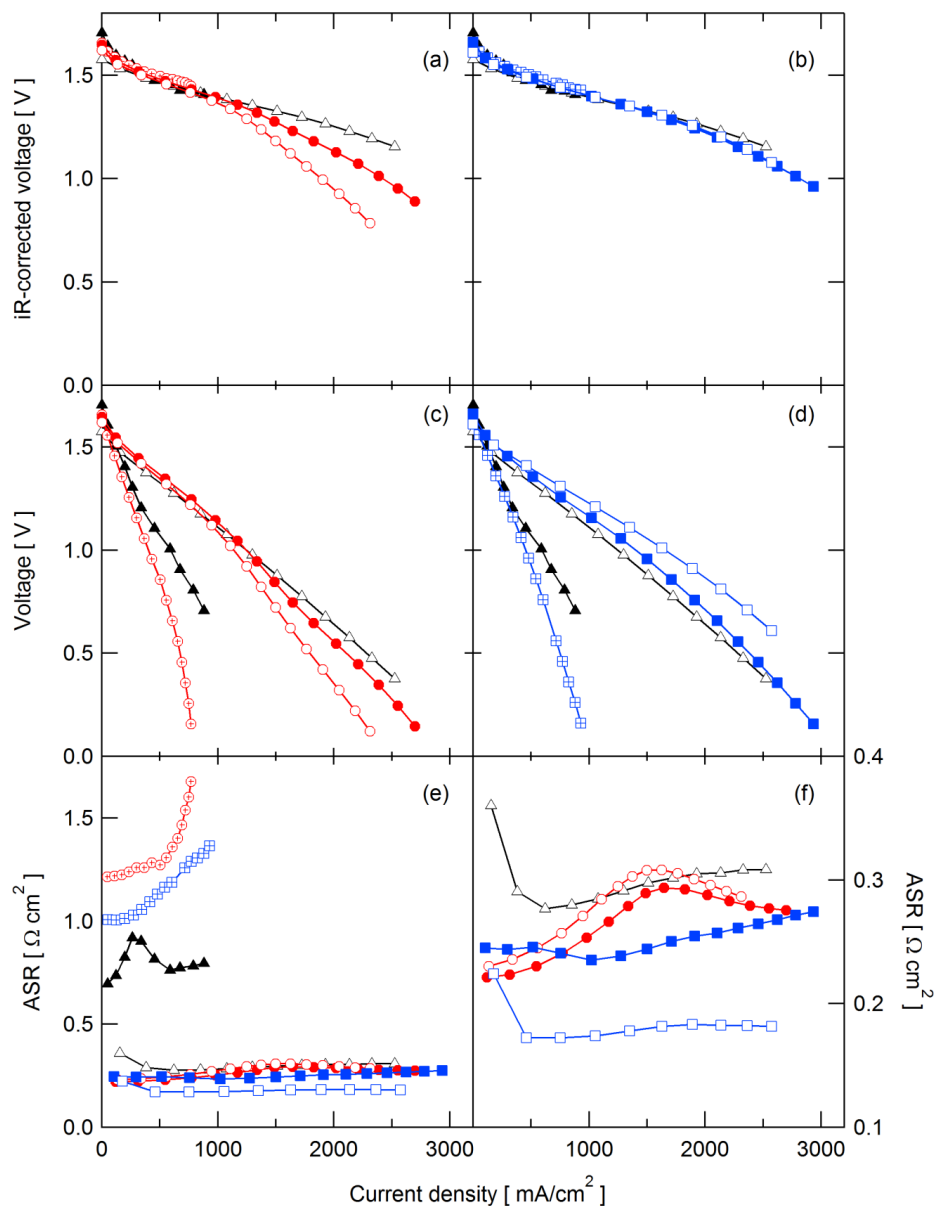
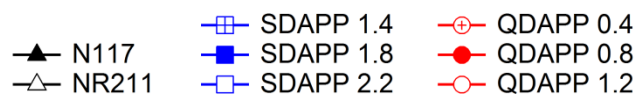


Figure 3.2. Polarization curves obtained at 100% SoC for QDAPP (a,c) and SDAPP (b,d) membranes, with Nafion for comparison: (a,b) iR-corrected and (c,d) actual cell voltages. ASR obtained during polarization curves for all membranes (e) and zoomed in on low-resistance membranes (f).

Symbols are as follows:



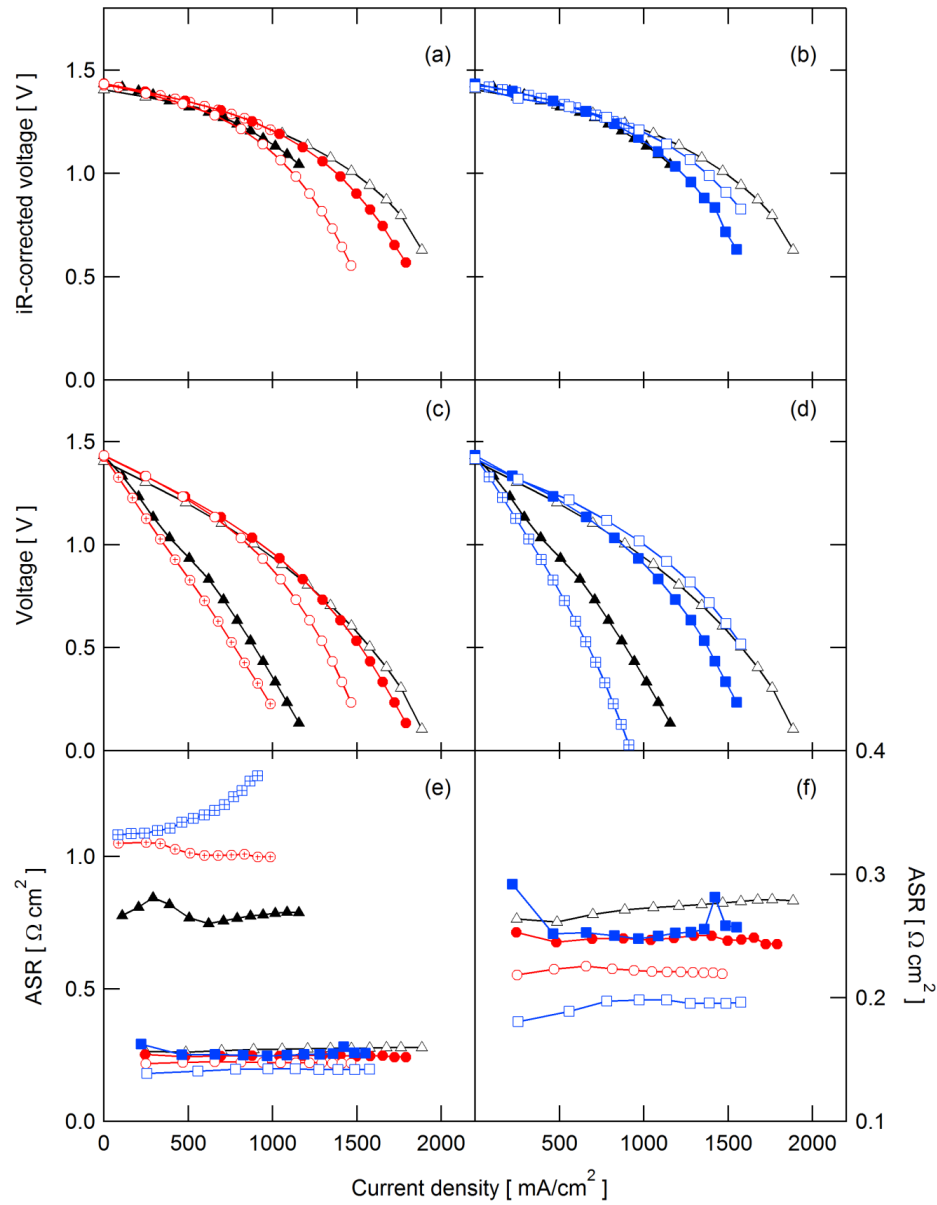
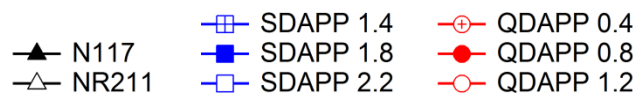


Figure 3.3. Polarization curves obtained at 50% SoC for QDAPP (a,c) and SDAPP (b,d) membranes, with Nafion for comparison: (a,b) iR-corrected and (c,d) actual cell voltages. ASR obtained during polarization curves for all membranes (e) and zoomed in on low-resistance membranes (f).

Symbols are as follows:



Nafion. This suggests an additional concentration polarization due to the membrane. This divergence at 100% SoC is seen primarily in QDAPP and not SDAPP, shown in Figure 3.3(a). As noted above, the uptake of acid into these membranes entails a shift in transport mechanism. The ‘natural’ tendency for transport in AEMs is to conduct anions, whereas in the CEM the tendency is for proton transport. Thus, it is likely that transport in the AEM includes a relatively high transference number for the bisulfate anion in comparison to the transference number for bisulfate in CEMs. Especially in the AEM, the membrane is no longer a single ion conductor. To allow the battery to perform, significant proton transport must also occur within the AEM in the aqueous pore solution within the polymer. In order to explain the apparent concentration polarizations at current densities above 1000 mA/cm^2 , we consider the electroneutrality requirement and the transference numbers of protons and bisulfate. Electroneutrality requires that ions (predominantly protons and/or bisulfate) cross the membrane to balance the electron transport occurring during charge or discharge. In the polarization curves in this work, only discharge is considered; ionic current through the membrane consists of a combination of protons traveling from the negative electrode to the positive and bisulfate traveling in the opposite direction. In SDAPP, it is expected that protons carry the bulk of the current; in QDAPP, bisulfate is expected to play a significant role. As current is passed, a buildup of bisulfate occurs on the negative side of the cell near the membrane, as bisulfate travels from the positive to negative electrode during discharge. We postulate that this buildup of bisulfate ions is at least partially responsible for the concentration polarization observed in QDAPP 0.8 and 1.2 at 50% SoC (QDAPP 0.4 did not reach high enough current to display the polarization due to prohibitively high ASR). Comparing QDAPP 1.2 to NR211 at a current density of $\sim 2.3 \text{ A/cm}^2$,

QDAPP 1.2 exhibited an additional 400 mV of concentration polarization, presumably due to the imbalance in bisulfate across the membrane. Of course, in the operating cell, transport of vanadium species is also important. The differences between the 50% and 100% SoC curves, and where the additional concentration polarization appears, are likely related to transport of the differing vanadium species when at 50% SoC and 100% SoC.

The uncorrected cell voltages reflect the performance of the cell with the inclusion of ohmic losses. Shown in Figure 3.2(c,d) and Figure 3.3(c,d), the performance of cells using QDAPP 0.8 and 1.2 and SDAPP 1.8 and 2.2 compare well with NR211, predicting operating voltages within ~100 mV of NR211 under 1.5 A/cm². These mid and high IEC QDAPP and SDAPP membranes show promise as membranes for enabling lower voltage losses at high current densities as a result of their low resistances. Even beyond 500 mA/cm², the cell voltage was above 1.0 V. QDAPP 0.4 and SDAPP 1.4 had significantly lower voltages because of their high ohmic loss, precluding high efficiency operation at high current density.

The OCV taken during polarization curves is shown in Table 3.2; for the 100% SoC curves, the OCV was highest for N117 (1.706V) and lowest for NR211 (1.577V), with the QDAPP and SDAPP membranes falling in the range between them. The difference in OCV can be attributed to crossover of VO₂⁺ and V²⁺ species, similar to the influence of fuel crossover on OCV in DMFCs.¹²⁹ Crossover is pronounced in high ion conduction films and thinner membranes (<30 micron), which leads to larger OCV drops. At 100% SoC, even small rates of crossover can have a large impact on OCV because the Nernst equation is very sensitive to small changes in concentration at high SoC, illustrated by the simple calculation below. The OCV of a VRFB is given by the following equation, neglecting the effect of protons:

$$E^0 = \frac{RT}{F} \ln \left(\frac{[\text{VO}_2^+] \times [\text{V}^{2+}]}{[\text{VO}^{2+}] \times [\text{V}^{3+}]} \right) \quad (3.4)$$

If it is assumed that a highly permeable membrane allows a 2% change in SoC in the electrolyte contained within the cell, the difference in OCV is much larger at 99% SoC than at 50% SoC. At 298 K, the thermodynamic difference in OCV is 57 mV as follows:

$$E^0(99\%) - E^0(97\%) = \frac{RT}{F} \left[\ln \left(\frac{0.99 \times 0.99}{0.01 \times 0.01} \right) - \ln \left(\frac{0.97 \times 0.97}{0.03 \times 0.03} \right) \right] = 0.057 \text{ V, whereas the difference}$$

in OCV between an SOC of 50% and 48% evaluates to 4 mV in a similar expression.

Table 3.2. The measured OCV during 50 and 100% SoC polarization curves.

	OCV at 50% SoC	OCV at 100% SoC
QDAPP 0.4	1.428	1.657
QDAPP 0.8	1.435	1.646
QDAPP 1.2	1.434	1.621
SDAPP 1.4	1.428	1.661
SDAPP 1.8	1.434	1.657
SDAPP 2.2	1.418	1.611
N117	1.435	1.706
NR211	1.406	1.577

The ASR in VRFBs is a combination of the ionic and electronic resistances in the cell. Ionic resistance results from the resistance of the membrane as well as the liquid electrolyte; ionic conductivity (including vanadium, protons, and sulfate) and thickness in the cell are the main determinants of the membrane resistance. Electronic resistance is due to the bulk resistance of the carbon paper and graphite flow fields as well as the contact resistance between these components in the cell assembly. In VRFBs, the majority of the ASR is attributed to the membrane,^{71,113} and in this study the flow field/electrode configuration were consistent between

builds; therefore, observed changes in the cell ASR are attributed to the membrane. At 50% SoC, the ASR is inversely related to IEC: the average ASRs between 0 and 500 mA/cm² for QDAPP 0.4, 0.8, and 1.2, were 1.05, 0.25, and 0.22 Ω cm², respectively; SDAPP 1.4, 1.8, and 2.2 were measured at 1.09, 0.25, and 0.19 Ω cm², respectively. However, at 100% SoC, QDAPP 0.8 has a slightly lower ASR than QDAPP 1.2, consistent with the trend in measured conductivities in sulfuric acid. Such behavior indicates that the conductivity of QDAPP is sensitive to the electrolyte environment. As previously discussed, the ion conduction mechanism in QDAPP may be strongly related to the acid/water uptake behavior. Thus, it follows that when SoC changes, which can affect acid uptake,¹²³ the membrane conductivity may also change. In contrast, the SDAPP membranes do not appear to have the same sensitivity to 100% SoC solutions. It is notable that the ASR is highly nonlinear as a function of IEC for both SDAPP and QDAPP: an increase of 0.4 meq/g from SDAPP 1.4 to 1.8 or QDAPP 0.4 to 0.8 decreases ASR from 1 Ω cm² to less than 0.3 Ω cm²; an additional 0.4 meq/g increase in IEC has little additional impact. As discussed above, the membranes exhibit complicated acid uptake behavior. That ASR responds non-linearly to IEC is further evidence that the acid uptake behavior is not straightforward. Furthermore, the nonlinearity may also suggest that the conductivity optimization cannot be achieved by solely increasing IEC.

At 100% SoC, the QDAPP 0.4 and SDAPP 1.4 membranes exhibit an ASR that sharply increases as a function of current density (30% increase in ASR at the maximum current density compared to OCV). Similar trends have been seen in fuel cells due to dry-out of the anode.¹³⁰ Though the membrane is in constant contact with liquid-phase sulfuric acid solution in the flow battery, it is still possible for the membrane to experience local decreases in water content if the

water diffusivity within the membrane cannot keep pace with electro-osmotic drag. Furthermore, these low IEC membranes are of particularly low water content in the first place. Previous fuel cell membrane work showed that water diffusivity and water content are positively correlated;¹³¹ thus, with membranes in which the water content is low, water diffusivity is low. This is the case for the low IEC membranes, as low IEC results in reduced water uptake. For QDAPP 0.8 and 1.2 at 100% SoC, the ASR also shows some dependence on current density, with a maximum appearing at $\sim 1.5 \text{ A/cm}^2$. At 50% SoC, the ASR shows little variation with current density. Elucidating the differences in ASR as functions of SoC and current density are outside the scope of this publication. From the results shown here, it appears that the anion exchange membrane, QDAPP, appears to be more sensitive to the solution conditions. As discussed above, concentration or transference effects also are likely to exhibit a strong influence on behavior.

It is noted that the ASR as measured in the cells is notably higher than that predicted by conductivity measurements in sulfuric acid (Table 3.1). For example, SDAPP 1.8 in sulfuric acid had an ASR of $0.067 \text{ } \Omega \text{ cm}^2$; in the cell with vanadium solution, it was between 0.250 and $0.300 \text{ } \Omega \text{ cm}^2$. The presence of vanadium has been shown to decrease membrane conductivity by a factor of 2 when the membrane is equilibrated in 1.7 M vanadyl sulfate / 5 M total sulfate solution, as discussed in detail elsewhere.¹²³ In that study, it was suggested that the presence of vanadium cations within the bulk water solution can interfere with the hydrogen bonding network, disrupting proton conduction via the Grotthus mechanism. We expect that the increase in ASR from the conductivity measurement to the measured in-cell ASR with vanadium is due to the presence of vanadium species within the membrane.

The overall contribution of membrane resistance to the overall cell polarization is significant, as shown in Figure 3.4 with data obtained from the 50% SoC polarization curves. With the low IEC QDAPP and SDAPP, the cell resistance accounts for at least 80% of the cell's overall polarization over the entire current density range, with N117 accounting for only slightly less. With the low resistance QDAPP and SDAPP and NR211, the membrane accounts for ca. 50% of the overall polarization at a current density of 250 mA/cm². As most VRFBs operate at or below this current density with comparable or higher ASR, it is clear that the membrane's ohmic resistance is a major contributor to voltage loss in most VRFB systems to date.

3.3.3 OCV decay

Differences in the OCV were observed during polarization curves; such differences are indicative of differing rates of vanadium permeation through the membrane. OCV decay experiments were carried out to qualitatively compare vanadium crossover between membranes in a straightforward manner, although detailed information about the permeation rates of the individual oxidation states of vanadium cannot be obtained from this experiment without additional instruments to measure the vanadium concentrations independently, e.g. UV-vis spectroscopy¹³² and potentiometric titration.¹³³ As the measured thickness of the QDAPP and SDAPP membranes were similar (40-60 μm), differences in the OCV decay are attributed to the vanadium ion permeability of each membrane. Shown in Figure 3.5 is the OCV decay for each membrane over time, including a comparison to Nafion; the profile is not expected to be linear and is described further by Sun and coworkers.¹³³ N117 closely overlaps the very similar SDAPP 1.4 and 1.8 results, while NR211 overlaps the SDAPP 2.2 data. QDAPP membranes can exhibit markedly slower OCV decay, as QDAPP 0.4 exhibited nearly 200 mV less OCV decay

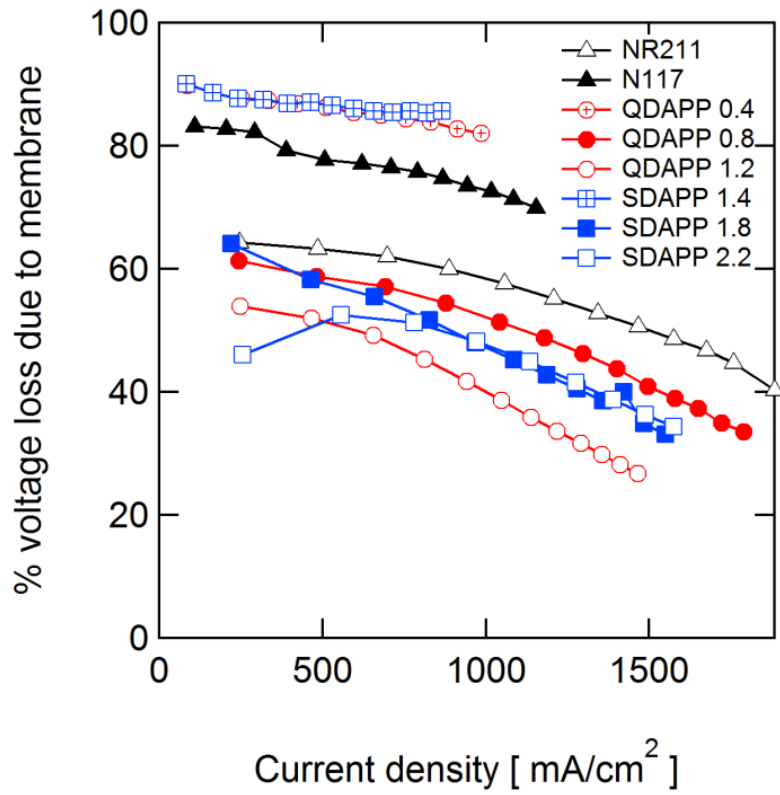
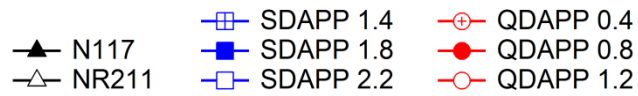


Figure 3.4. Fraction of total voltage loss due to the membrane resistance in the cell obtained during 50% SoC polarization curves.

Symbols are as follows:



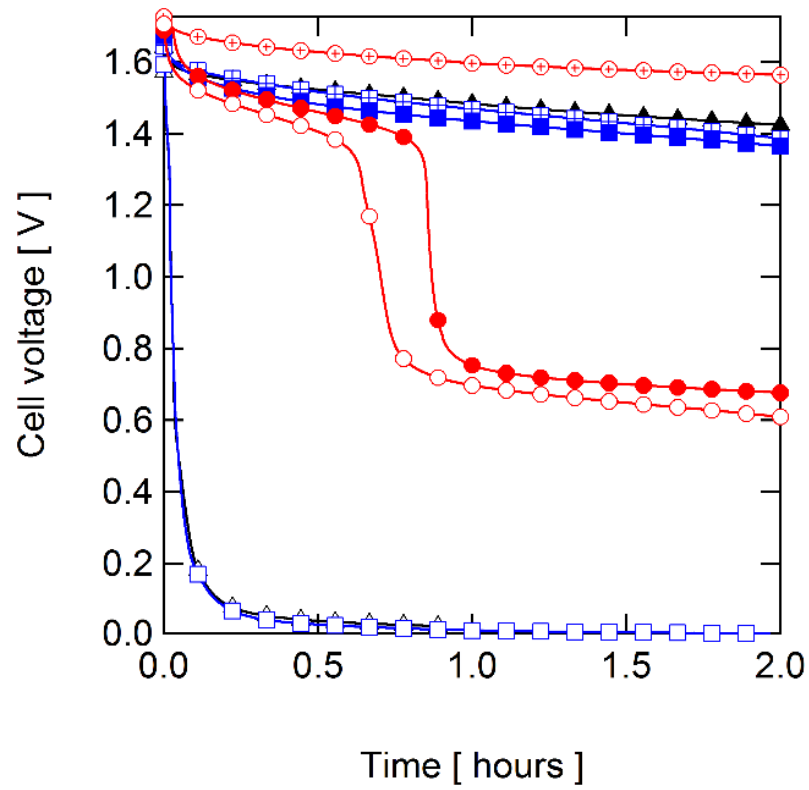
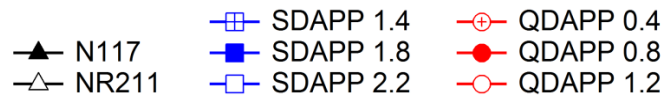


Figure 3.5. Open circuit voltage decay from 100% SoC in a static environment. Symbols are as follows:



than N117 and SDAPP 1.4 and 1.8. Interestingly, QDAPP 0.8 and 1.2 did not prevent OCV decay more readily than N117 or SDAPP 1.4 and 1.8. In References 88 and 120 we reported estimates of the permeability of the VO^{2+} ion (K_V) through the membranes. Table 3.3 shows the permeabilities of the QDAPP and SDAPP membranes relative to N117. The measured permeability in QDAPP membranes is similar to that in the SDAPP membranes: $K_V(\text{QDAPP 1.2})/K_V(\text{SDAPP 2.2}) \sim 1.14$, $K_V(\text{QDAPP 0.8})/K_V(\text{SDAPP 1.8}) \sim 1.00$, and $K_V(\text{QDAPP 0.4})/K_V(\text{SDAPP 1.4}) \sim 0.44$.^{88,120} Also, dramatic decreases in vanadium permeability with decreasing IEC were observed for both membrane types, such that $K_V(\text{QDAPP 1.2})/K_V(\text{QDAPP 0.4}) \sim 14$ and $K_V(\text{SDAPP 2.3})/K_V(\text{SDAPP 1.4}) \sim 36$.^{88,120} Based on the VO^{2+} permeability alone, the OCV decay should be rather similar for each IEC pair. However, both the low and high IEC QDAPP had slower OCV decay than their low and high IEC SDAPP analogs. The middle IEC QDAPP, however, exhibited a faster decline, with a sharp drop occurring after ~ 1 h while the middle IEC SDAPP did not show the sharp drop even after 2 h.

Table 3.3. VO^{2+} permeabilities of QDAPP and SDAPP relative to permeability in N117. Low IEC refers to SDAPP 1.4 & QDAPP 0.4, mid refers to SDAPP 1.8 & QDAPP 0.8, and high refers to SDAPP 2.2 & QDAPP 1.2.

IEC	SDAPP	QDAPP
Low	0.037	0.042
Mid	0.331	0.330
High	1.337	0.589

Based on simple electrostatics, it is expected that QDAPP would exhibit a slower OCV decay in comparison with SDAPP, as the positively charged functional groups in QDAPP should impede vanadium transport relative to the negatively charged functional groups in SDAPP as a result of Donnan exclusion. Note, however, that we are working in a domain in which Donnan exclusion is overcome and the primary effects are subtler than might be expected from

electrostatics alone. The consequences of Donnan breakthrough means that water/acid uptake are much more important, as vanadium ions will diffuse through the bulk liquid within the membrane. Thus, increased IEC leading to more water/acid uptake should also lead to higher vanadium permeability in both QDAPP and SDAPP. The permeability measurements as well as the OCV decay confirm this hypothesis. Importantly, increasing the IEC of QDAPP membranes does not result in lower permeability. Thus, the idea that AEMs prevent crossover or vanadium permeation is not necessarily true in the concentrated electrolyte environment typical of VRFBs.

3.3.4 Cycling

The cycling performance of each membrane was compared by evaluating coulombic, voltage, and energy efficiencies for 20 cycles, with the first cycle for each cell tested shown in Figure 3.6. The QDAPP 0.4 and SDAPP 1.4 membranes are not presented here since their high ASR precluded cycling at 200 mA/cm². The cycling behavior of the membranes was relatively stable: as shown in Figure 3.7, the voltage efficiency (VE) was virtually unchanged from cycle 1 to cycle 20 for all cells. The coulombic efficiency (CE) was stable in all cases with the exceptions of NR211 and SDAPP 2.2. Differences in coulombic efficiency are primarily affected by the membrane, as it is the only variable changed between tests. It is expected that the tests adopting membranes with high vanadium permeability result in lower CE, as self-discharge occurs when vanadium species cross the membrane and react with the charged V²⁺ and VO₂⁺ species. The CEs observed generally agree with the OCV decay experiments. The SDAPP 2.2 and NR211 membranes, with rather rapid OCV decay, had CEs below 50%. SDAPP 1.8 had the highest CE, followed by QDAPP 0.8, QDAPP 1.2, and then N117; all of these membranes were between 94 and 96% CE. Other than N117, these results follow the same trend as the OCV

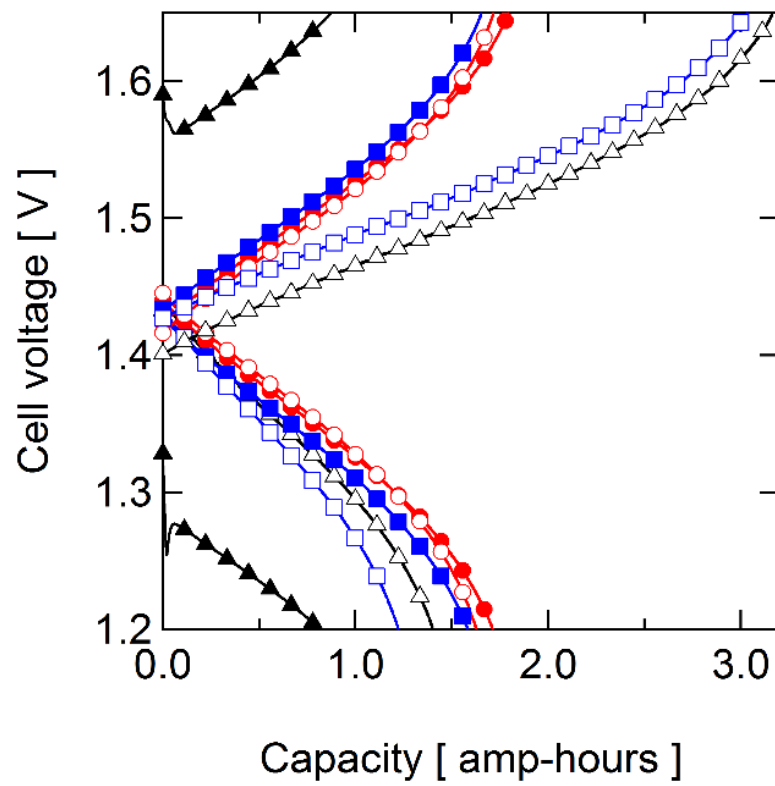


Figure 3.6. First charge/discharge cycle voltage profile.

Symbols are as follows:

- | | | |
|---------|-------------|-------------|
| ▲ N117 | ■ SDAPP 1.8 | ● QDAPP 0.8 |
| △ NR211 | □ SDAPP 2.2 | ○ QDAPP 1.2 |

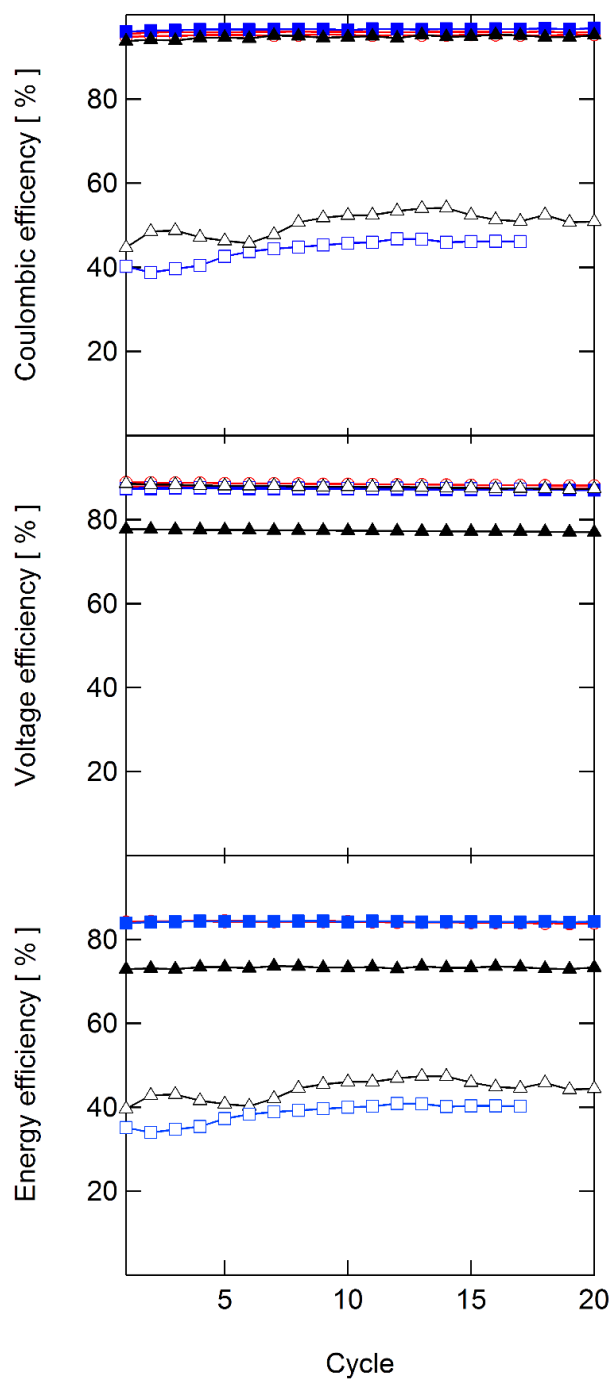


Figure 3.7. Coulombic, voltage, and energy efficiencies obtained during cycling.

Symbols are as follows:

- | | | |
|---------|-------------|-------------|
| ▲ N117 | ■ SDAPP 1.8 | ● QDAPP 0.8 |
| △ NR211 | □ SDAPP 2.2 | ○ QDAPP 1.2 |

decay, with SDAPP 1.8 showing the slowest OCV decay (corresponding to the highest CE), followed by QDAPP 0.8 and then QDAPP 1.2. It is noted that while QDAPP 0.8 and 1.2 appear to be significantly worse than N117 and SDAPP 1.8 in terms of OCV decay, the CEs were in fact very similar. These results show that while the OCV decay experiment is useful as a qualitative tool for comparing vanadium permeability, CE cannot be predicted solely by the OCV decay experiment. The discrepancy may be due to the fact that the OCV decay experiment only measures diffusional crossover statically and neglects the electro-osmotic and pressure-driven fluxes that are present in an operating battery.⁷² The timeframe sampled in the two experiment types is different and the condition of the electrolyte varies substantially during cycling. Differences in the voltage efficiency (VE) are attributed to differing ohmic drops, as the iR -free voltages for all cells were very similar at 200 mA/cm² as measured in the polarization curves. Other than N117, which had a relatively low VE of 77% due to high ASR, the other five membranes cycled had very similar VEs (87-88%), illustrating that though the resistance is often considered to be a dominating factor in battery performance, the VE difference at the relatively high current density of 200 mA/cm² is not greatly affected by differing ASRs. The energy efficiency (EE) metric combines the VE and CE; the EE is relevant when comparing the tradeoffs between low conductivity membranes (low VE, high CE) and high conductivity membranes (high VE, low CE). Though NR211 and SDAPP 2.2 had some of the lowest observed ASRs, the poor CE dominates, with EEs of ~46 and 40%, respectively. In contrast, N117, with its high CE, pays a penalty in the VE for its relative thickness, resulting in an EE of 73%. SDAPP 1.8, QDAPP 0.8, and QDAPP 1.2 have the best overall performance in terms of EE, all ~85%, as they have high VE and CE. In comparing to N117, the SDAPP and QDAPP

membranes show an increase in EE of over 10% at the relatively high current density of 200 mA/cm². To further illustrate the tradeoff (or lack thereof) between achieving low permeability and high conductivity, the CE, VE, and EE are plotted against the ASR measured during cycling in Figure 3.8. Interestingly, high ASR does not necessarily result in drastically lower VE and low ASR does not necessarily result in low CE.

While coulombic, voltage, and energy efficiency are important factors in evaluating membranes, it is also important to monitor the capacity fade. This phenomenon is in part due to imbalances in the vanadium concentrations in each half-cell that build up as a result of crossover. As one side of the battery is depleted in vanadium, the total charge that can be stored in the electrolyte decreases, resulting in capacity fade. While VRFBs are touted for the ability to rebalance the electrolyte periodically, minimizing capacity fade is desirable to lower the maintenance cost associated with rebalancing operations. Figure 3.9 shows capacity fade, both in absolute terms and normalized with respect to the first cycle for each membrane. It is typically believed that membranes with low vanadium permeability are expected to exhibit decreased rates of capacity fade; however, this is only true if diffusion-based crossover dominates other transport phenomena. SDAPP 1.8 showed the lowest rate of capacity fade, losing only 6% of its capacity after 20 cycles; both QDAPP and Nafion lost over 15% of their capacity after 20 cycles. The erratic behavior of the SDAPP 2.2 capacity is attributed to membrane instability – as the ASR decreased for the first few cycles, the effective voltage window grew, increasing capacity. It is interesting that both Nafion and QDAPP showed similar rates of normalized capacity fade, as the CE for NR211 was significantly lower than that of N117 and both QDAPP membranes.

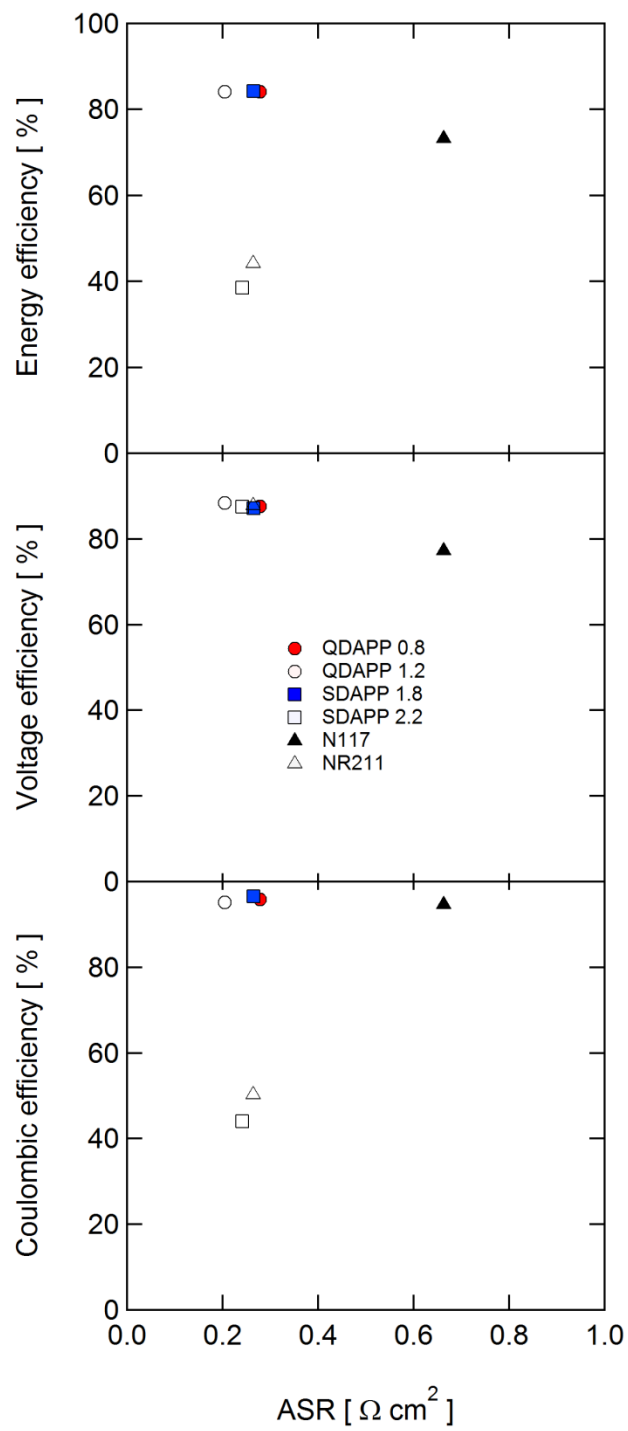


Figure 3.8. Coulombic, voltage, and energy efficiencies plotted against the average ASR measured during cycling.

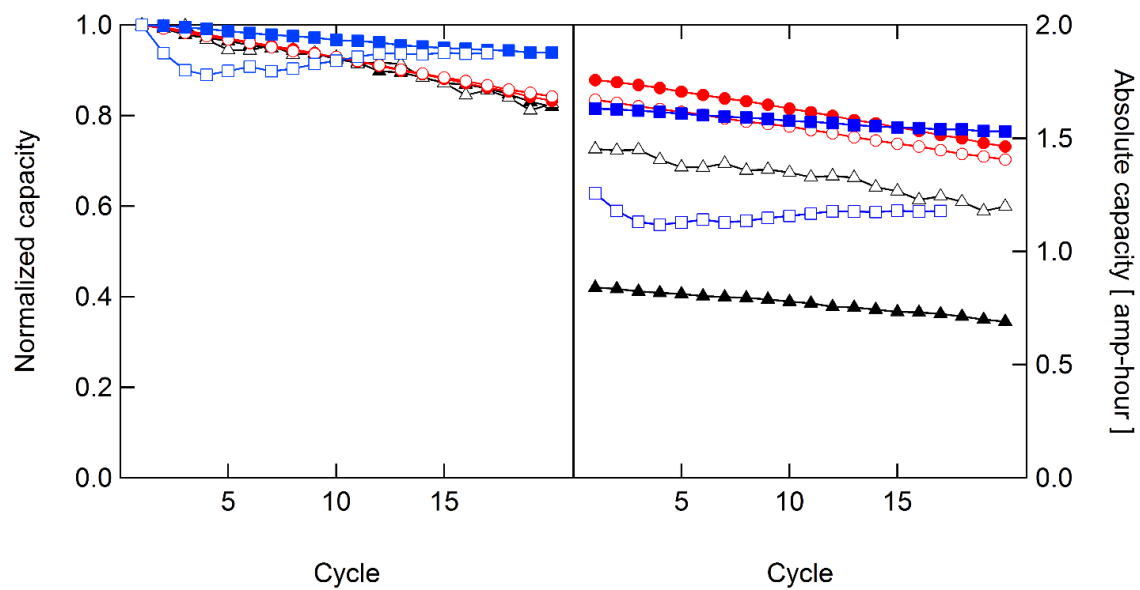


Figure 3.9. Discharge capacities obtained during cycling. Left: normalized to cycle 1 capacity. Right: absolute capacity.

Symbols are as follows:

- ▲— N117 —■— SDAPP 1.8 —●— QDAPP 0.8
- △— NR211 —□— SDAPP 2.2 —○— QDAPP 1.2

This finding suggests that capacity fade and CE are not strongly linked. Migration, diffusion, and convective forces can all cause crossover of vanadium ions, reducing CE; however, some of these modes of crossover may occur preferentially in one direction. For example, the negative side of the battery is always at a lower potential than the positive side, and thus migration may always act to drive the positively charged vanadium ions toward the negative side. The diffusion coefficient of vanadium ions through the membrane is dependent on the oxidation state of the vanadium, i.e., VO_2^+ diffuses more rapidly through the membrane than V^{2+} ;¹³⁴ this mismatch in diffusion coefficient can result in a net imbalance in vanadium concentration. Side reactions can also contribute to capacity fade.⁹³

Though QDAPP is an AEM, and SDAPP and Nafion are CEMs, the capacity fade does not appear to depend strongly on functional groups in the membrane. Again, this appears to correlate with the OCV decay results: the nature of the side chains in the membrane – cationic or anionic – does not seem to have a significant impact on vanadium permeation for membranes with comparable physical properties. This reinforces the notion that the overall rate of net crossover is not strongly dependent on diffusion along the charged functional groups, and more likely related to transport through the bulk acid/water solution in the membrane.

The absolute capacity is also an important metric to compare. Because a large portion of VRFB cost is due to the vanadium,²⁴ increasing the vanadium utilization is critical to achieving competitive cost. For equal volumes of electrolyte, then, the absolute capacity that can be discharged is of great importance. QDAPP 1.2 and 0.8, along with SDAPP 1.8, are the best performers in terms of absolute discharge capacity, with cycle 1 capacities between 1.6 and 1.8 Ah, 80-90% of the 2 Ah theoretical total capacity. The low capacity of N117 (0.8 Ah) is

attributed to the high ohmic drop; the cutoff potentials during cycling are reached prematurely. The poor absolute discharge capacity in NR211 (1.4 Ah) and SDAPP 2.2 (1.2 Ah) are attributed to high rates of vanadium crossover.

The ASR measured at the end of each discharge step is shown in Figure 3.10. Other than SDAPP 2.2 and N117, the membranes showed rather stable ASRs over time, indicating membrane stability in an operating cell over relatively short time periods. The slight decrease in the ASR of SDAPP 2.2 could be indicative of a short-term and non-catastrophic membrane degradation and explains the capacity increase for the SDAPP 2.2 membrane after a few cycles.

3.4 Conclusions

In this work, a comprehensive comparison of anionic and cationic Diels Alder poly(phenylene)s (QDAPP and SDAPP, respectively) and Nafion membranes in cells was carried out. Flow batteries assembled with QDAPP and SDAPP were shown to have ASRs as low as those assembled with Nafion 211; based on polarization curve analysis, the measured ASR was below $0.3 \Omega \text{ cm}^2$. Cycling with overall energy efficiencies of 85% for SDAPP 1.8 and QDAPP 0.8 and 1.2 at a current density of 200 mA/cm^2 were achieved. These membranes had coulombic efficiencies above 95%, slightly better than the thick Nafion 117, while their voltage efficiencies of 88% matched that of the thin Nafion 211.

The QDAPP membranes were most sensitive to operating conditions, with changes in ASR as a function of current density and a complicated relationship between IEC and ASR at 100% SoC. Additionally, apparent concentration polarizations were observed with QDAPP membranes at very high current densities. OCV decay was positively correlated with IEC; QDAPP was shown to have a rate of self-discharge in comparison with SDAPP and Nafion in

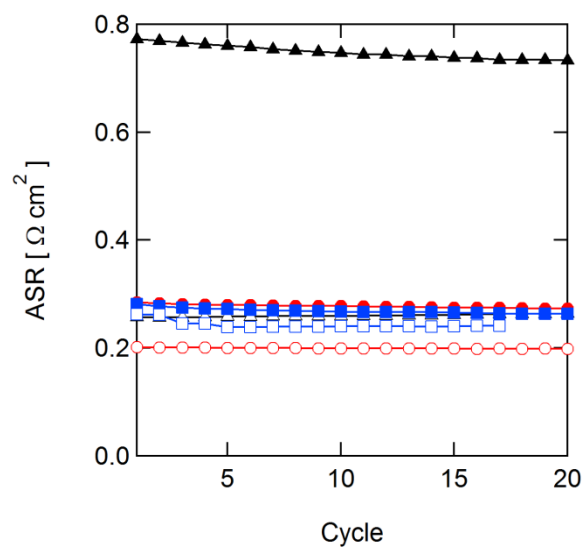


Figure 3.10. ASR measured at end of charging (solid symbols) and discharging steps (hollow symbols) during cycling.

Symbols are as follows:

- | | | |
|---------|-------------|-------------|
| ▲ N117 | ■ SDAPP 1.8 | ● QDAPP 0.8 |
| △ NR211 | □ SDAPP 2.2 | ○ QDAPP 1.2 |

spite of the fact that QDAPP is an AEM and the others were CEMs. Thus, under high acid concentrations typical in VRFBs, AEMs may not inhibit vanadium crossover as effectively as is typically assumed. The observed trends with vanadium permeation as well as membrane conductivity suggest that the ion conduction mechanism likely occurs in a bulk liquid phase.

CHAPTER 4
THE CELL-IN-SERIES METHOD: A NOVEL TECHNIQUE FOR ACCELERATED
ELECTRODE DEGRADATION IN REDOX FLOW BATTERIES

Abstract

This chapter is revised based on the published paper with permission:¹³⁵

Alan M. Pezeshki, Robert L. Sacci, Gabriel M. Veith, Thomas A. Zawodzinski, and Matthew M. Mench. “The cell-in-series method: a technique for accelerated electrode degradation in redox flow batteries.” *Journal of The Electrochemical Society* 163(1) (2016): A5202-A5210. [DOI: 10.1149/2.0251601jes] Copyright 2003, The Electrochemical Society.

My primary contributions to this work were the experimental design, collection, reduction, and interpretation of data, and composition of the manuscript. Sacci assisted in experimental design and composition of manuscript. Veith assisted in collection and interpretation of XPS data.

4.1 Introduction

In Chapters 2 and 3, improved cell performance through optimization of electrode and membrane materials was achieved. In this chapter, initial exploration of performance degradation is carried out to verify the stability of the high performance electrodes identified in Chapter 2. We present a methodology and initial findings for studying performance degradation in VRFBs. The energy efficiency loss in a typical VRFB cycling experiment is deconvoluted into contributions from decreased electrode performance and increased ohmic resistance within the membrane. Capacity fade, often attributed to crossover alone, is examined and the relative contributions of crossover and increased cell overpotential are discussed. Electrode changes are the focus of this study; therefore, changes in the membrane related to long-term durability are not discussed in great detail in this work.

A review of degradation-related publications was presented in Section 1.3.4. These previous studies show a link between aging and oxidation of the surface.^{8,11} The question of how

aging-induced oxidation affects the chemistry of an already-oxidized surface, and ultimately the electrode performance, is of interest.

Typical cycling experiments involve varying the SoC and alternating the direction of current, making it difficult to determine when electrode degradation occurs. To resolve the effects of SoC and charge/discharge condition on the surface chemistry of the electrode, we developed a novel cell-in-series (CIS) technique that maintains a constant SoC at a particular charge/discharge condition for indefinite periods of time. The CIS technique was used at high and low voltages to artificially stress the electrodes, which resulted in rapid decreases in performance relative to a cell that underwent typical cycling. This indicates that the CIS is a useful tool for accelerated VRFB testing. The technique is broadly applicable to flow batteries involving two liquid-phase redox reactions; it cannot be applied to hybrid flow batteries in which one electrode undergoes electroplating or electrodisolution because a steady state cannot be maintained.

Overall, this work presents the CIS technique as a tool to age electrodes at different sets of specified steady-state conditions. The use of XPS demonstrates how an analytical method can be used to identify specific changes in the physicochemical properties of the electrode due to differing operating conditions within the battery. The double layer capacitance of the electrodes was also measured and used as a proxy for the electrochemically active surface area. The surface oxygen content (from XPS) and surface area were assessed as two possible causes of the observed electrode performance degradation.

4.2 Experimental methods

In this work, electrodes are degraded at typical conditions in a cycling experiment, high and low SoC under charge and discharge conditions via the CIS method, and by chemical means through soaking in electrolyte solution. Polarization curves are used to characterize electrochemical performance and XPS is used to quantify oxygen content of selected electrodes. Capacitance measurements are used to estimate the electrochemically active surface area.

4.2.1 Setup

Cell architecture

Single-cell flow batteries using the no-gap architecture¹⁰⁴ with a single-channel serpentine flow field design were used. One layer of SGL 10AA carbon paper (SGL Group) compressed to 70% of its original thickness was used as the electrode in both sides of the cell. Geometric active areas of 5 and 25 cm² were used. All 5 cm² electrodes were heat treated in 42% oxygen / 58% nitrogen (Airgas) at 400 °C for 30 h prior to use;⁶¹ 25 cm² electrodes were used as received. Nafion 117 (DuPont) was used as the membrane in all cells. Cell temperatures were controlled at 30 °C with an Arbin FBTS 2000. Electrochemical measurement and control for cycling and CIS testing were performed with an Arbin FBTS 2000. Electrochemical measurement and control for CV and EIS used to determine the capacitance were carried out with a Bio-Logic Instruments VSP potentiostat. Polarization curves were obtained with the Bio-Logic VSP potentiostat coupled to a 20 A booster.

Electrolyte solutions

Solutions of 1.7 M vanadium ions in 5 M total sulfate were prepared from vanadium sulfate oxide hydrate (Alfa Aesar, 99.9%) and sulfuric acid (Alfa Aesar, ACS grade). Initial charging was performed with a 2:1 catholyte:anolyte volume ratio in a 25 cm² cell at 1.8 V until a cutoff current of 10 mA/cm² was reached. One half of the catholyte solution was then

discarded to obtain a 1:1 volume ratio of ca. 100% SoC catholyte and anolyte solutions.

Electrolyte tanks were purged with nitrogen (Airgas, UHP) to prevent oxidation of the vanadium species. Separate sets of solution were used for soaking, CIS, cycling, and polarization curve experiments as described below.

Cycling

A single-cell battery with 5 cm² geometric active area was used to carry out cycling at a current density of 200 mA/cm². Cutoff voltages of 1.0 V and 1.65 V for discharge and charge, respectively, were used. 50 mL of catholyte and anolyte were circulated at 90 mL/min.

Cell-in-series

In this work, the CIS method is introduced as a way to maintain constant conditions for flow battery testing. Two single-cell batteries were used, as shown in Figure 4.1; each battery is controlled by an independent channel on the potentiostat. The first cell, which will be described as the “cell of interest” in the remainder of this work, consists of a 5 cm² geometric active area with heat treated carbon paper electrodes; the second cell, described as the “counter-cell,” consists of a 25 cm² geometric active area with untreated carbon paper electrodes. 50 mL of catholyte and anolyte were recirculated for the duration of testing with a dual channel peristaltic pump (Cole Parmer) at 20 mL/min through the cell of interest and then through the counter-cell before returning to the electrolyte reservoirs. For cases in which the cell of interest was galvanostatically controlled, the counter-cell was potentiostatically controlled; when the cell of interest was potentiostatically controlled, the counter-cell was galvanostatically controlled. A summary of these control schemes is listed in Table 4.1.

Table 4.1. Summary of electrochemical data for cell-in-series experiments. Positive currents denote charging; negative currents denote discharging.

Expt.	Cell of interest (5 cm ²) control mode	Counter-cell (25cm ²) control mode	SoC	Cell of interest average voltage (V)	Coulombic efficiency
A	+100 mA	1.0 V	Low	1.289	91.6%
B	+1000 mA	1.0 V	Low	1.501	98.3%
C	−100 mA	1.7 V	High	1.530	90.2%
D	−1000 mA	1.7 V	High	1.206	97.4%
E	0.6 V	+100 mA	Low	0.600	91.4%
F	1.8 V	−100 mA	High	1.800	89.5%

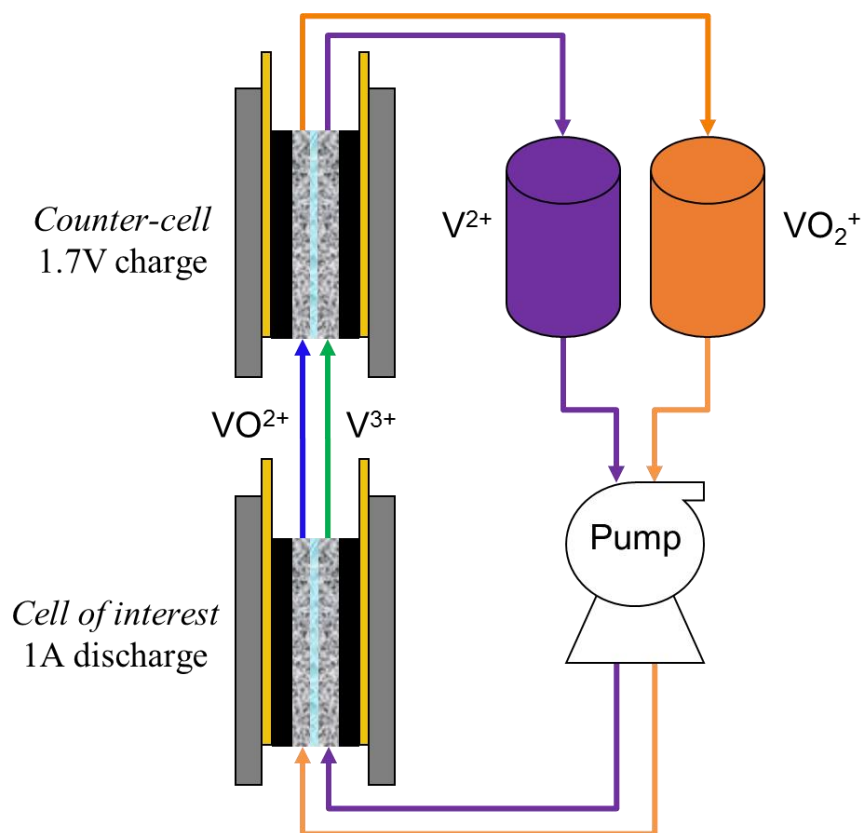


Figure 4.1. Schematic of CIS set-up with discharge occurring in cell of interest and recharge occurring in counter-cell.

Soaks

The 100% SoC solutions (V^{2+} and VO_2^+) were obtained as described above. The ~0% SoC solutions (V^{3+} and VO^{2+}) were obtained by discharging 100% SoC solutions until a cutoff potential of 0.2 V was reached; an OCV of ca. 1.2 V was observed. Strips of the heat treated electrode material were immersed in vials of the prepared solutions and purged with nitrogen and sealed. Soaks were carried out for 3 d and 6 d at room temperature.

4.2.2 Electrochemical measurements

Polarization curves

Polarization curves were obtained with separate sets of electrolyte solutions with volumes of ca. 400 mL. In the first set of experiments, the polarization curves were taken with cells that were previously cycled or run in the CIS set-up; in these cases, the cell was drained of electrolyte solution and tanks were replaced with the polarization curve solution tanks. In the second set of experiments, cells were built with electrodes that had been previously soaked in electrolyte solution but not electrochemically cycled. In these cases, electrodes soaked in catholyte were used as the positive electrode and electrodes soaked in anolyte were used as the negative electrode. During all polarization curve measurements, the counter-cell was removed from the fluid circuit (i.e., electrolyte flowed only through the cell of interest).

For all polarization curves, a relatively high flow rate of 90 mL/min was used to minimize concentration polarization. The catholyte and anolyte were ca. 50% SoC, obtained by coulometric discharge of the 100% SoC solution. Because large volumes of electrolyte were used and the current passed was low, and charge and discharge nearly balanced out, changes in SoC during polarization curves were minimal. Polarization curves were obtained with potential steps beginning at OCV and then in increments of ± 20 mV. The current value was taken as the average

over the last 15 s for each potential step, after a steady-state current had been reached (less than 5 s was required to reach steady-state).

Electrochemical impedance spectra were obtained during the potentiostatic control steps to measure the HFR, which was taken as the intercept of the Nyquist spectrum with the real axis. The areal specific resistance (ASR) was obtained by multiplying the HFR by the cell geometric area. The ohmic drop was calculated multiplying ASR by the current density; this value was subtracted from the applied cell voltage for iR -correction.

Capacitance

The capacitance of the electrode materials was obtained in an ex situ three electrode cell. Measurements were obtained after samples were cleaned (described in the XPS section below). A single layer of carbon paper was clamped between graphite clips and immersed in 0.5 M sulfuric acid and used as the working electrode in conjunction with a mercury sulfate reference electrode (Pine Instruments) and platinum mesh counter electrode. The carbon paper was preconditioned with 10 cycles of cyclic voltammetry carried out between -0.5 and 0.5 V at a scan rate of 50 mV/s, followed by EIS performed at constant applied voltages of -0.5 to 0.5 V in 0.1 V increments.

X-ray photoelectron spectroscopy

Used or electrolyte-soaked electrode materials from three day CIS operation were triple rinsed in DI water and dried at 75 °C in air for 2 h prior to XPS analysis. Samples were loaded into an ultra-high vacuum chamber which was maintained at 10^{-8} Torr or less during measurement. Spectra were taken with a PHI 3056 spectrometer with an Al K_{α} x-ray source (1486.6 eV) at 350 W. Survey scans were taken with 0.5 eV energy steps and a pass energy of 93.9 eV; high resolution scans were taken with 0.05 eV energy steps and a pass energy of 23.5

eV. Spectra were charge-corrected by setting the highest intensity carbon peak to 284.8 eV. The C1s and O1s high resolution scans were processed by subtracting a Shirley-type background and then normalized by the maximum intensity within the same sample.

4.3 Results and discussion

4.3.1 Cycling

Representative cycling data for a VRFB operated at 200 mA/cm² are shown in Figure 4.2(a). The cell exhibited stable coulombic efficiency while the voltage efficiency (VE) declined slightly from 78% to 75% over the course of the experiment. After 54 cycles (6 d of operation, ~3 h/cycle), the capacity faded to 66% of the first cycle capacity. It has been well established that crossover affects capacity by causing an imbalance in the vanadium concentrations; the side with less vanadium restricts the total capacity of the battery, resulting in capacity fade. The capacity can be restored by rebalancing electrolyte to the initial concentrations of vanadium in each half-cell.¹³⁶ The electrolytes were rebalanced after the 54th cycle and the solution was recharged in a separate cell to verify that the vanadium concentrations were restored to the first cycle values. The initial charge capacity of the electrolyte after the rebalance operation was 99% of the initial charge prior to the first cycle, indicating that side reactions were not responsible for significant capacity fade under the cycling conditions used in this experiment.

Charge and discharge profiles for cycles 1, 54 (pre-rebalance), and 55 (post-rebalance), presented in Figure 4.2(b), show a 50 mV increase in the charging voltage between cycle 1 and cycle 54 in the linear region of the charge curve, while the discharge profiles showed a 55 mV decrease in the same region. Imbalances in the vanadium concentration can explain part of this shift, as concentration imbalances can impact the OCV and therefore the charging and

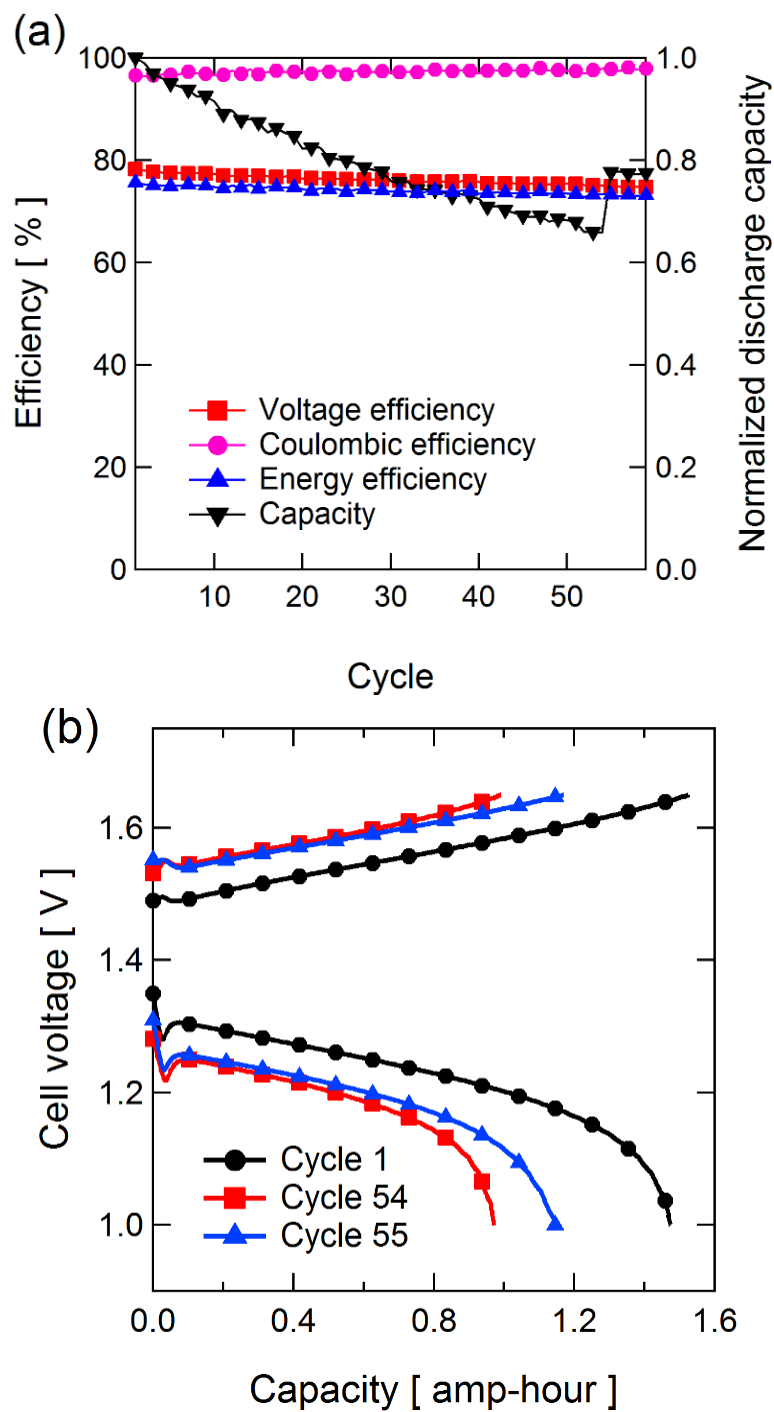


Figure 4.2. Results for battery cycled at 200 mA/cm² with electrolyte solution rebalance between cycles 54 and 55: (a) voltage efficiency, coulombic efficiency, and discharge capacity and (b) charge and discharge profiles.

discharging profiles. However, even after rebalancing and restoring the initial vanadium concentrations, the cycle 55 charging and discharging profiles were similar to the cycle 54 profiles, with only a 5 mV decrease in the charge profile and a 7 mV increase in the discharge profile. Though vanadium concentrations were restored after cycle 54, the next cycle's capacity was only 78% of the first cycle's capacity, indicating that electrolyte crossover only caused a 12% drop in capacity while another process caused capacity to drop an additional 22%.

The observed 22% decrease in capacity can be explained by an increase in the battery overpotentials over the course of cycling. An increase in the charging overpotential results in reaching the upper voltage limit at a lower SoC, effectively cutting the charge capacity. Likewise, on discharge, a larger overpotential results in reaching the lower voltage limit at a higher SoC, decreasing the discharge capacity. As a result, the OCV after charging is lower and after discharging is higher, which partially explains the changes in the charge and discharge profiles. The remaining portion of the shift is due to the increase in overpotentials, not the equilibrium potential. In this work, polarization curves are utilized to measure the changes in the battery overpotential.

In electrochemical cells, overpotentials are attributed to electrochemical activation (charge transfer), ohmic, and concentration polarizations.⁹⁷ Polarization curves were obtained before cycle 1 and after cycle 54 to identify changes in the cell overpotential. Use of a separate solution ensured that the results were independent of crossover effects that occur during cycling. The polarization curves shown in Figure 4.3 include both the iR -corrected and uncorrected data. Because the iR -corrected curves remove the ohmic overpotential from the membrane, changes in the iR -corrected curves in Figure 4.3 are attributed to changes in the kinetic performance of the

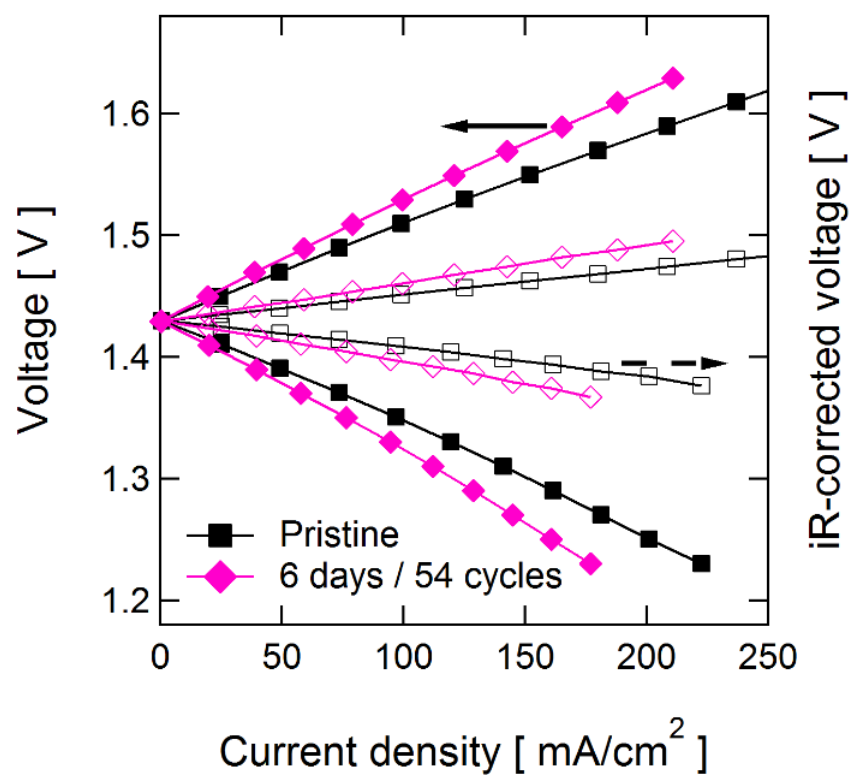


Figure 4.3. Polarization curves before and after 54 cycles at 200 mA/cm². Solid symbols reflect uncorrected data; hollow symbols are iR-corrected. Left and right axis scales are identical.

electrode surface, changes in the mass transport behavior within the cell, or a combination of the two. A 20 mV increase in the sum of the activation and mass transport overpotentials at a current density of 200 mA/cm², from 45 mV pre-cycling to 65 mV post-cycle 54, was observed. More work must be done in order to conclusively resolve the activation/kinetic overpotential increase and the mass transport/concentration overpotential increase. An increase in the activation overpotential is indicative of a decrease in the electrode's electroactive surface area, a decrease in the electrode activity, or a combination of the two. A decrease in activity is due to inherent changes in the nature of the electrode surface and in the case of a carbon electrode is related to the structure of the carbon itself as well as the presence of heteroatoms, such as oxygen. Few studies discuss changes in the electrode due to usage in an operational VRFB. Regarding properties that might alter electrode kinetics, Trogadas et al. observed a decrease in the active surface area of carbon felt electrodes of 37% after 60 h of cycling due to fiber agglomeration.⁸ Rudolph et al. speculated that a loss of oxygen-containing functional groups on the negative electrode resulted in decreased electrode activity.^{9,137} Changes in mass transport, if present, are likely attributable to changes in the electrode morphology that impact electrolyte flow. One such change may be related to fiber agglomeration observed in Reference 8, which would affect the electrode tortuosity. Another possible mechanism that could cause such changes would be the dislodging of carbon particles from the electrode. These particles could eventually clog portions of the electrode, impeding the bulk transport of vanadium species throughout the electrode. We mention these as two possible mechanisms by which transport can be affected within the electrode; other mechanisms are possible and should be investigated. The VRFB literature to date does not comment on changes in mass transport that may occur during cycling.

The ASR measured during discharge at a current density of 200 mA/cm² increased from 0.66 to 0.77 Ω cm² after 6 d of cycling; over the same time period, the ASR during charge increased from 0.55 to 0.64 Ω cm². Vijayakumar et al. observed that VO²⁺ ions can foul Nafion-based membranes,⁹⁰ reducing conductivity and increasing the cell resistance. Translated to the cycling experiment at 200 mA/cm², the increase in ASR resulted in 18 mV of additional overpotential during charging and 22 mV during discharging. Therefore, the decline in the cell's cycling performance is caused by an increase in the membrane resistance as well as decreased electrode performance, which must result from worsening kinetic properties, mass transport, or a combination of the two. Both components experienced an approximate 20 mV increase in overpotential, meaning that the cell's overall performance decline is due in equal parts to membrane and electrode performance loss. A summary of the contributions to capacity fade through cycle 54 of cycling is shown in Figure 4.4. Given that the previously described polarization curves demonstrate that the increases in overpotential due to the membrane and electrodes are equal in magnitude, the 22% capacity fade due to increased cell overpotential, described above, is ascribed evenly to membrane and electrode contributions.

We briefly note that one might expect a 50 mV increase in the linear region of the charging profile and a 50 mV decrease in the linear region of the discharging profile to result in a much larger drop in VE than the observed 3% (78% to 75%.) However, because voltage cutoffs are used to end the charge and discharge steps (1.65 and 1.0 V, respectively), the average voltage cannot change to the same extent that the overpotential does. For example, the cycle 1 average charge voltage was 1.562 V, while the cycle 55 average charge voltage was 1.589 V, an increase of only 27 mV; this is much lower than the overall 50 mV shift observed in the overall charge

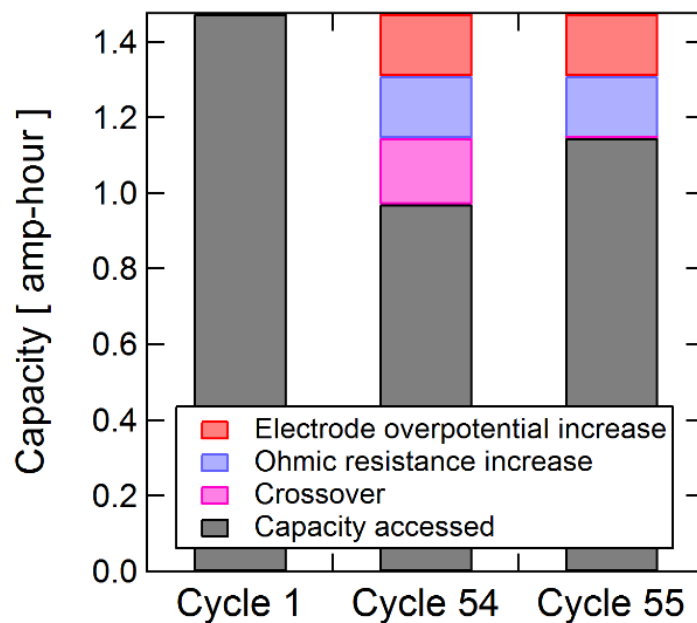


Figure 4.4. Capacity fade after 54 cycles attributed to crossover, increased membrane resistance, and decreased electrode performance, denoted as the sum of increased transport and kinetic overpotential.

profile. The use of different voltage cutoffs or state-of-charge cutoffs instead of voltage cutoffs to increase the charge and discharge windows would decrease capacity fade, but result in lower voltage efficiencies over time as the cell overpotential increases.

4.3.2 Cell-in-series

A summary of the conditions tested and the resulting electrochemical data is shown in Table 4.1. For simplicity, this portion of the discussion focuses on the four conditions (experiments A–D) in which the cell of interest was galvanostatically controlled and the counter-cell was potentiostatically controlled. Potentiostatic control in the counter-cell is desirable, as the large active area ensures a low current density and therefore low overpotentials. In this manner, very high and very low SoC operating conditions can be maintained: holding the counter-cell at 1.7 V yields ca. 95% SoC based on coulombic calculations; a potential hold at 1.0 V results in ca. 5% SoC. Galvanostatic control is chosen in the cell of interest to ensure the desired current is reached. Though steady state currents should lead to steady voltages, the voltage declined for discharging cells (A, B) by over 100 mV and increased by 20 mV for charging cells (C, D), as seen in Figure 4.5(a). Some portion of the change in the cell voltage can be explained by crossover, as the self-discharge due to crossover decreases the OCV. When the OCV is decreased, the cell voltage with passage of current will also decrease; the changes in concentration due to crossover can also have minor impacts on the concentration and activation overpotentials. Other changes in the cell voltage independent of crossover are attributed to decreasing electrode performance, discussed in the polarization curve section below in more detail, and increasing membrane resistance. The current in the counter-cell in each case was extremely stable over the course of the experiment, shown in Figure 4.5(b). The steady current

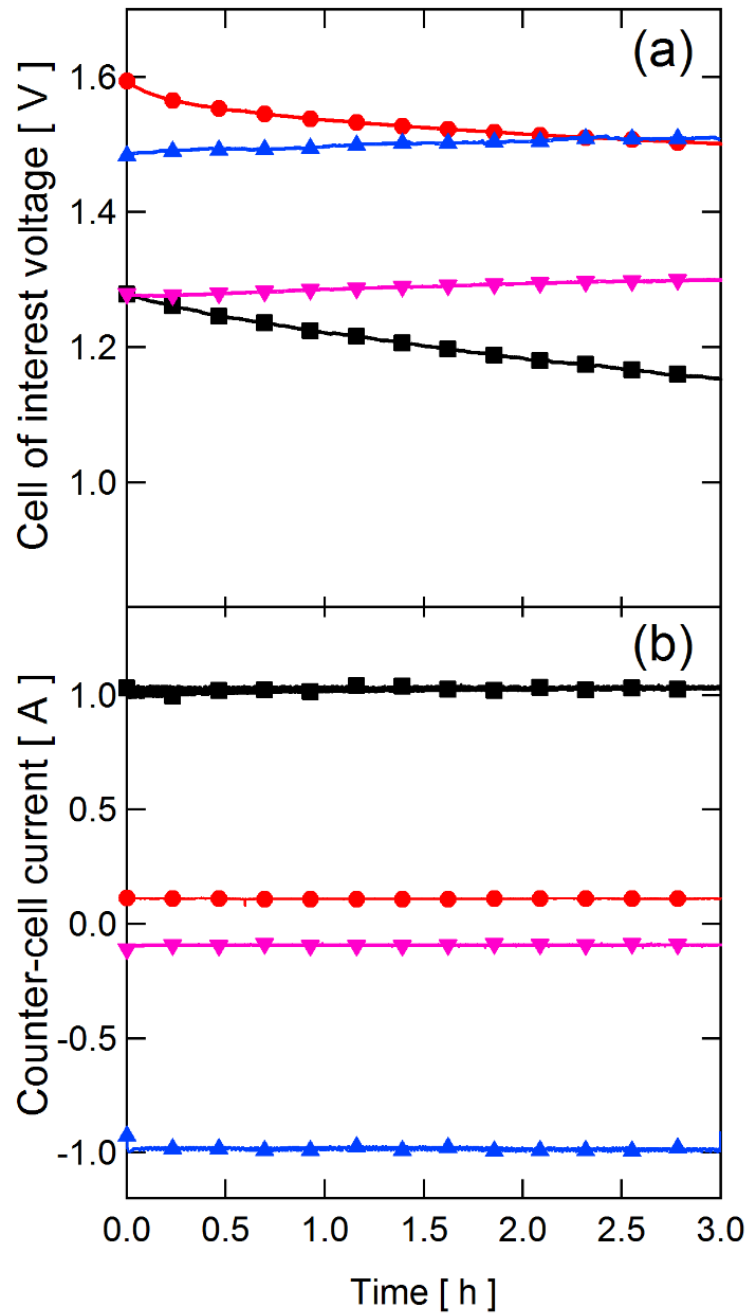


Figure 4.5. Electrochemical data for experiments A–D, in which the cell of interest was galvanostatically charged: (a) cell of interest voltage and (b) counter-cell current.

Symbols refer to experiments as follows: (▼) A, Low SoC +20 mA/cm², (▲) B, Low SoC +200 mA/cm², (●) C, High SoC –20 mA/cm², (■) D, High SoC –200 mA/cm²

indicates that a relatively steady SoC was achieved. It is noted that the charging cell always had a slightly higher current than the discharging cell due to crossover that occurs in both the cell of interest and the counter-cell.

To achieve extreme conditions in experiments E and F, i.e. charging while at high SoC and discharging while at low SoC, potentiostatic control is used in the cell of interest and galvanostatic control is used in the counter-cell. Because the cell overpotentials increase over time, maintaining galvanostatic control in the cell of interest while charging at high SoC would result in very high cell voltages that are unrealistic for VRFB operation due to high rates of undesirable gas evolution reactions and corrosion of the graphite blocks. Therefore, the cell of interest must be controlled potentiostatically. The counter-cell is controlled galvanostatically to ensure that current will also pass in the cell of interest; potentiostatic control in both cells with continued increase in the cell of interest overpotential would eventually result in no current passed.

The coulombic efficiency in Table 4.1 is calculated by dividing the average discharge current by the average charge current. Though a detailed discussion of coulombic efficiency is beyond the scope of this chapter, it is noted that some information regarding crossover is available from the coulombic efficiencies found with the CIS experiment, as crossover is what drives the coulombic efficiency to be less than 100%. For example, experiments carried out at low current (A, C, E, F) had a coulombic efficiency of 90–92%, while those at high current (B, D) had a coulombic efficiency of 97–98%, implying that crossover occurs at higher rates when the cell operates at lower current densities. These results agree qualitatively with recent literature:

where the authors also found that increased current density operation results in improved coulombic efficiency.¹³⁸

For further insight into the relative rates of migration and diffusion and how these affect the net crossover, and ultimately coulombic efficiency, see Reference 138. Experiments at high SoC had more rapid crossover than those at low SoC: at high current, the coulombic efficiency of experiment D (97.4%) was lower than B (98.3%), and at low current, experiments C and F (90.2, 89.5%) had lower coulombic efficiencies than A and E (91.6, 91.4%). These results are logical in that the passage of the charged V^{2+} and VO_2^+ species through the membrane results in more self-discharge, and thus effectively faster crossover, than the passage of the discharged V^{3+} and VO^{2+} species. In summary, the CIS technique could be useful in parametrically studying crossover as a function of operating parameters with relative ease.

4.3.3 CIS/Soak polarization curves

As described above, *iR*-corrected polarization curves in this work are indicative of a combination of activation and mass transport losses. As shown in Figure 4.6(a) and Figure 4.6(b), operation at a fixed voltage, whether at low SoC and discharging (experiment E, 0.6 V hold, -20 mA/cm^2) or at high SoC and charging (experiment F, 1.8 V hold, $+20 \text{ mA/cm}^2$) serves to greatly decrease electrode performance. It is noted that the increase in overpotential is observable at low current densities (20 mA/cm^2), which suggests a decrease in kinetic performance. The slope of the polarization curve increases throughout the curve, which may indicate that transport within the cell also declines. More work must be done to determine the chief contributor to electrode performance loss. For both experiments E and F, there was an increase in *iR*-corrected overpotential at a current density of 100 mA/cm^2 from ca. 25 mV before

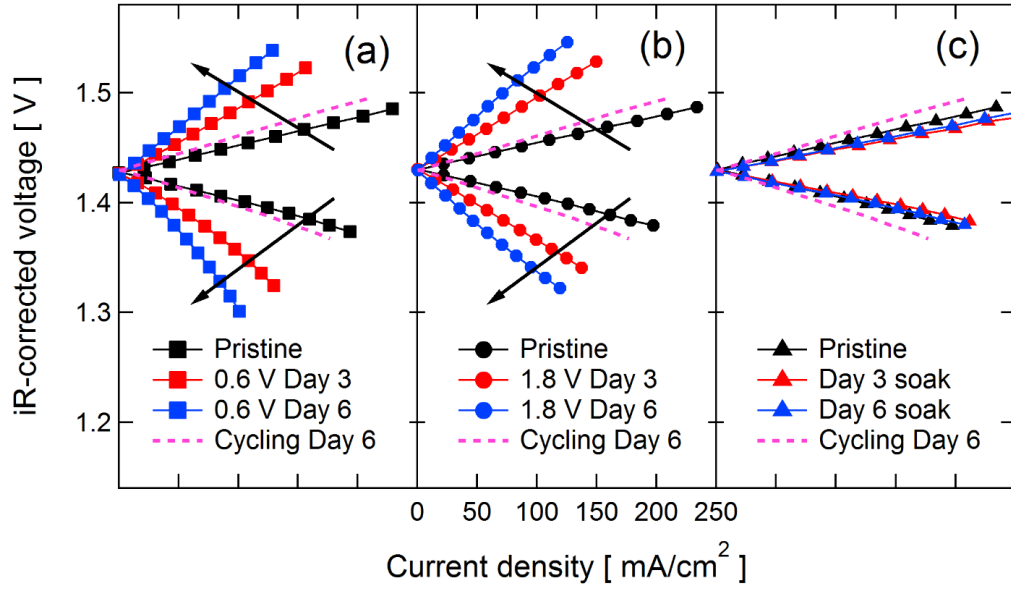


Figure 4.6. iR-corrected polarization curves taken after initial build, 3 d, and 6 d: (a) cell-in-series experiment E: potential hold at 0.6V and at low SoC, (b) cell-in-series experiment F: potential hold at 1.8V and at high SoC, and (c) soaked in high SoC solution. Curve for cell cycled for 6 d shown for reference.

CIS operation to 65 mV and 100 mV after 3 d and 6 d of CIS operation, respectively. Since the increases in overpotential are similar, the detrimental changes in the electrode performance cannot be attributed solely to charging or discharging. In comparison, the overpotential at 100 mA/cm² observed in the cycling experiment increased from 25 mV pre-cycling to 35 mV after 6 d of cycling. The increase in overpotential due to CIS operation (75 mV) was thus sevenfold larger than the increase in overpotential due to cycling (10 mV). This indicates that the experimental conditions in E and F likely simulate much longer cycling time, which is logical since cycling experiments reside in the neighborhoods of 0.6 or 1.8 V for very short periods of time. These tests may be a valuable method in evaluating the durability of electrode materials due to the accelerated performance degradation observed.

The effects of high SoC electrolyte on the electrodes, without the presence of any electrochemical effects, is shown to be minimal with respect to performance, as the polarization curves in Figure 4.6(c) indicate that the *iR*-corrected overpotentials actually slightly decrease after 3 d and 6 d of electrolyte exposure. Overall, then, the polarization curves suggest the decline in electrode performance cannot be attributed to the chemical effects of exposure to strong oxidizing (VO₂⁺) or reducing agents (V²⁺). Rather, the loss in performance likely originates from electrochemical processes (the passage of current). Furthermore, soaking electrodes in the electrolyte is not a sufficient method by which electrode durability can be tested, though it is often used in predicting the long-term stability of ion exchange membranes used in VRFBs.^{88,89}

4.3.4 Physicochemical characterization

The electrode surface is the determining factor for the reaction kinetics and thus the activation overpotential. The relevant surface properties include the electrochemically active surface area as well as the surface chemistry, which affects the activity of the surface. As described in the introduction, it has been claimed that the presence of certain oxygen functional groups reduces the activation overpotential for vanadium redox reactions. In the following sections, changes in the surface area and oxygen functional groups as a result of usage in the battery and their potential contributions to performance loss are discussed.

Capacitance

The double layer capacitance is used as a proxy for the surface area, i.e., it is assumed that the surface area is proportional to the double layer capacitance. It is noted that the presence of oxygen functional groups can affect the capacitance; however, these changes are not expected to affect the capacitance by more than 25%.¹³⁹ In order to estimate the capacitance, an equivalent circuit model consisting of a constant phase element in series with a resistor was used to fit the impedance data obtained in the three electrode cell, similar to the analysis performed by Sun et al.⁹³ The double layer capacitance was estimated at each voltage following Brug et al.:¹⁴⁰

$C_{dl} = (Q_0 R_{\Omega}^{1-\alpha})^{1/\alpha}$ and is shown in Figure 4.9 in the Appendix. The cyclic voltammogram in Figure 4.10 in the Appendix was taken immediately prior to obtaining impedance data. A sample fit is also shown in Figure 4.11 in the Appendix.

No clear trend was observed in the capacitance in relation to SoC or operating conditions; i.e., some of the samples exposed to catholyte experienced increased capacitance while others experienced decreased capacitance, and likewise for those exposed to anolyte. In addition, there were no trends relating poor electrochemical performance to changes in capacitance: the

electrodes soaked in 100% SoC catholyte experienced a 50% decrease in capacitance relative to the pristine electrode, while the electrodes soaked in 100% SoC anolyte experienced a small increase in capacitance. The cell built with these electrodes as the positive and negative electrodes, respectively, then, had an overall decrease in the surface area. However, the electrode performance was improved, as shown in Figure 4.6(c). Furthermore, the changes in capacitance are small when compared to the effect of the initial heat treatment, in which the capacitance increases by a factor of 200.⁶¹ Therefore, the data suggest that a change in the surface area cannot explain the majority of the observed increase in electrode polarization.

XPS

XPS spectra focused on the O1s region are presented for electrodes subjected to the CIS tests or soaked in electrolyte. The C1s region also shows changes, but the changes are less apparent due to the high concentration of C–C species and are therefore not shown. The O1s peak maximum is typically at or around 533.5 eV, and is attributed to C–O bonds; spectral intensity which appears at 532 eV as a shoulder to the main peak is attributed to C=O bonds. Two versions of the same data are shown: the O1s spectra normalized to the C1s peak shows the relative concentration of oxygen on the carbon surface within each sample; the O1s spectra normalized to the O1s peak shows the peak shape and therefore the relative distribution of C–O to C=O bonds. The oxygen content of the pristine electrode surface was 2.5%; after soaking in sulfuric acid, surface oxygen increased to 5.5%. The acid-soaked electrode is used as the relevant reference point. No observable quantities of sulfur from the sulfuric acid were present in the XPS spectra. A summary of oxygen contents is shown in Table 4.2.

Table 4.2. Atomic composition of electrode surface for cell-in-series and electrolyte soak experiments as determined by XPS analysis, sorted from maximum to minimum oxygen content.

Expt.	Oxygen content (atomic %)	Carbon content (atomic %)	Electrode Polarity	SoC	Current density (mA/cm²)
V(V) soak	9.3	90.7	+	High	N/A
F	8.3	91.7	+	High	+20
C	8.0	92.0	+	High	-20
D	6.9	93.1	+	High	-200
B	6.4	93.6	+	Low	+200
A	5.8	94.2	+	Low	+20
B	5.7	94.3	-	Low	+200
E	5.7	94.3	+	Low	-20
D	5.5	94.5	-	High	-200
V(IV) soak	5.5	94.5	+	Low	N/A
acid soak	5.5	94.5	N/A	N/A	N/A
A	5.1	94.9	-	Low	+20
V(III) soak	5.1	94.9	-	Low	N/A
F	4.4	95.6	-	High	+20
E	3.5	96.5	-	Low	-20
V(II) soak	3.1	96.9	-	High	N/A
pristine	2.5	97.5	N/A	N/A	N/A

As shown in Figure 4.7(a), exposure to V^{2+} decreased the oxygen content from 5.5% in the acid-soaked sample to 3.1%; V^{3+} decreased the oxygen content to 5.1%, VO^{2+} showed no effect, and VO_2^+ increased the oxygen content to 9.3%. Indicated in Figure 4.7(b), there is a clear difference in the C–O/C=O surface chemistry after exposure to the electrolytes, the catholyte inducing more C=O bonding relative to C–O than the anolyte, evident in the increased spectral intensity at 532 eV.

Shown in Figure 4.7(c), SoC was the dominant force in affecting the oxygen content in the positive electrode, as the electrode always exhibited a higher oxygen content at high SoC – 6.9% or greater, compared to 6.4% or less for low SoC – independent of whether the cell was charging or discharging and independent of the magnitude of the applied current. The direction of current (i.e., charging vs discharging) was not important at the low current density: at both low and high SoC, the + and –20 mA/cm² spectra are nearly overlaid. The effect of the magnitude of the applied current was most apparent in the bonding in Figure 4.7(d): the high current density experiments, independent of high or low SoC, enhanced the C=O bonding relative to the C–O bonding. The effect of SoC is secondary, though at the lower current density, the high SoC induced more C=O bonding, similar to what was observed in the soaking experiments described previously. That the C=O bonding was enhanced by both high current densities and electrolyte soaking is somewhat puzzling, as one might expect the electrolyte soaks and the low current density experiments to be similar because a low current density is closer to the equilibrium or zero current density experienced during electrolyte soaking.

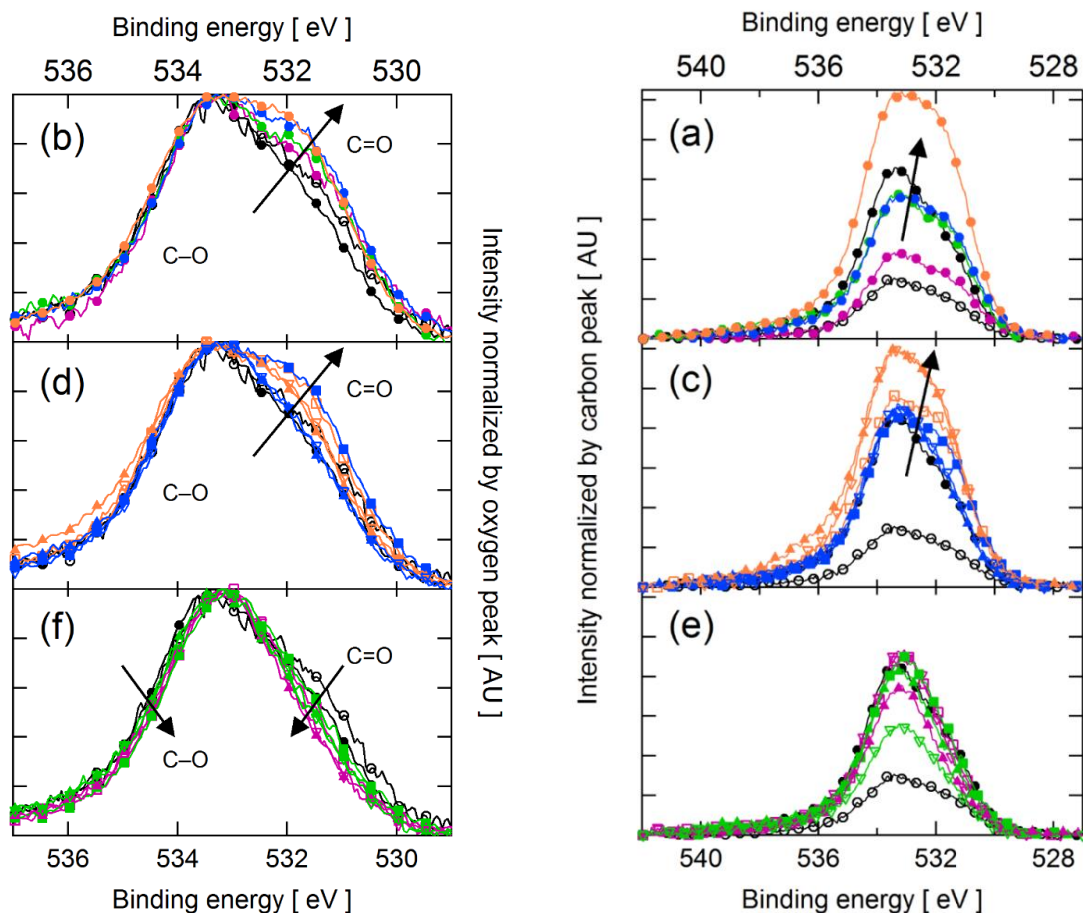


Figure 4.7. XPS O1s spectra for electrodes subjected to soaking and cell-in-series operation for 3 d: (a) soaked electrodes normalized by C1s peak, (b) soaked electrodes normalized by O1s peak, (c) positive electrodes normalized by C1s peak, (d) positive electrodes normalized by O1s peak, (e) negative electrodes normalized by C1s peak, and (f) negative electrodes normalized by O1s peak. Pristine ($\circ$) and acid soaked ($\bullet$) included for reference in all frames.

Color scheme refers to electrode polarity and SoC as follows: ($\bullet$) + high SoC, ($\bullet$) + low SoC, ($\bullet$) – low SoC, ($\bullet$) – high SoC. Symbol shape refers to experimental condition as follows: ($\bullet$) soaked, (∇) -20 mA/cm^2 , ($\blacktriangle$) $+20 \text{ mA/cm}^2$, ($\blacksquare$) $+200 \text{ mA/cm}^2$, ($\square$) -200 mA/cm^2 . (a), (c), and (e) are plotted on identical vertical axes.

Apparent from the spectra for the negative electrodes, shown in Figure 4.7(e), is that the oxygen content on the negative electrode was generally similar to or less than that observed with the sulfuric acid soak, opposite of what was observed on the positive side. No clear trends appear that link oxygen content to SoC, magnitude of current, or direction of current. However, the C=O bonding, shown in Fig. 7(f), exhibited a slight decrease relative to the C–O bonding in all cases, and furthermore, a high SoC typically reduced the C=O bonding more than a low SoC.

The overall XPS results, qualitatively shown in Figure 4.8, suggest that the electrode surface chemistry is indeed affected by operating conditions. Relative to soaking in acid, an electrode in the positive half-cell of the battery undergoes significant oxidation when at a high SoC under a variety of operating conditions, while the positive electrode at low SoC and the negative electrode at both low and high SoC both show little evidence of oxidation under similar applied currents. The general trend of oxidation of the positive electrode surface agrees with other literature, though the amounts vary significantly. With the carbon papers used in this work, the highest post-mortem oxygen content observed was 9.3%, much lower than the 40% observed after 65 hours of cycling⁸ or 18–30% observed after 50 min of overcharge.¹¹ While more investigation is needed, these results are an indication that carbon paper and carbon felts likely exhibit different operational lifetimes under continued electrochemical stress.

The surface chemistry of the carbon electrode was affected by soaking in the vanadium electrolyte as well as during VRFB operation. However, the electrode performance was only affected by VRFB operation. Because drastically different electrode overpotentials were observed for electrodes with similar oxygen content, the results seem to indicate that the oxygen content of the electrode surface does not play a major role in decreasing the electrochemical

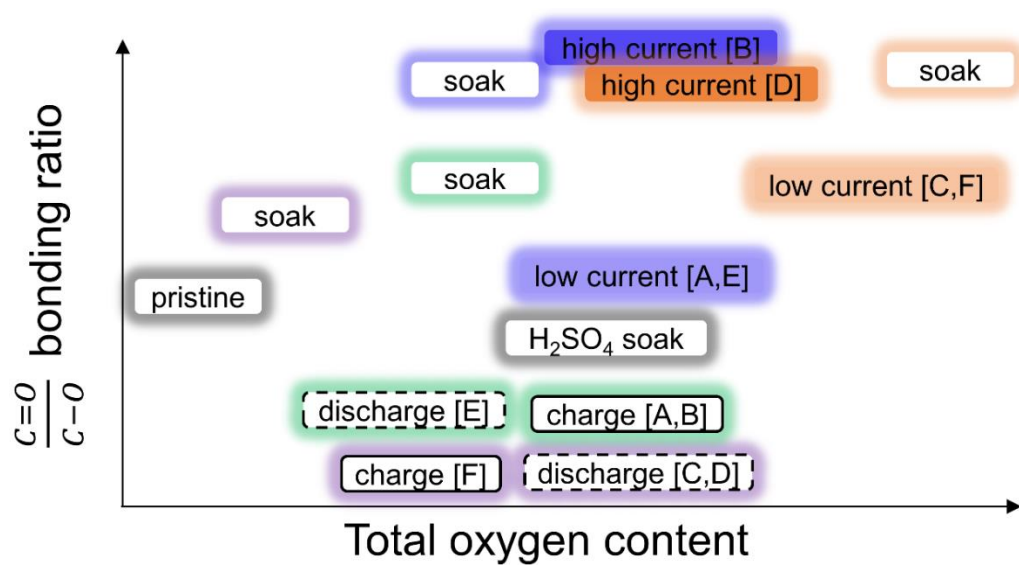


Figure 4.8. Qualitative comparison of oxygen content and bonding for electrodes analyzed with XPS.

performance of the carbon materials tested. Melke et al.⁶⁰ found that heat treated carbon materials do not rely upon carboxyl or hydroxyl groups to facilitate the vanadium redox reactions. Combined, these results suggest that oxygen groups may not play a significant role in the vanadium redox reactions. These findings contrast with the theory advanced in References 9 and 137 that the loss of oxygen functional groups on the anode contributes to increased cell polarization. Thus, more work is required to determine the cause(s) of electrode performance loss, as the surface area and oxygen-related surface chemistry were found to be unlikely causes for the changes observed in electrode performance in this work. It is noted that degradation mechanisms may differ for felt vs. paper-based electrodes.

4.4 Conclusions

In this work, we show the origin of changes in the energy efficiency that occurred in a typical cycling experiment. The combined activation and concentration polarization increased from 25 mV pre-cycling to 45 mV after 54 cycles at 200 mA/cm²; ohmic overpotential, presumably due to membrane fouling, increased 20 mV. These increases in overpotential together contributed 22% to the observed capacity fade after 54 cycles, while crossover accounted for 12%. The CIS set-up was then introduced as a method to study constant conditions in flow battery testing, and reasonably constant conditions were achieved. We demonstrate that charging at high SoC and discharging at low SoC can be used to accelerate performance loss in VRFBs, and that the CIS design can therefore assist in material durability evaluation. Analysis of the polarization curves suggests that both the charging and discharging process contribute to decreased electrode performance; therefore, neither process is solely responsible for performance

loss. Simple exposure to electrolyte with no electrochemical cycling had no significant effect on the kinetic performance of the electrode.

Electrode samples from CIS experiments and from electrolyte soaks were analyzed with XPS to determine changes in the surface chemistry. High SoC induced the most oxidation on the positive electrode, with oxygen content of up to 9.3%; the negative electrode exhibited oxidation similar to that caused by soaking in sulfuric acid, around 5.5%. Changes in the C–O/C=O chemistry were primarily related to the polarity of the battery and were more sensitive to operating conditions on the positive electrode. XPS results in conjunction with polarization curve analysis suggest that the oxygen content on its own may not play a large role in electrode performance for the electrode materials tested, and therefore that aging-related changes in oxygen cannot explain the observed electrode performance loss.

The CIS technique, which allows for constant condition testing, provides a platform for these insights into how SoC, magnitude of current, and direction of current affect degradation mechanisms in VRFBs. The use of XPS to examine oxygen content is a demonstration of how the CIS can be used in conjunction with an analytic technique to study targeted physicochemical properties of the electrode as a function of SoC and applied current. The study of electrodes after cycling does not allow the freedom to distinguish which portion of the charge/discharge cycle (i.e., at which SoC, charge or discharge) might contribute to changes in the material properties, which is where the CIS can be of great benefit. This work rules out changes in oxygen functionality and surface area as likely causes of the loss in electrode performance. More work must be done to better understand how other physicochemical properties change during battery operation, and which properties are important to declining performance.

While the CIS technique is used in this work to study the effect of a constant condition on the electrode in VRFBs, it should be noted that the technique could be applied to other flow battery chemistries and experiments. The CIS can be used to study membrane durability in a manner similar to how electrodes were studied in this work. Membrane permeability measurements could also be taken at constant SoC from an operating battery. The CIS can also provide a useful platform for other types of flow battery experiments. Short-term experiments that would benefit from a constant SoC, including polarization curve analysis, could utilize a counter-cell to maintain SoC, as opposed to a single-pass configuration which requires a large volume of electrolyte or low flow rates in order to conduct a constant SoC experiment. Symmetric cells¹⁰¹ are another useful tool to conduct constant SoC experiments; one may find the CIS technique advantageous because SoC can be changed by changing conditions in the counter-cell, whereas a symmetric cell requires changing of the electrolyte solution to change SoC.

4.5 Appendix

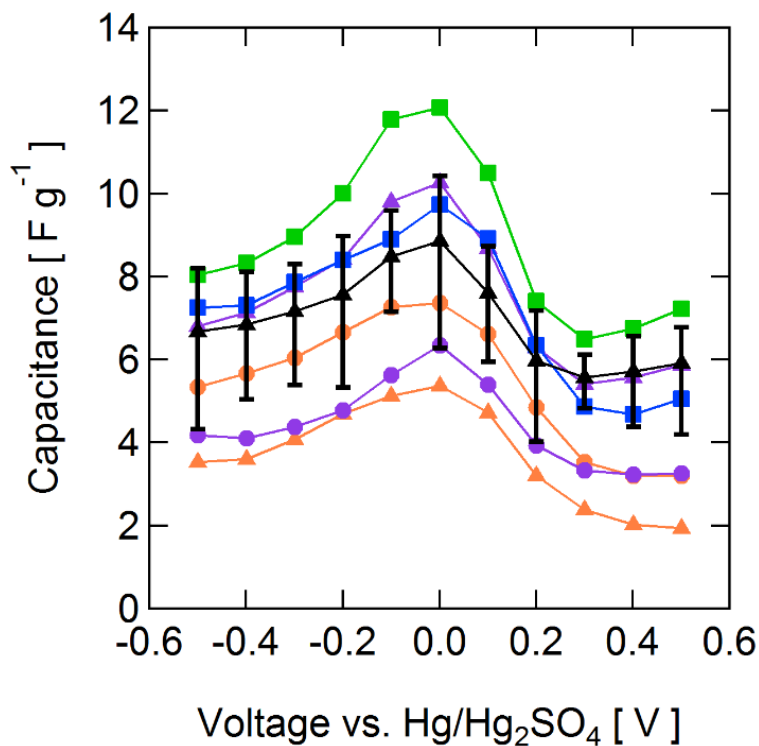


Figure 4.9. Capacitance values obtained for pristine and post-soak and post-CIS operation obtained from EIS at 100 mV increments. Error bars obtained from fitting.

Symbols refer to polarity, state of charge, and experimental conditions as follows:

- (▲) Pristine
- (▲) VO₂⁺ soak
- (▲) V²⁺ soak
- (●) + high SoC (experiment E)
- (●) - high SoC (experiment E)
- (■) + low SoC (experiment F)
- (■) - low SoC (experiment F)

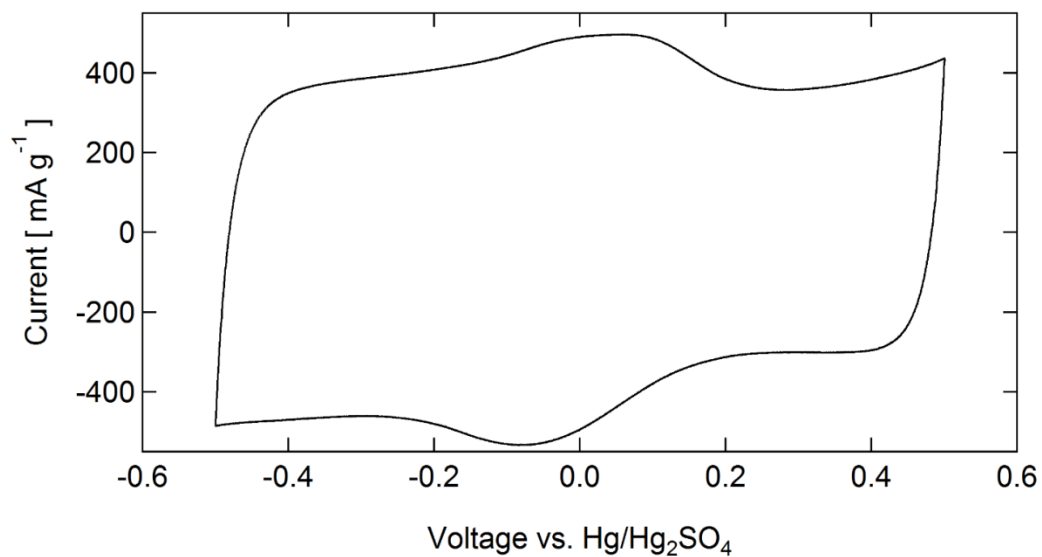


Figure 4.10. Cyclic voltammogram obtained immediately prior to electrochemical impedance spectroscopy for pristine electrode material.

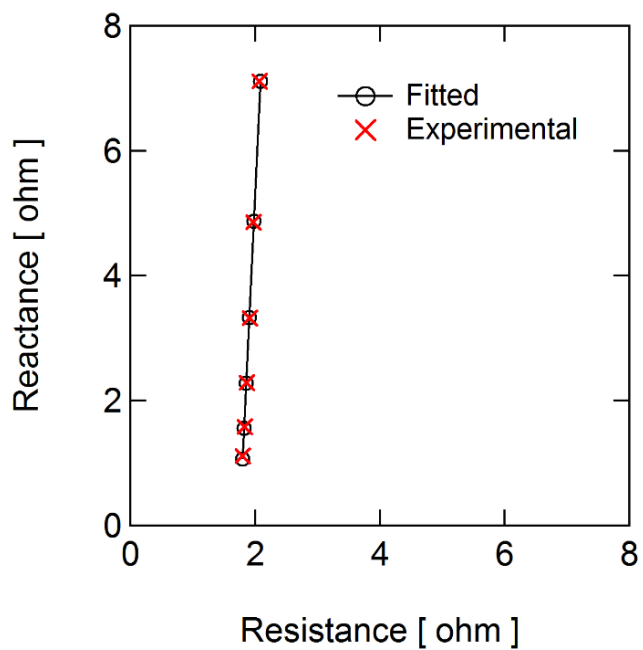


Figure 4.11. Fitting obtained with impedance spectrum taken with pristine electrode at -0.3 V. Frequency ranges from 0.11 Hz to 0.77 Hz.

CHAPTER 5
IMPROVED ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY METHOD FOR
ELUCIDATION OF OVERPOTENTIALS IN REDOX FLOW BATTERIES

Abstract

This article hasn't been published anywhere, nor will it be before I turn in the final version of my ETD, so I didn't include a publication statement. A manuscript will be submitted for publication. This work was authored by Alan M. Pezeshki, Robert L. Sacci, Frank M. Delnick, Douglas S. Aaron, and Matthew M. Mench.

My primary contributions to this work were the experimental design, collection, reduction, and interpretation of data as well as composition of the manuscript. Sacci assisted interpretation of data and composition of manuscript. Delnick assisted application of impedance model to data and composition of manuscript.

5.1 Introduction

RFB architecture has remained relatively unchanged, with cell designs largely utilizing an architecture where porous electrodes are pressed against a patterned graphite plate.^{23,104} For a given redox chemistry, cell optimization involves selection of electrodes that provide sufficient kinetic activity and membranes with acceptable conductivity and minimal crossover of the redox active materials. The electrode morphology and flow field pattern in concert with the flow rate define the hydrodynamics within the cell. The hydrodynamics control the transport of electroactive species and the cell pressure drop, which is the source of parasitic pumping losses. The use of diagnostic techniques to determine quantitatively how the electrodes, membrane, and flow field contribute to battery overpotential provide an avenue for continued optimization for any redox chemistry. Additional motivation for the work presented in this chapter was to employ methods to understand the origin of performance degradation in Chapter 4.

As described in Chapter 1, commonly used techniques involving CV or RDE are applicable for planar electrodes, but cannot resolve kinetics and transport within porous

materials.^{42,141} EIS is a powerful tool that can be used to identify and resolve the sources of resistance within an electrochemical device, with deconvolution of porosity effects.¹⁰⁰ This permits the quantitative measurement of the effect of electrode and flow field properties on these limiting resistances.

In this work, we describe an experimental method to obtain finite diffusion resistances with operationally relevant flow rates (25 mL min⁻¹) through the use of a pulse dampener in conjunction with peristaltic pumps. The method is applied to a series of experiments in which the flow fields, vanadium concentration, and electrode material were varied. The model developed by Sun et al.⁶⁹ was used to interpret the complex impedance data. Through resolution of the three sources of overpotential, the impact of cell design on electrochemical kinetics, mass transport, and ohmic processes within the cell was determined quantitatively. Using this approach, one can determine the limiting processes for any liquid-phase chemistry/material combination, allowing optimization efforts to focus on improving the rate-limiting steps in the RFB.

5.2 Methods

5.2.1 Experimental set-up

Cell testing was carried out on a single-cell 5 cm² geometric active area flow battery.¹⁰⁴ Two flow field patterns were tested: 1) a square active area single-channel serpentine (2.23 x 2.23 cm) and 2) a rectangular flow-through design (4 x 1.25 cm) shown in Figure 5.1. Cells were built with one layer of electrode on each side of the membrane separator. The electrode materials were carbon paper (SGL 10AA, ~360 μ m thickness, compressed to 240 μ m) and carbon felt (SGL GFD3, ~3 mm thickness, compressed to 2 mm). Electrodes were soaked in nitric acid (70%, Alfa Aesar) for 10 minutes and then rinsed with deionized water five times. The separator

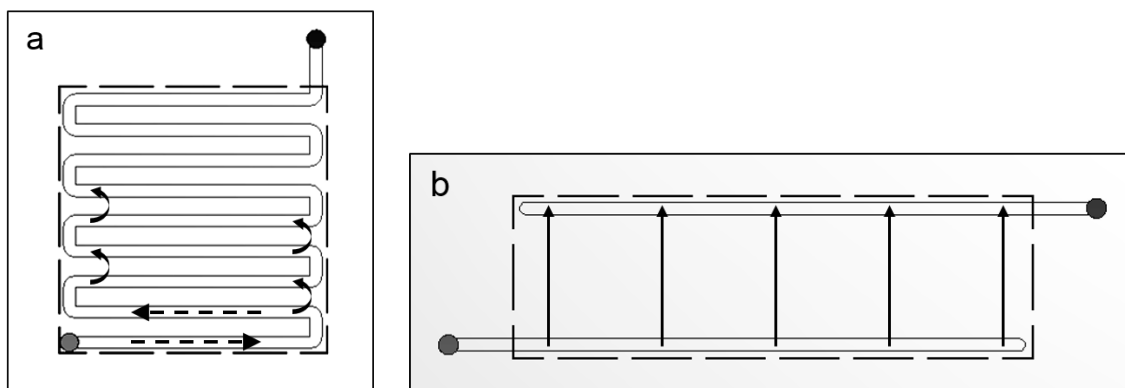


Figure 5.1. Flow field patterns. In the serpentine design (a), electrolyte bypass flow in the channels is shown as dashed lines. Flow over the lands (through the porous electrode) is shown as curved arrows. In the flow-through design (b), all flow is forced through the electrode and primarily travels in the in-plane direction denoted by the solid arrows.

was a Nafion N117 membrane (Ion Power), pretreated by immersion in 1 M sulfuric acid at 80 °C for 30 min followed by immersion in deionized water at 80 °C for 30 min. Two negative electrolyte solutions were prepared by electrolysis of VOSO_4 (Alfa Aesar, 99.9%) dissolved in a sulfuric acid supporting electrolyte (Alfa Aesar, ACS grade). Prior to electrolysis, the solutions were filtered to remove impurities.^{86,142} The first solution nominally consisted of 0.5 M total vanadium in 4 M sulfuric acid; the second was composed of 1.5 M total vanadium in 3.0 M sulfuric acid. A lower acid concentration was used with the higher vanadium concentration to preserve the total dissolved sulfate concentration. Both solutions were coulometrically tuned to 50% SoC, i.e. equal V^{2+} and V^{3+} concentrations in a separate cell. Nitrogen was purged over the solutions to prevent oxidation of the vanadium species.

The experimental set-up is shown in Figure 5.2. The symmetric cell configuration was used; i.e. the negative electrolyte was circulated through both sides of the cell in one continuous fluid circuit.^{64,101} In this circuit, fluid flows from the electrolyte reservoir into the pump, enters a pulse dampener, is fed into the cell, and returns to the electrolyte reservoir. The dampener

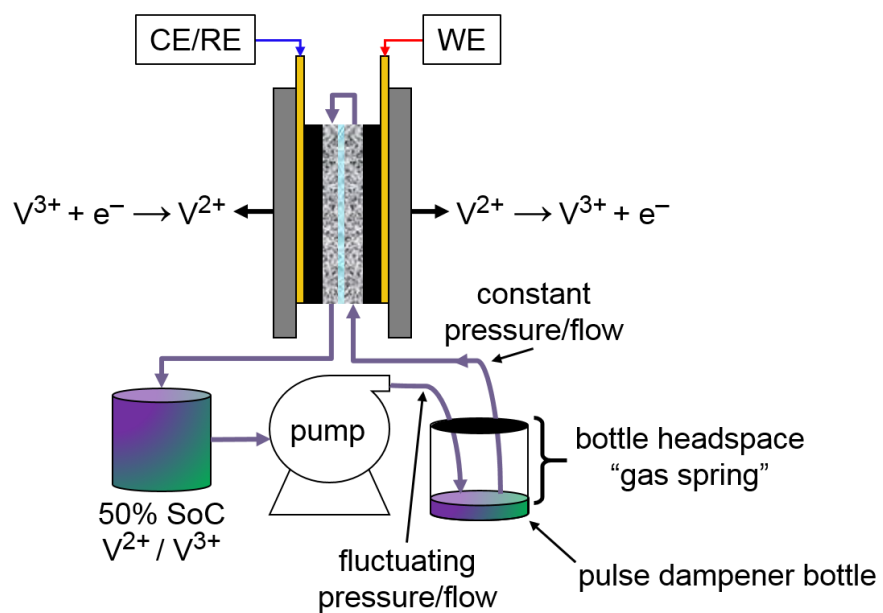


Figure 5.2. Schematic of the symmetric cell setup with pulse dampener.

consists of a sealed glass bottle with two ports. Pulsing from the pump is dampened by the gas headspace. Prior to startup, the bottle dampener was purged with nitrogen. During startup, pressure in the dampener builds until the bottle pressure reaches the cell pressure drop associated with the desired flow rate.

A Bio-Logic Instruments VSP potentiostat coupled to a 20 A booster was used for electrochemical measurement and control in a two-electrode configuration as shown in Figure 5.1. The cell temperature was controlled at 30 °C. The cell was filled with the 0.5 M vanadium solution and then preconditioned using five potentiostatic cycles, with each cycle consisting of a +200 mV imposed cell overpotential for 30 minutes followed by a –200 mV imposed cell overpotential for 30 minutes. After preconditioning, the polarization curve was recorded. The cell was then drained and the reservoirs were switched to the 1.5 M vanadium solution for another polarization measurement. Polarization curves were obtained by incrementing the cell overpotential from 0 to +200 mV in 25 mV increments. At each step, the voltage was held constant for 30 seconds, followed by the acquisition of impedance data using 5 mV sinusoidal perturbations. A two-electrode configuration was used because the impedance spectra collected relative to a reference electrode were distorted. A sample distorted spectrum is included in Figure 5.14 in the Appendix.

5.2.2 Symmetric cell considerations

The symmetric cell configuration has been demonstrated in the literature as a useful tool for certain flow battery diagnostics;^{36,64,69,101} the primary benefit is that the solution reservoir maintains the same SoC throughout the experiment. Because the cell is operated at 50% SoC and the transfer coefficients of the V^{2+}/V^{2+} couple are 0.5,⁶⁹ the cell overpotential should be evenly

distributed between both sides of the cell.¹⁰¹ When the cell overpotential was 200 mV, both electrodes were at 100 ± 10 mV relative to their open circuit voltage, measured with the use of an Hg/HgSO₄ reference electrode in contact with the membrane. At open circuit, the assumption that the charge transfer resistance across the whole cell can be divided by two to obtain the single-electrode charge transfer resistance holds rigorously. It is noted that the change in concentration across one electrode is no more than 3.5% of the total vanadium concentration: the maximum current at 0.5 M total vanadium concentration was below 660 mA at flow rate of 25 mL min⁻¹. Because the cell is operated at 50% SoC, these small changes in the inlet concentration are not expected to appreciably affect the exchange current or charge transfer resistance even when not at open circuit. Because the cell architecture is also symmetric with respect to the electrodes, any ohmic losses not occurring through the separator are also evenly divisible between the two sides. The finite diffusion resistance measured consists of the sum of both half cells; near 50% SoC, the split should be nearly even between both sides.

5.2.3 Fitting data to complex impedance model

The single-electrode model developed by Sun and coworkers for the VRFB⁶⁹ was adopted to fit the open circuit impedance data for each of the eight configurations tested. The model was modified to account for the fact that the impedance data was collected for a whole cell via

$$AZ_{\text{cell,model}} = 2 \times AZ_p + ASR_{\text{series}} + i\omega L \quad (5.1)$$

where $AZ_{\text{cell,model}}$ is the model-predicted area specific impedance of the whole cell, AZ_p is the area specific impedance of one electrode in the VRFB and is calculated according to the previously developed protocol,⁶⁹ ASR_{series} is the area specific series resistance of the cell, and L

is the inductance of the leads. The model parameters described in this work are consistent with the notation used in Reference 69.

In addition to the universal gas constant R and the Faraday constant F , the fixed model parameters were the temperature T , the geometric active area of the cell A , the electrode thickness b , the ionic specific resistivity of the liquid electrolyte ρ_1 , the electronic specific resistivity of the electrode material ρ_2 , the concentrations of the reduced and oxidized species c_R and c_O , the diffusion coefficients of the reduced and oxidized species D_R and D_O ,¹⁴³ and the specific double-layer capacitance C_{dl} . The values for these fixed parameters are shown in Table 5.2 in the Appendix. The ionic specific resistivities were based on the reported conductivities of V^{2+} and V^{3+} electrolytes,¹³⁶ and the electronic specific resistivities were based on manufacturer specifications. It is noted that the concentrations were determined coulometrically and were not exactly 0.5 and 1.5 M total vanadium; however, throughout the text, the concentrations are described nominally as 0.5 and 1.5 M for simplicity.

The fitted parameters were the total internal surface area A_t , the exchange current for a differential unit element of surface area i_0 , the constant phase element (CPE) power factor P , the boundary layer thickness a , the geometric shape factor f defined in Reference 69, and the additional parameters L and ASR_{series} . A non-linear least squares regression in MATLAB was performed allowing the fitted parameters to vary until the quantity $\sum_{F_j} |AZ_{cell,experimental} - AZ_{cell,model}|$ over the entire frequency range (all F_j) was minimized. The values for these fitted parameters at open circuit are included in Table 5.3 in the Appendix.

The area-specific resistances ASR_{hf} (distributed ohmic due to ionic and electronic resistance), ASR_{ct} (charge transfer), and ASR_{fd} (finite diffusion) for the open circuit impedance spectra are calculated for a single electrode:⁶⁹

$$ASR_{\text{hf}} = b \frac{\rho_1 + \rho_2}{3} + b \frac{\rho_1 \rho_2}{3(\rho_1 + \rho_2)} \quad (5.2)$$

$$ASR_{\text{ct}} = \frac{A}{A_t} \frac{RT}{F i_0} \quad (5.3)$$

$$ASR_{\text{fd}} = \frac{A}{A_t} \frac{a}{f} \frac{RT}{F^2} \left(\frac{1}{C_R D_R} + \frac{1}{C_O D_O} \right) \quad (5.4)$$

These resistances can be integrated with respect to current density to obtain the overpotential associated with each process:⁶⁹

$$\eta_x = \int_0^i ASR_x(i) di \quad (5.5)$$

where x represents the series ohmic, distributed ohmic, charge transfer, and finite diffusion processes, with i representing the current density. To find the total cell overpotential due to each process, the model-calculated single-electrode overpotential η_x was doubled for each process other than the series resistance.

5.2.4 Calculation of rate constant

The exchange current I_0 for an electrode is related to the open circuit charge transfer resistance $R_{\text{ct},0}$ by⁹⁶

$$R_{\text{ct},0} = \frac{RT}{\eta F I_0} \quad (5.6)$$

$R_{\text{ct},0}$ is simply the model-extracted ASR_{ct}/A at open circuit. Assuming a one-electron Butler-Volmer kinetic model, the exchange current I_0 and rate constant k_0 are related by⁹⁶

$$I_0 = F A_{t,\text{corrected}} k_0 c_O^\alpha c_R^{1-\alpha} \quad (5.7)$$

In Eq. 5.7, the total surface area is corrected according to a procedure developed by Brug et al.¹⁴⁰ and used by others.¹⁴⁴ The double-layer capacitance of a CPE is found according to:

$$CPE_{dl,corrected} = Q^{\frac{1}{P}} \left(\frac{R_e R_{ct}}{R_e + R_{ct}} \right)^{\frac{1}{P}-1} \quad (5.8)$$

where Q and P are the CPE constants and R_e and R_{ct} are the ohmic and charge transfer resistance, respectively. Using the following equations to find the inputs for Eq. 5.8, we can find $A_{t,corrected}$.

$$Q = A_t \times C_{dl} \quad (5.9)$$

$$R_e = \left(\frac{ASR_{series}}{2} + ASR_{hf} \right) / A \quad (5.10)$$

$$R_{ct} = ASR_{ct} / A \quad (5.11)$$

All of the parameters on the right-hand side of Eqns. 5.9-5.11 are obtained from the model fit as described above. Finally, we find the corrected surface area:

$$A_{t,corrected} = \frac{CPE_{dl,corrected}}{C_{dl}} \quad (5.12)$$

Substituting into Eq. 5.7, the rate constant k_0 is obtained.

5.3 Results and discussion

In the following sections, the complex impedance data and model fits are shown. Then, insights from impedance are used to discuss the effects of electrode material, flow field pattern, and vanadium concentration on charge transfer, finite diffusion, and ohmic processes. Afterward, the overpotentials from each process are summed to obtain the impedance-resolved polarization curves⁶⁹ and the limiting process for each cell is discussed.

5.3.1 Model fit

The complex impedance spectra, shown in Figure 5.3 and Figure 5.4, exhibit clear resolution of the charge transfer and finite diffusion processes. The distributed resistance is due to the parallel resistances of the ionic and ohmic resistances through the thickness of the electrode and often appears as a linear feature at the high frequency portion of the complex impedance spectrum.¹⁰⁰ This feature is especially apparent in the spectra collected with GFD3 electrodes at 0.5 M total vanadium concentration. The higher frequency semicircle is the charge transfer process and the lower frequency feature is the finite diffusion process. The open circuit fits in Figure 5.5 and Figure 5.6 show very good agreement between the model fit and experimental data. It is noted that equivalent circuits would not be able to capture the distributed resistance. Additionally, with sufficiently high exchange current, the charge transfer feature is no longer a semicircle and cannot be described by an equivalent circuit.¹⁰⁰

An example of the calculated intercepts of the complex impedance data with the real axis according to Eqns 5.2-5.4 is shown in Figure 5.7 for the GFD3 electrode. These resistances are plotted as a function of current density for the flow-through 0.5 M vanadium 10AA electrode case in Figure 5.8. The subsequent integration to obtain the overpotentials due to each process is shown in Figure 5.8 as well.

5.3.2 Charge transfer process

Rate constant measurement

Rate constants for the V^{2+}/V^{3+} reaction under various conditions are summarized in Table 5.1. The rate constant measured for the GFD3 electrode under all conditions was between 2.6 and $3.2 \times 10^{-5} \text{ cm s}^{-1}$. The 10AA electrode rate constant was measured between 7.6 and

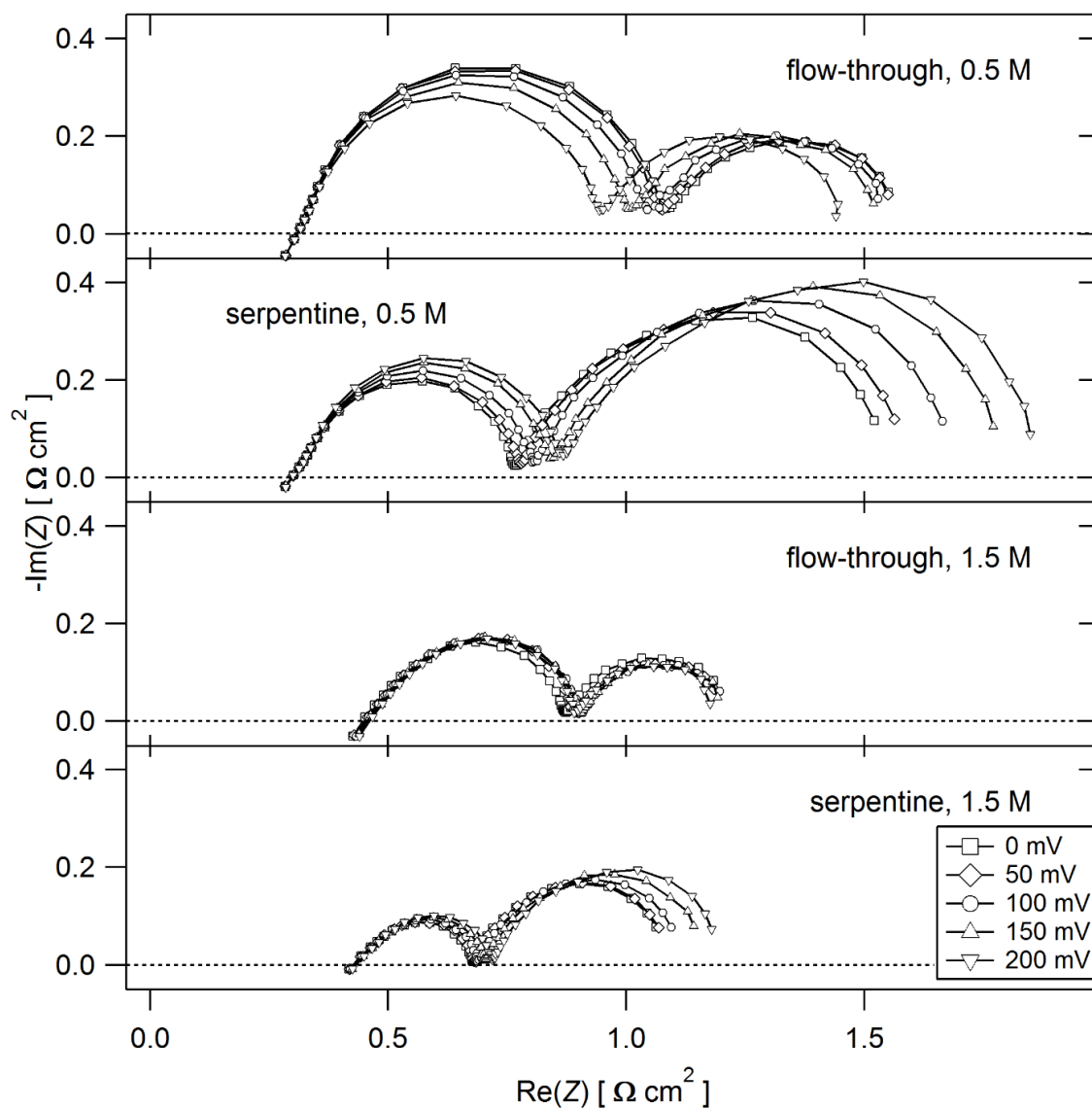


Figure 5.3. Whole cell complex impedance spectra for 10AA electrodes with flow rate 25 mL/min and at 30 °C. Spectra are labeled with the flow field and total vanadium concentration. Applied overpotential is for the whole cell.

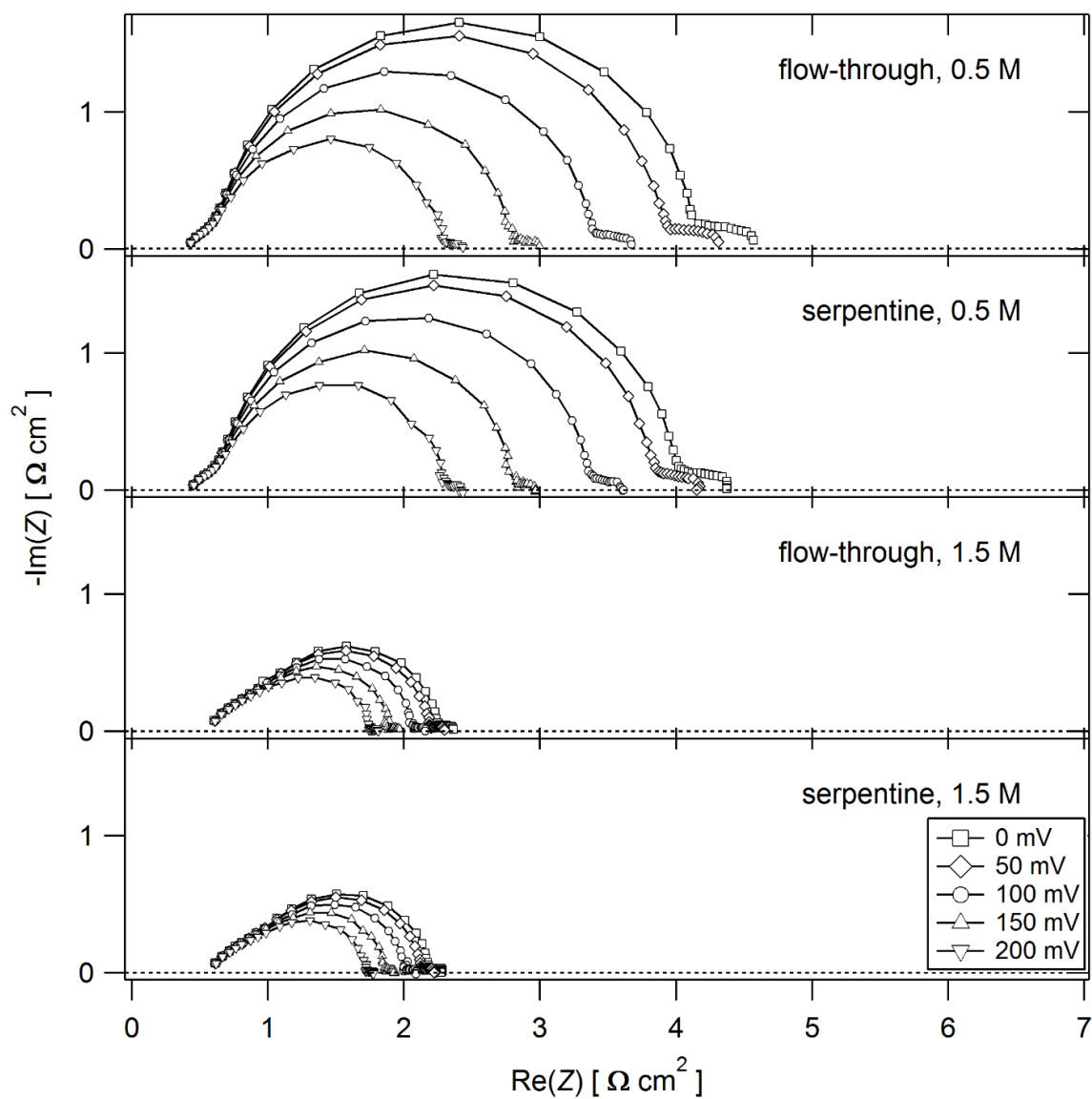


Figure 5.4. Whole cell complex impedance spectra for GFD3 electrodes with flow rate 25 mL/min and at 30 °C. Spectra are labeled with the flow field and total vanadium concentration. Applied overpotential is for the whole cell.

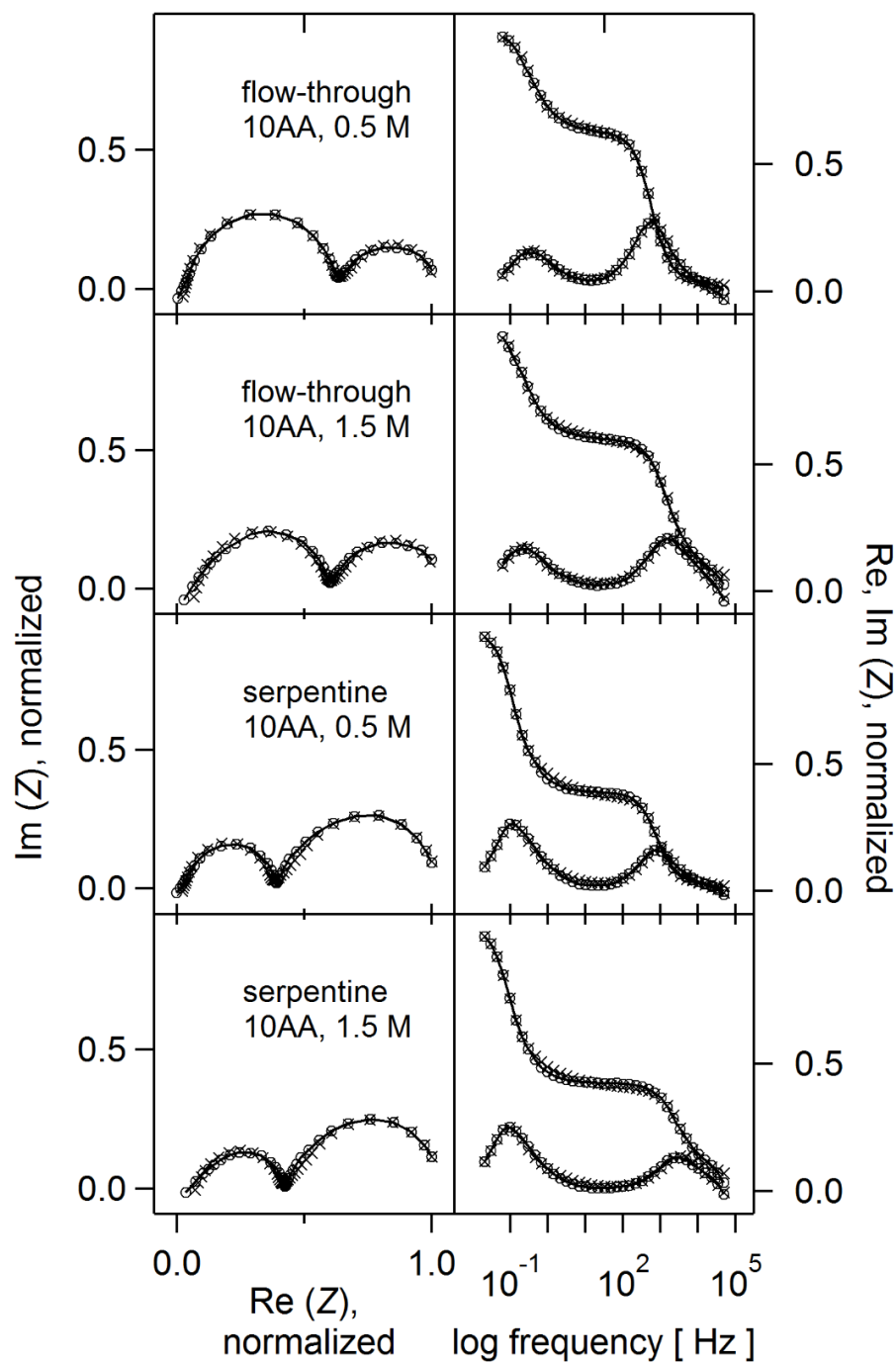


Figure 5.5. Model fit ($\circ$) to experimental data ($\times$) for 10AA electrodes. Left: Nyquist plot. Right: Bode plot. The real impedances were normalized by first subtracting $\min(\text{Re}(Z))$ from all points and then dividing by the quantity $[\max(\text{Re}(Z)) - \min(\text{Re}(Z))]$. Imaginary impedances were normalized only by dividing by the quantity $[\max(\text{Re}(Z)) - \min(\text{Re}(Z))]$.

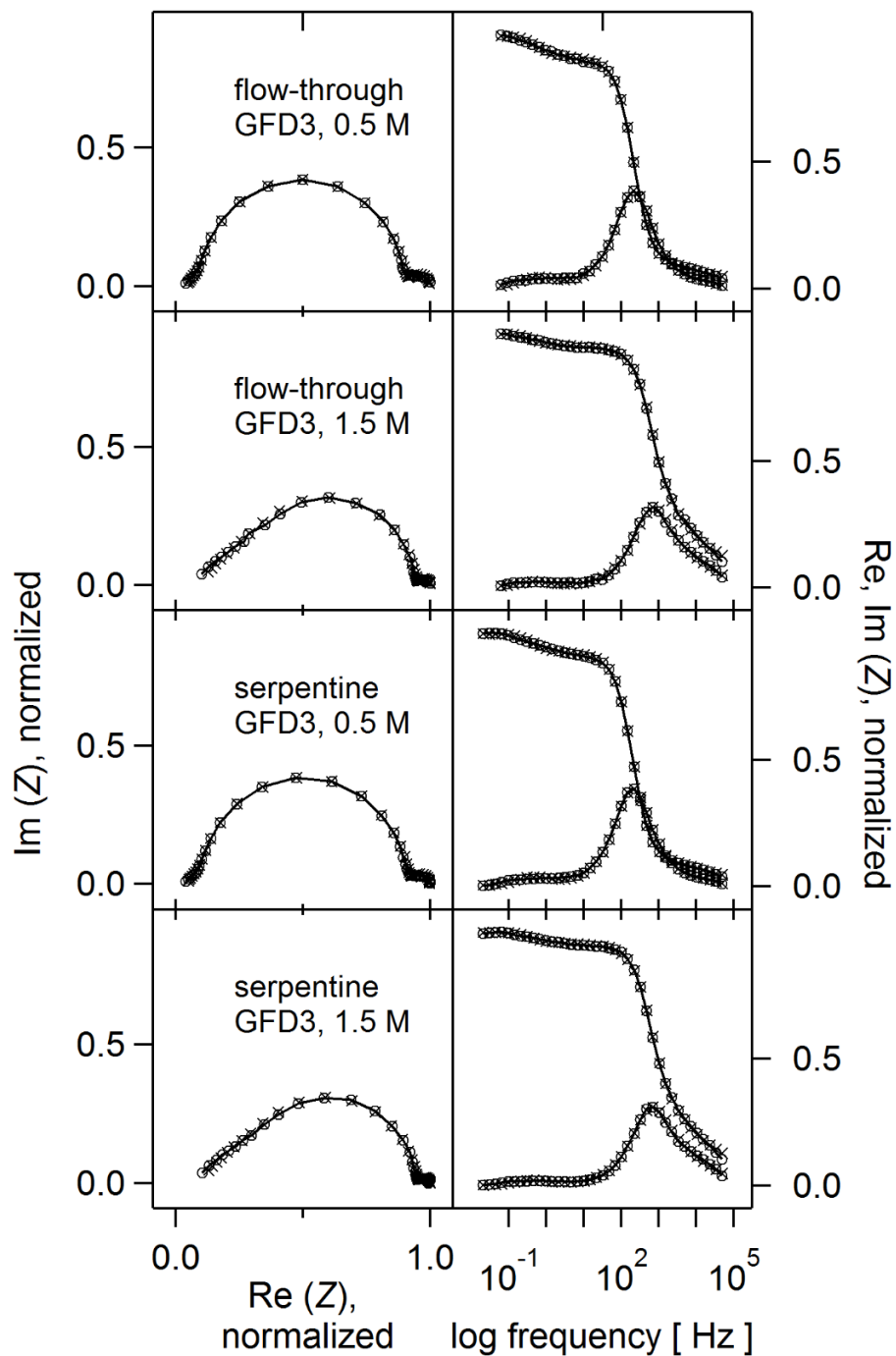


Figure 5.6. Model fit ($\circ$) to experimental data ($\times$) for GFD3 electrodes. Left: Nyquist plot. Right: Bode plot. The real impedances were normalized by first subtracting $\min(\text{Re}(Z))$ from all points and then dividing by the quantity $[\max(\text{Re}(Z)) - \min(\text{Re}(Z))]$. Imaginary impedances were normalized only by dividing by the quantity $[\max(\text{Re}(Z)) - \min(\text{Re}(Z))]$.

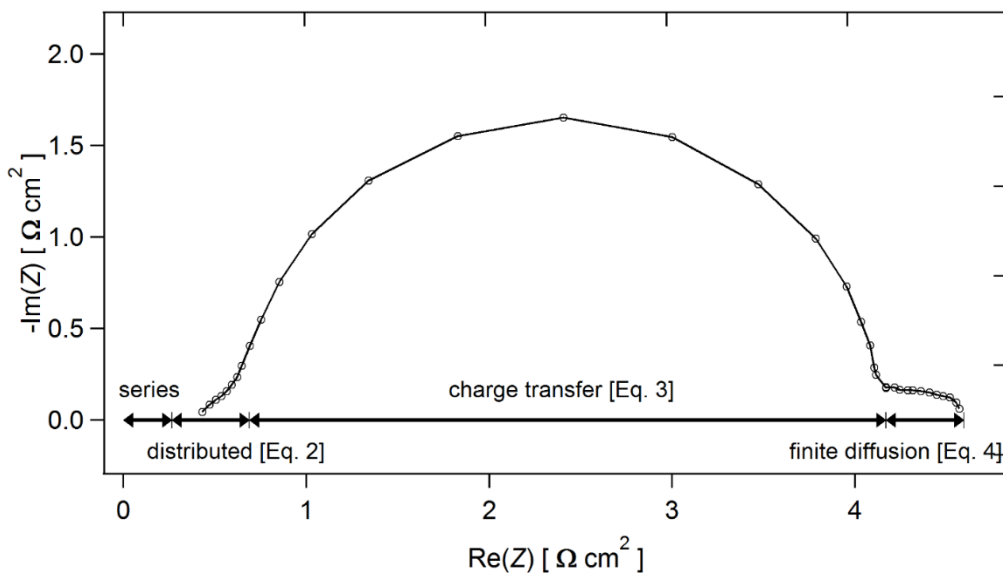


Figure 5.7. Resolved resistances according to low-frequency approximations in Eqns. 5.2-5.4 for the open circuit complex impedance spectrum of the GFD3 electrode with flow-through flow field and 0.5 M vanadium concentration.

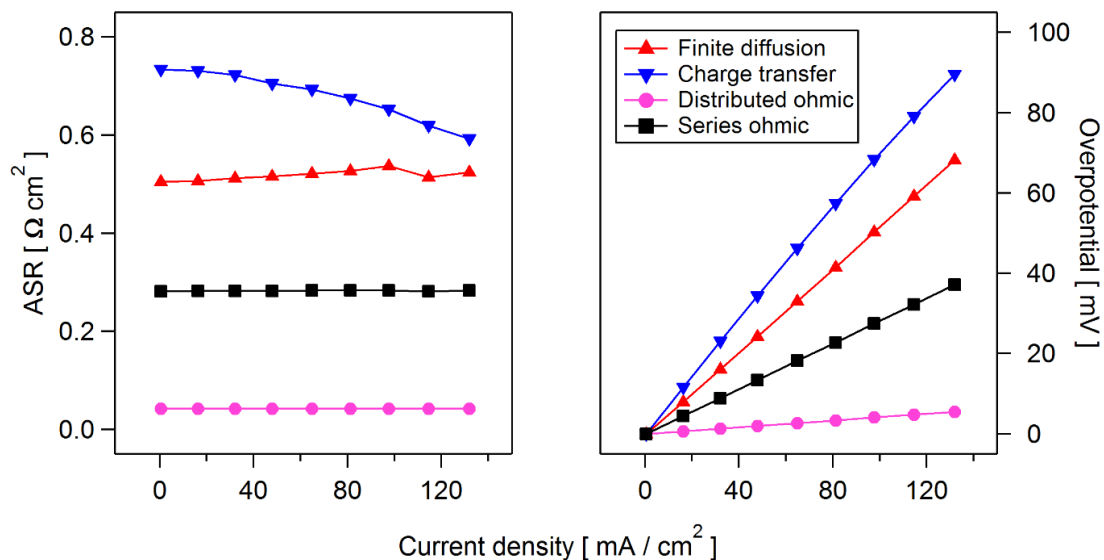


Figure 5.8. Area-specific resistances and integrated overpotentials. Resistances were extracted by fitting the data to the impedance model at each current density. Data shown are for 10AA electrodes with flow-through flow field at 0.5 M vanadium concentration.

$15.0 \times 10^{-5} \text{ cm s}^{-1}$. The rate constant for GFD3 was lower than for 10AA by at least a factor of two, indicating that the activity of the carbon felt is lower than that of the paper. It is hypothesized that this is due to differences in material properties, particularly the degree of graphitization.

Table 5.1. Rate constant and effective area of single 5 cm^2 electrode in the cell.

Electrode	Flow field	c (M)	k_0 ($10^{-5} \text{ cm s}^{-1}$)	A_{eff} (cm^2)
10AA	flow-through	0.5	7.6	170
		1.5	8.2	110
	serpentine	0.5	10.9	220
		1.5	15.0	110
GFD3	flow-through	0.5	2.8	98
		1.5	3.2	84
	serpentine	0.5	2.6	110
		1.5	3.0	97

Overall kinetic performance

Shown in Figure 5.9 are the charge transfer/activation overpotentials for all conditions tested. GFD3 exhibited a much larger activation overpotential than 10AA. When holding flow field constant, the activation overpotential for GFD3 was $\geq 3\times$ greater than the activation overpotential of 10AA across the entire range of current density. As discussed previously, the rate constant for GFD3 is lower than that of paper, which partially results in the higher activation overpotential. The remaining difference is because the GFD3 surface area is lower than the 10AA surface area.

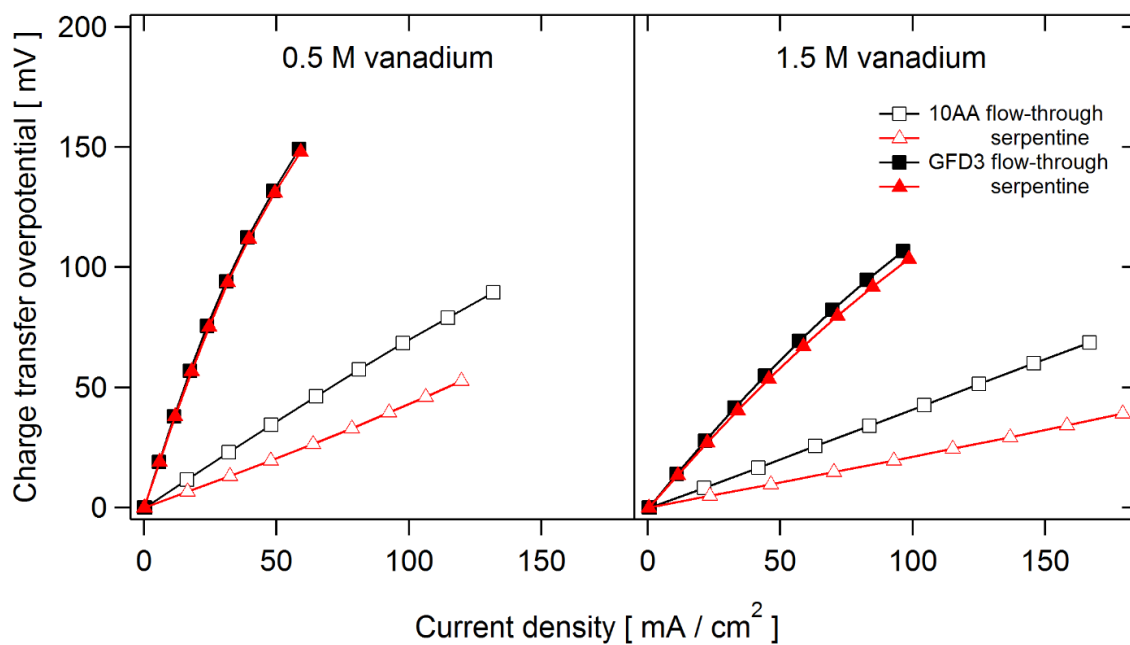


Figure 5.9. Charge transfer overpotential. Left: 0.5 M total vanadium concentration. Right: 1.5 M total vanadium concentration.

For 10AA, the flow field pattern had a large impact on activation overpotential; it was nearly 2× higher for 10AA used in conjunction with the flow-through pattern in comparison with 10AA used with the serpentine pattern. The impedance data suggest a difference in surface area; the 10AA electrode in the serpentine cell was measured at 220 cm² of effective surface area in comparison with the 170 cm² in the flow-through cell. For GFD3, the serpentine pattern also resulted in a higher surface area relative to flow-through, though the difference was much smaller (110 vs. 98 cm²). Electrodes removed from cells built with the serpentine pattern often appear to have an imprint of the flow channels, which is an indication that the electrode material flexes some degree into the channels; the flow-through pattern has little space for such flexing. The flexing into the channels may expose more surface area. Thus, flow field pattern may play a role in affecting the effective surface area of the electrode and the magnitude of its role is dependent on electrode material. Further study with additional flow field patterns is needed to shed light on this phenomenon.

5.3.3 Finite diffusion processes

The finite diffusion process is dependent on the bulk concentration of the electroactive species and the Nernstian diffusion layer thickness, which can vary throughout the electrode as a result of the electrode morphology and non-uniform electrolyte velocity. In this work, electrode morphology refers to properties including the tortuosity and porosity. A higher porosity typically results in a lower tortuosity. Qualitatively, a high electrolyte velocity in the electrode decreases the boundary layer thickness, reducing the finite diffusion resistance and concentration polarization. Additionally, uniform electrolyte distribution (good mixing) through the electrode should decrease concentration polarization as the bulk concentration is maintained throughout

the electrode. High porosity and low tortuosity promote uniform electrolyte distribution. The flow field pattern can also play a major role in determining the magnitude and distribution of the electrolyte velocity through the electrode.⁶³

As shown in Figure 5.10, the concentration polarizations were much higher for 10AA electrodes with both flow fields and both concentrations in comparison with GFD3. At the 0.5 M vanadium concentration and a current density of 50 mA cm^{-2} , the concentration polarization was less than 12 mV for GFD3 (both flow fields) while for 10AA it was 25 mV (flow-through) and 40 mV (serpentine). The flow field strongly affected transport with 10AA electrodes, as the flow-through design resulted in a significant decrease in concentration overpotential relative to the serpentine, especially at 0.5 M vanadium concentration. With GFD3 as the electrode, the flow field pattern had virtually no effect on the concentration polarization. These observations can be explained by first considering the electrode material properties and then considering the transport mechanisms of the two flow fields.

The 10AA material is less porous than GFD3 (10AA compressed porosity: 80%, GFD3 compressed porosity: 90%¹⁴⁵) and a single layer of 10AA is significantly thinner than the GFD3 (compressed thickness, $240 \text{ }\mu\text{m}$ vs. 2 mm). The differences in porosity and thickness result in a significant difference in pressure drop. The pressure drop measured in the flow-through cell at a flow rate of 25 mL min^{-1} for one layer of 10AA was $\sim 12 \text{ psi}$, while a single layer of GFD3 exhibited a $\sim 1 \text{ psi}$ pressure drop.

Mass transport in the serpentine flow field design relies on both passive diffusion of vanadium from the channels into the electrode and forced advection of vanadium by electrolyte flowing into the electrode across lands in the flow field (depicted by the arrows in Figure 5.1a).

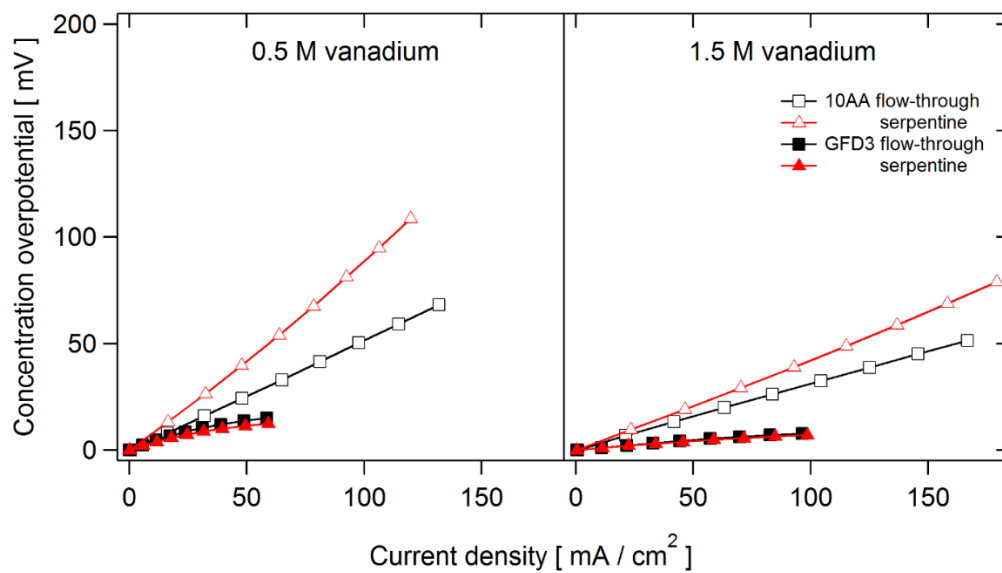


Figure 5.10. Concentration overpotential. Left: 0.5 M vanadium concentration. Right: 1.5 M total vanadium concentration.

The pressure drop along the channel versus through the electrode determines how much flow jumps into the electrode and how much bypasses in the flow field channel; this mode of electrolyte transport can result in non-uniform velocity distributions within the electrode.^{63,145} A low pressure drop in the in-plane direction of the electrode results in a large fraction of the electrolyte flowing into the electrode. Conversely, with high-pressure drop materials, less flow is forced through the electrode resulting in a lower electrolyte velocity in the electrode.^{63,145} Therefore, with serpentine flow fields, one expects lower concentration polarization with electrode materials that have a lower inherent pressure drop; the lower pressure drop through GFD3 can explain the much lower concentration polarization than 10AA with the serpentine design.

The flow-through design has no channels for bypass flow; thus, all electrolyte is forced through the electrode, and the electrolyte velocity in the electrode is determined by the cross-sectional area. The electrolyte velocity in the electrode is always greater than the electrolyte velocity with the same electrode and a serpentine flow field because there can be no bypass flow. Additionally, the flow-through pattern results in a uniform velocity distribution in the in-plane direction of the electrode. Therefore, one expects a lower concentration polarization with the flow-through design in comparison with the serpentine design; this result was confirmed as shown in Figure 5.10. The difference in concentration polarization with GFD3 between the serpentine and flow-through designs was negligible. This can be explained by the low pressure drop in GFD3; most of the flow with the serpentine design already travels through the electrode because the serpentine channels do not carry much bypass flow. The end result is that the serpentine and flow-through designs have very similar flow profiles within the GFD3 electrode.

Thus, the flow-through design cannot provide significant improvement with respect to transport in GFD3, and the concentration polarization is the same for both flow fields.

The expected effect of tripling concentration is to decrease the finite diffusion resistance and overpotential by 67%. In GFD3, the concentration overpotential decreased by 50%. In 10AA, the concentration overpotential decreased by only 25-30%.

5.3.4 Ohmic resistance

The ohmic resistance was resolved into the series and distributed resistances and is shown in Figure 5.11. The series resistance is the sum of the membrane ionic resistance, electronic contact resistances, and the electronic resistance through the flow field and collector. The distributed resistance is calculated in Eq. 5.2 and is the parallel combination of the electronic and ionic resistances in the electrode and liquid electrolyte, respectively.

The series resistances were ~ 0.28 and $\sim 0.41 \text{ } \Omega \cdot \text{cm}^2$ at 0.5 and 1.5 M vanadium concentration, respectively, and were independent of flow field and electrode configuration as represented in Figure 5.11. Assuming all series resistance was in the membrane and a membrane thickness of $177 \text{ } \mu\text{m}$, the implied membrane ionic conductivities are 0.063 and 0.043 S/cm at 0.5 and 1.5 M vanadium concentration, respectively. These values are consistent with those measured by Tang et al.¹²³

The distributed resistances with 10AA were 0.042 and 0.062 $\Omega \cdot \text{cm}^2$ with 0.5 and 1.5 M vanadium concentration, respectively; with GFD3, the distributed resistances were 0.42 and 0.59 $\Omega \cdot \text{cm}^2$. The GFD3 compressed thickness was $8\times$ the compressed thickness of 10AA and nearly entirely explains the $10\times$ difference in distributed resistance. The remaining 20% difference is due to the difference in electrical conductivities, reported by the manufacturer as

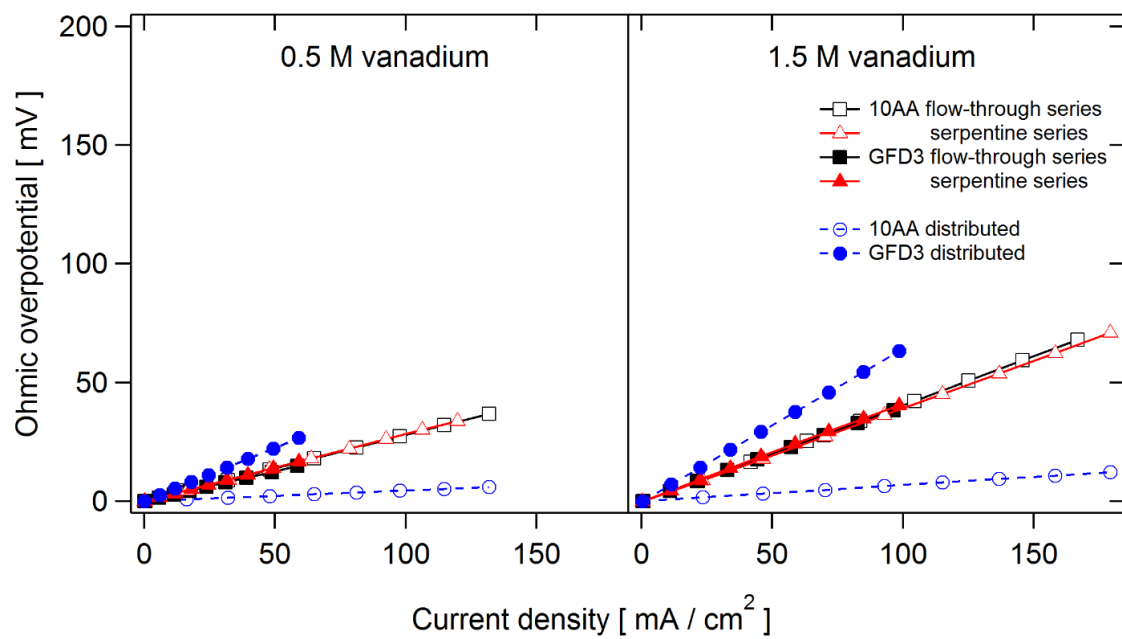


Figure 5.11. Ohmic overpotential separated into series and distributed resistances. Left: 0.5 M total vanadium concentration. Right: 1.5 M total vanadium concentration.

0.012 and 0.30 $\Omega\cdot\text{cm}^2$ for 10AA and GFD3, respectively. The relatively small difference in distributed resistance in spite of the large difference in electrical resistivity is because the ionic resistance is approximately an order of magnitude larger than either of the electronic resistances, and so the distributed resistance is dominated by ionic resistance.

These results show the significance of electrode thickness in determining the overall ohmic resistance. With thick carbon felts, 60% of the ohmic resistance is due to the distributed ohmic resistance of the electrode and electrolyte. With thin carbon papers, the membrane dominates the total ohmic resistance, accounting for 87% of the total. The ohmic resistance of a battery with GFD3 felt and no membrane would exceed that of a cell built with 10AA and Nafion 117.

5.3.5 Overall cell behavior

Figure 5.12 displays the overall polarization curves. The 10AA electrodes always had a higher current density than GFD3 electrodes at a given overpotential, independent of flow field and concentration. The 1.5 M vanadium concentration outperformed 0.5 M vanadium concentration if the electrode materials were the same. However, although concentration increased by a factor of three, the current density increased by less than a factor of two, suggesting that there are diminishing returns for increased concentration in terms of current density. With continual increases in ohmic resistance, there may be a point at which increased vanadium concentration may actually decrease the current density at a given overpotential. The flow field had no impact on the overall performance for GFD3. For 10AA, the effect of flow field was dependent on concentration. At 0.5 M vanadium, the flow-through design exhibited better performance; at 1.5 M vanadium, the serpentine was superior. These differences can be

explained by the differences in activation and concentration polarization, discussed in sections 3.1.2 and 3.2.

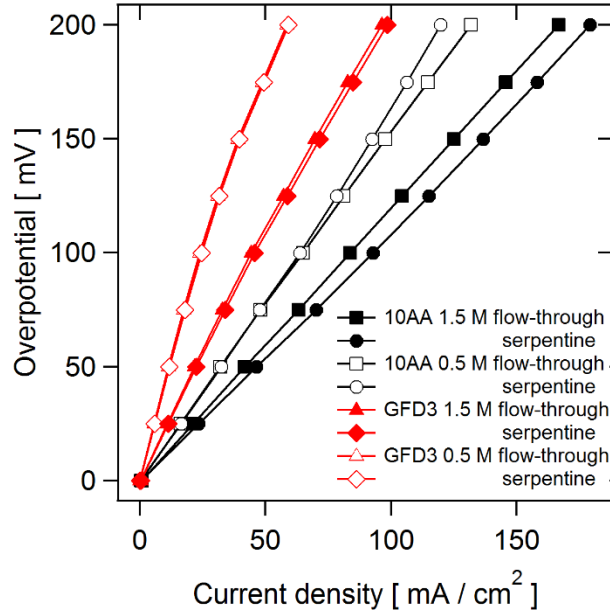


Figure 5.12. Overall polarization curves, all conditions.

The impedance resolved polarization curves are shown in Figure 5.13, which allow straightforward analysis of the relative contribution of each process to the total overpotential. The impedance-resolved voltage matches the potentiostat-imposed voltage to within 4% for the GFD3 1.5 M vanadium concentration cases and to within 1% for all other cases. This extremely good agreement means that all contributions to overpotential are quantified.

The limiting process for 10AA electrodes cannot be attributed to solely one process. At 200 mV total overpotential, finite diffusion losses accounted for 55% and 40% of the total overpotential with the serpentine flow field and 35% and 25% with the flow-through design at low and high concentration, respectively. Activation overpotential was 25% and 20% with the serpentine and 45% and 35% with the flow-through designs at low and high concentrations,

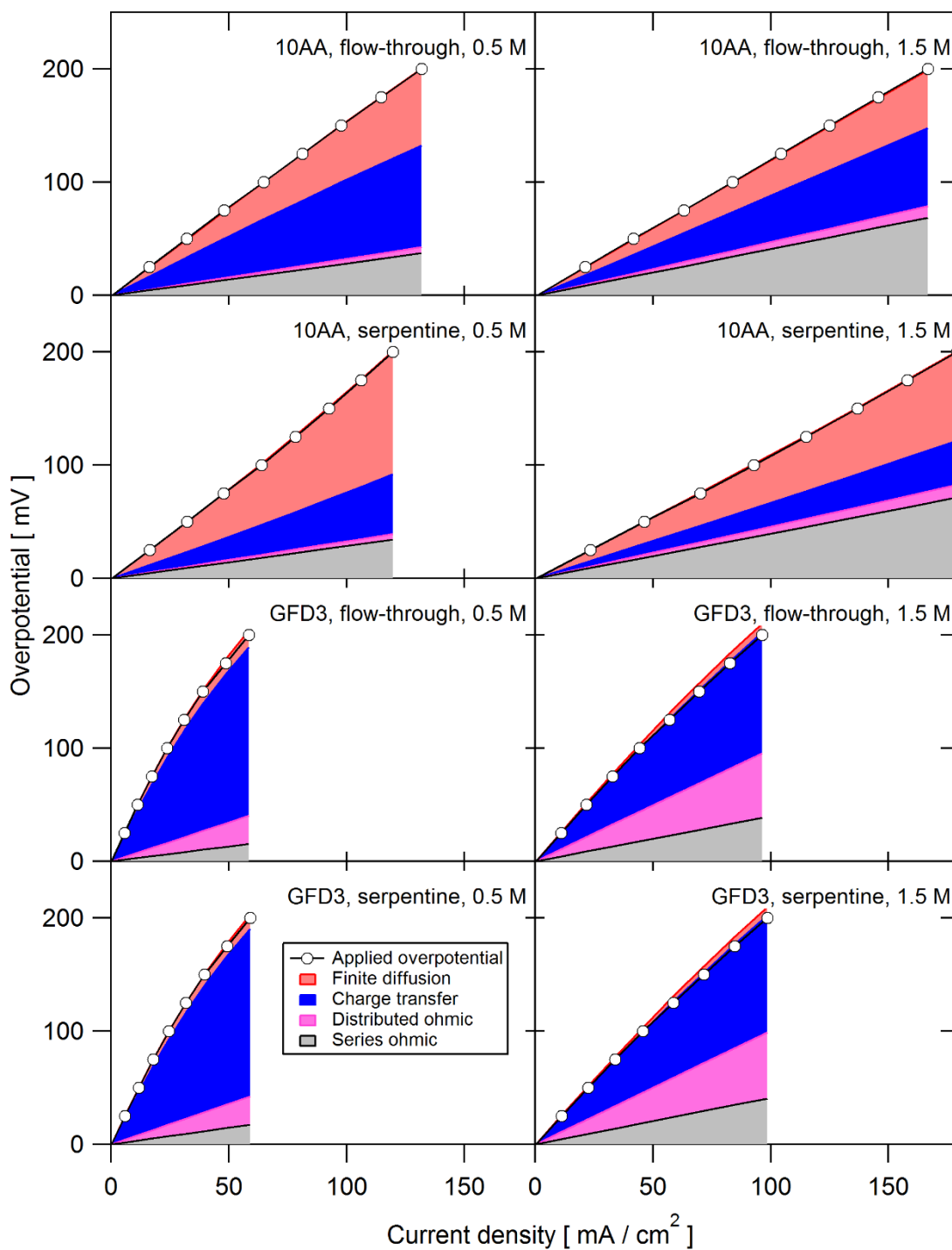


Figure 5.13. Impedance-resolved polarization curves showing the contributions of ohmic, charge transfer, and finite diffusion overpotentials. Open circles represent the potentiostat-imposed overpotential.

respectively. Total ohmic losses were 20% and 40% of the total at low and high concentration, respectively. Transport losses can be partially mitigated with flow field design. Ohmic polarization is a relatively small contributor at low vanadium concentration, but becomes the largest source of overpotential at higher concentration, though it is still below half of the total. The distributed ohmic resistance is small relative to all other resistances.

The limiting process for GFD3 electrodes is very clearly the charge transfer process: with both flow fields, it is 70% of the total polarization at low concentration and 50% at high concentration. Concentration polarization is negligible at both concentrations with less than 10% of the total overpotential at 0.5 M vanadium concentration and less than 5% at 1.5 M vanadium concentration. Ohmic resistance is a small contributor at low concentration, growing to about 45% at high concentration. The distributed resistance is the more significant of the two sources of ohmic resistance.

This work highlights some of the tradeoffs of using a felt or paper-based carbon electrode. Ohmic losses with felt are much higher due to the thickness, but finite diffusion overpotential is much lower. Using thinner paper electrodes can greatly decrease the ohmic resistance, but a higher finite diffusion overpotential results. Off-the-shelf 10AA paper is kinetically more facile than GFD3 felt. However, it has been shown that a variety of pretreatments can be used to improve the kinetics;¹³ thus, kinetics in off-the-shelf materials need not be a determining factor in electrode material choice. An ideal electrode would be thinner than the commercially available felts today (GFD3 is among the thinnest), but would maintain their favorable transport properties. Thin electrodes based on gas diffusion layers such as the 10AA in this work must have improved transport properties to minimize concentration overpotential.

The reader should take note of the fact that the results presented in this work are only relevant for the V^{2+}/V^{3+} couple. The limiting process for the positive side of the VRFB (VO_2^+/VO^{2+}) is likely different, given that the kinetics on the positive side are faster than that on the negative side.^{36,62,141} Because commercial VRFBs operate at concentrations above 1.5 M vanadium concentration, where ohmic overpotential started to dominate the negative symmetric cell in this work, one might predict that the ohmic resistance would be the dominant source of overpotential in full cells under practical operating conditions. Given that increased vanadium concentration has competing effects on voltage efficiency – increase in ohmic overpotential and decrease in charge transfer and finite diffusion overpotentials – efforts to continually increase vanadium concentration will ultimately result in a tradeoff between increased energy density and decreased cell efficiency and power density.

5.4 Conclusions

The use of a pulse dampener to obtain quantitative information about the finite diffusion resistance with EIS at a practical flow rate and with relatively short experimental time was presented. The method can be a useful diagnostic tool for electrochemical characterization of the growing number of redox couples used in RFBs. In this work, the effects of electrode material, flow field design, and concentration on charge transfer, finite diffusion, and ohmic resistance and overpotential were determined with respect to the V^{2+}/V^{3+} redox couple in a VRFB.

Charge transfer was the dominant source of overpotential with GFD3 electrodes; finite diffusion was negligible. For 10AA-based cells, all three sources of overpotential contributed significant portions to the total cell overpotential. Flow field design had a significant impact on the finite diffusion overpotential with 10AA. The distributed resistance with GFD3 felt was

larger than the membrane in large part to the thickness of the electrode, while in 10AA-based cells, the membrane resistance was the largest contributor to ohmic overpotential.

5.5 Appendix

Table 5.2. Fixed parameters for model input.

Fixed parameters	Value	Units	Description
A	5	cm^2	defined by cell geometry
b (10AA)	0.24	mm	defined by cell geometry
b (GFD3)	2	mm	defined by cell geometry
C_{dl}	20	mF/cm^2	typical dl capacitance
D_O	1.10×10^{-6}	cm^2/sec	Ref. 143
D_R	0.57×10^{-6}	cm^2/sec	Ref. 143
T	303.15	K	controlled
c_O, c_R (low conc.)	0.28	mol/L	coulometric measurement
c_O, c_R (high conc.)	0.76	mol/L	coulometric measurement
ρ_1 (low conc.)	2.61	$\Omega \cdot \text{cm}$	calculated (Ref. 136)
ρ_1 (high conc.)	3.88	$\Omega \cdot \text{cm}$	calculated (Ref. 136)
ρ_2 (10AA)	0.012	$\Omega \cdot \text{cm}$	manufacturer specification
ρ_2 (GFD3)	0.3	$\Omega \cdot \text{cm}$	manufacturer specification

Table 5.3. Table of model output fitted parameters at open circuit for each experimental case.

Flow field	electrode	V conc. (M)	At	i0 (10^{-3})	P	a (10^{-4})	f	L (10^{-7})	ASR series
flow-through	10AA	0.5	260	1.3	0.95	9	0.18	3.9	0.28
		1.5	370	1.8	0.87	12	0.09	3.8	0.41
	GFD3	0.5	140	5.5	0.96	7	0.32	2.1	0.26
		1.5	160	1.2	0.93	8	0.46	1.3	0.41
serpentine	10AA	0.5	230	2.8	0.99	16	0.22	1.9	0.29
		1.5	270	4.6	0.91	18	0.15	2.4	0.39
	GFD3	0.5	160	5.0	0.96	8	0.38	1.9	0.29
		1.5	190	1.1	0.92	9	0.47	1.5	0.42

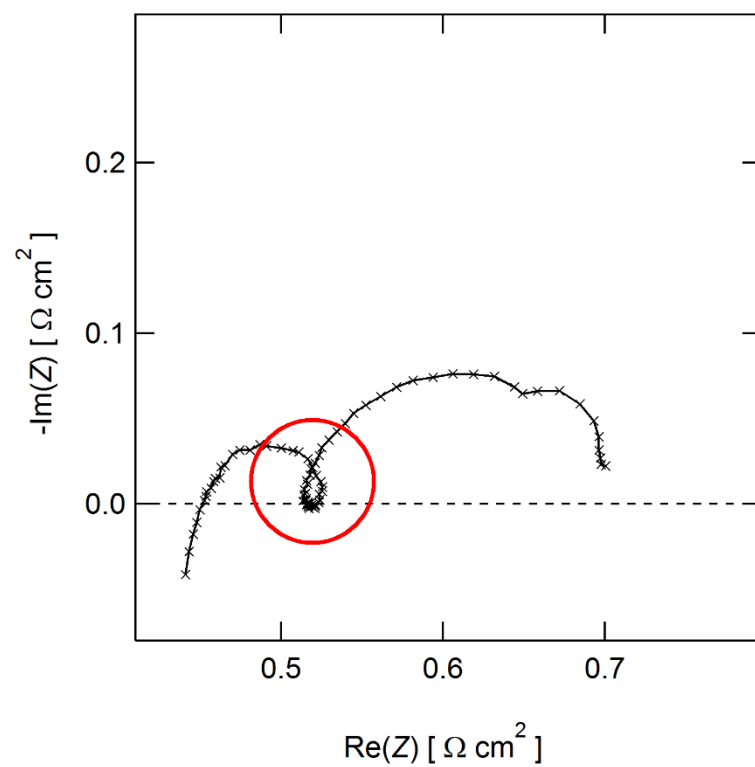


Figure 5.14. Distorted EIS spectrum.

CHAPTER 6
IMPEDANCE-RESOLVED BEGINNING-OF-LIFE ELECTROCHEMICAL
PERFORMANCE AND DURABILITY OF TREATED CARBON FELT ELECTRODES
IN VANADIUM REDOX FLOW BATTERIES

Abstract

This article has not been published anywhere, nor will it be before I turn in the final version of my ETD, so I didn't include a publication statement. A manuscript will be submitted for publication. This work was authored by Alan M. Pezeshki, Robert L. Sacci, M. Cyrus Daugherty, Katie L. Browning, Rose E. Ruther, Frank M. Delnick, Craig A. Bridges, Gabriel M. Veith, and Matthew M. Mench.

My primary contributions to this work were the experimental design, collection, reduction, and interpretation of all data, and composition of the manuscript. Sacci contributed to experimental design and interpretation of all data. Daugherty performed the SEM and assisted in collection of EDS data. Browning assisted in collection of XPS data. Ruther assisted in collection and interpretation of Raman data. Delnick contributed to interpretation of impedance data and application of model to data. Bridges assisted in ammonia heat treatments. Veith assisted in collection of XPS data.

6.1 Introduction

Numerous and varied treatments have been applied to improve electrode performance in VRFBs, as described in Section 1.3.3. Improved kinetics via the addition of nitrogen or oxygen-containing surface functionalities is commonly assumed to be the mechanism for performance gains. Typically, the durability/stability of these treated materials is evaluated by performing a cycling experiment and investigators declare that an electrode material is “stable” upon observing a stable voltage efficiency. However, as shown in Chapter 4, electrode degradation can manifest as a decrease in capacity fade, even if the voltage efficiency does not change significantly. Crossover further convolutes cycling experiments. This chapter aims to evaluate the effects of a series of treatments on a single baseline material with respect to initial performance as well as the beginning-of-life performance degradation over the course of a day.

Phenomenological understanding of performance changes as a result of treatment and as function of time/usage in the battery is obtained.

In Chapter 4, initial studies of degradation in the high performance heat treated SGL 10AA material from Chapter 1 were carried out. However, the polarization curve analysis used was not sufficient to describe the origin of degradation in the material. As described in Section 1.3.4, knowledge of degradation in electrode materials is limited in the literature. While EIS can provide rich information regarding cell performance, its application to study performance in redox flow batteries has been limited. Its use has typically been limited to ex situ three electrode cells in which the electrode material does not necessarily behave as it would in a constructed flow battery cell, where convection is important and cell architecture influences ohmic resistance. The use of EIS to study performance as a function of time during a cycling experiment is complicated by the changes in SoC that occur during operation; crossover additionally exacerbates compositional changes. Therefore, analysis of impedance data taken periodically during cycling experiments in which SoC/electrolyte composition change makes it difficult to draw meaningful conclusions about why electrode performance changes over time, though recent work has attempted to do so.⁸⁷

In Chapter 5, we applied EIS in a symmetric cell to study the impact of electrode material, vanadium concentration, and flow field design on overall cell performance. A macrohomogeneous porous electrode impedance model was utilized to calculate relevant physical parameters including surface area and rate constants based on experimental data and known system physical properties. In this chapter, EIS is again applied, this time to observe the effects of electrode pretreatment as well as the evolution of cell performance. The symmetric cell

method is again employed in order to maintain a constant electrolyte composition and to avoid the confounding effects of changing SoC on impedance spectra.

6.2 Experimental methods

6.2.1 Experimental set-up

The VRFB in this work was a 5 cm² active area cell with a rectangular flow-through flow field design. The separator, a Nafion 117 membrane (Ion Power), was first pretreated by immersing in 1 M H₂SO₄ for 30 minutes at 80 °C and then immersed in deionized water for 30 minutes at 80 °C. One layer of GFD3 carbon felt (SGL carbon) was used as the electrode on both sides of the battery. Including the untreated material, a total of nine variations of the material were tested. The eight thermal and/or chemical pretreatments are detailed in Section 6.2.2. A stock solution of 0.5 M vanadium / 4 M sulfuric acid was prepared by dissolution of VOSO₄ (Alfa Aesar, 99.9%) in a sulfuric acid (Alfa Aesar, ACS grade) solution. The stock solution was filtered after preparation.^{86,142} 50% SoC positive (0.25 M VO²⁺/0.25 M VO₂⁺) and negative (0.25 M V²⁺/V³⁺) electrolyte solutions were prepared coulometrically by electrolysis of the stock solution in a separate cell.

All measurements were carried out in a symmetric cell configuration;^{36,64,69,101} that is, for a given experiment, the same electrolyte solution was circulated through both sides of the cell. A pulse dampener was used to obtain noise-free impedance data at low frequency as in Chapter 5. The pressure drop across the cell was measured with a gas-phase pressure transducer (Omega), which was hydraulically connected to the dampener bottle headspace. Because the electrolyte flows through both sides of the cell, the pressure drop reported is for the whole cell. The cell temperature was controlled at 30 °C and a flow rate of 25 mL min⁻¹ was used for all testing.

6.2.2 Treatments

The baseline material was untreated carbon felt. Eight pretreatments were performed. These treatment conditions with abbreviations referenced hereafter in the text are listed in Table 6.1. Heat treatments were carried out in a tube furnace. The furnace was purged with nitrogen gas at 200 mL min⁻¹ for 1 h prior to heat treatment. Reactant gases flowed at 200 mL min⁻¹ during the temperature ramp and treatment. The furnace temperature was ramped from room temperature to the treatment temperature over 2 h. The reactant gases, temperatures, and hold times at the treatment temperature are specified in Table 6.1. The oxygen treatment was based on very early electrode modification work.⁵⁴ Ammonia is a reducing agent, in contrast to the oxidizing environment of the enriched oxygen treatment; the nitrogen treatment provided a control for the high temperature of the ammonia treatment.

Table 6.1. Electrode treatment parameters.

Sample name	Treatment type	Reactants	Temp. (° C)	Hold time
Raw	Untreated			
HtO	Heat treat	42% O ₂ /58% N ₂	400	15 h
HtN	Heat treat	N ₂	900	1 h
Am1	Heat treat	NH ₃	900	1 h
Am4	Heat treat	NH ₃	900	4 h
HyB	Hydrothermal	1:3 HNO ₃ /H ₂ SO ₄	60	1 h
HyA	Hydrothermal	1:3 HNO ₃ /H ₂ SO ₄	80	1 h
NAS	Soak	HNO ₃	ambient	10 min
Hyt	Hydrothermal + heat treat	1:3 HNO ₃ H ₂ SO ₄ NH ₃	80 900	1 h 4 h

Hydrothermal treatments based on a previous study⁵⁷ were performed in a Teflon-lined autoclave (Columbia International, HTC230-V50) at 60 °C and 80 °C. Solutions of 30 mL of concentrated H₂SO₄ (Alfa Aesar, ACS grade, 96%) and 10 mL of concentrated HNO₃ (Alfa

Aesar, 70%) were used for both treatments. After the carbon felt was added to the mixed acid solution, the vessel was sealed and immersed in a water bath at the treatment temperature. The reactor vessel's internal temperature reached the treatment temperature after 30 min and was held at that temperature for an additional 60 min. Then, the carbon felts were immediately removed and rinsed in deionized water at least five times and stored in deionized water for 8 h prior to battery testing.

The nitric acid soak consisted of soaking the carbon felt in a concentrated nitric acid (Alfa Aesar, 70%) bath for 10 min. This is a common method for cleaning off the shelf carbon materials. The felt was then rinsed in deionized water at least five times and then placed into the battery for testing.

The final treatment combined elements of the hydrothermal and heat treatments. First, the felt was hydrothermally treated at 80 °C in the mixed acid solution described above. After rinsing in deionized water, the felt was dried under vacuum at ambient temperature and placed in the tube furnace. The heat treatment was carried out in the same manner as the Am4 sample. In the following sections, when “ammonia heat treated electrodes” are referenced, they do *not* include this material, which is hereafter referred to as the “mixed” treatment.

6.2.3 Electrochemical protocol

The cell was operated as a two-electrode cell as described in Chapter 5; thus, all cell voltages reported here are across the whole cell. All impedance measurements were taken by holding the DC potential steady for 30 s, followed by acquisition of the impedance data with a 5 mV sinusoidal perturbation from 50 kHz to 60 mHz.

After cell assembly, a solution of deaerated 4 M H_2SO_4 was pumped through the cell. Cyclic voltammetry was performed with a scan rate of 50 mV/s with a voltage window of -0.4 to $+0.4$ V. Then, EIS was carried out at -0.2 , 0 , and $+0.2$ V DC polarizations.

After CV and EIS measurements with sulfuric acid, the cell was drained and refilled with 50% SoC vanadium solution to evaluate the beginning of life electrochemical performance and durability, in which a total of 20 electrochemical cycles were performed. Each cycle comprised a 30 min $+200$ mV imposed cell overpotential followed by a 30 min -200 mV imposed cell overpotential. This protocol simulates a cycling experiment because alternating the imposed potential on the cell switches the half-cell reaction occurring on each side of the cell between charging and discharging. Open circuit EIS measurements were obtained after every cycle. After every five cycles, a full polarization curve with EIS was taken, obtained in 25 mV increments from 0 to $+200$ mV.

Following the ~ 25 h protocol described above, the cell was flushed twice with sulfuric acid solution. Then, the CV and EIS measurements with 4 M H_2SO_4 were performed as described above.

6.2.4 EIS data fitting

Fit to physical model

The EIS spectra for all treatments except the two ammonia heat treatments were fitted as described in Chapter 5. In that work, the single-electrode model developed by Sun et al.⁶⁹ was modified to account for the fact that the impedance data obtained were for a whole cell. It is noted here that as a result of the alternating of potential cycles, both electrodes in the cell were aged in the same manner. Therefore, the requirement that both electrodes behave similarly kinetically for whole cell impedance analysis as described in Chapter 5 is valid. Relevant

parameter values, i.e. electrode surface area, rate constant, and various resistances, were calculated as described in Chapter 5, with one exception: the distributed ohmic resistance. In Chapter 5, the resistances due to each process were estimated according to the low frequency approximations described in Reference 69. When the exchange current is low, the low frequency approximation for the distributed resistance is no longer valid. The distributed resistance was calculated by subtracting the charge transfer, finite diffusion, and series resistances from the total cell resistance, which was taken as the lowest frequency intercept of the data with the real axis.

Fit to equivalent circuit

The impedance spectra collected for the ammonia heat treated electrodes could not be fit to the macrohomogeneous porous electrode model used for the other treated electrodes due to the presence of a third feature at high frequencies that is attributed to ionic resistance as a result of the pore geometry.^{100,146} In these cases, the spectra were fit to an equivalent circuit at frequencies below where the pore geometry feature appeared. A Randles circuit was used for the fit. In this circuit, a series resistance was connected to a parallel combination of a constant phase element and a series combination of a charge transfer element and a bounded Warburg element. The series resistance in this circuit represents the sum of the membrane and distributed ohmic resistances.

The CPE power factor in all cases was 1; therefore, the double-layer capacitance equated directly to the fitted CPE capacitance. The surface area A was calculated based on a specific double-layer capacitance of $20 \mu\text{F cm}^{-2}$. The rate constant k_0 was calculated according to the following equations, based on the one-electron Butler-Volmer kinetic model,⁹⁶

$$i_0 = F A k_0 c_O^\alpha c_R^{1-\alpha} \quad (6.1)$$

$$R_{ct,0} = \frac{RT}{F i_0} \quad (6.2)$$

where i_0 is the exchange current, F is the Faraday constant, $c_{O,R}$ are the oxidized and reduced species concentrations, α is the exchange coefficient, $R_{ct,0}$ is the open circuit charge transfer resistance from the equivalent circuit fit, R is the universal gas constant, and T is the temperature.

6.2.5 Materials characterization

After the completion of cell testing, the electrode materials were removed from the battery, rinsed and stored in deionized water, and then dried under vacuum at ambient temperature. Electron dispersive spectroscopy (EDS), XPS, and Raman spectroscopy were used to probe the surface chemistry. SEM was used to examine the fiber morphology. XPS spectra were obtained and processed as described in Chapter 4. An Alpha 300 confocal Raman microscope (WITec, GmbH) was used to collect Raman spectra. A 532 nm excitation laser (spot size $1\ \mu\text{m}^2$) and 20 $\times$ objective lens were used. Individual spectra acquisition times were 45 s. Representative samples were taken as the average of three to four spot spectra from different fibers within the felt. The D:G band ratio was calculated as the ratios of the peak heights after a linear baseline was subtracted.

6.3 Results and discussion

Each electrode material was electrochemically characterized by the electrochemical protocol described in Section 6.2.3. The first portion of the results discusses the effect of treatment on the electrode used for the positive half-cell reactions. The overall performance is shown with time evolution, followed by deconvolution of the impact of treatment on the ohmic, charge transfer, and finite diffusion processes. Similar results are discussed for electrodes used

for the negative half-cell reactions. Finally, the ex situ EDS, XPS, and Raman results are presented.

6.3.1 Positive electrode

Overall performance

Polarization curves taken at the beginning and end of each experiment are shown in Figure 6.1. At a cell overpotential of 200 mV, the first polarization curve for the four hour ammonia heat treatment had the highest current density of 370 mA cm⁻²; the nitric acid soak resulted in the lowest current density of 270 mA cm⁻². The top five performers were all heat treated in some fashion, while the bottom four included the untreated, nitric acid soaked, and hydrothermally treated materials. Overall, the positive electrode benefits modestly from treatment.

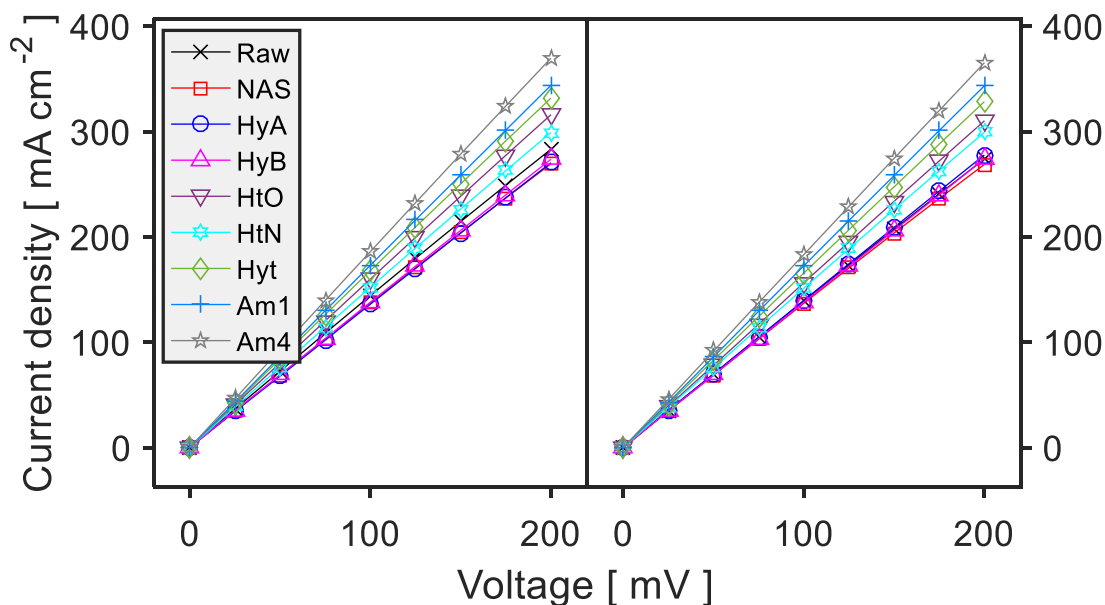


Figure 6.1. Polarization curves obtained at the beginning (left) and end (right) of each experiment. The voltage refers to the total voltage applied across the whole cell.

The average current measured during each potentiostatic step is shown in Figure 6.2. It is immediately obvious from the normalized currents that the performance appears to be stable. The largest decrease in current was the untreated electrode with a nearly negligible 5% decline. The largest increase, observed in the high temperature hydrothermal sample, was 4%. Thus, independent of treatment, the positive electrode appears to suffer from very little degradation and in some cases even shows marginal performance improvement.

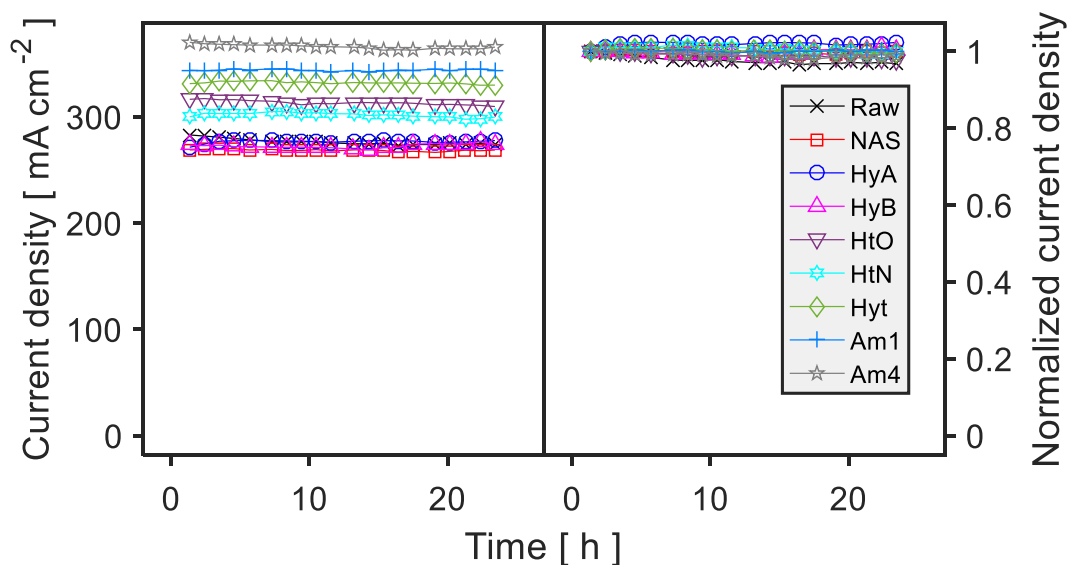


Figure 6.2. Average current measured during each potentiostatic step. Left: actual value. Right: current normalized to first potentiostatic step for the same treatment.

EIS spectra

The open circuit spectrum in Figure 6.3 for the untreated electrode is representative of all treatments, except the ammonia heat treatments. The magnitudes of the charge transfer feature varied in size for the individual treatments. The charge transfer and ionic resistance features overlapped significantly; the low frequency finite diffusion resistance feature was clearly resolved. The four hour ammonia treatment is also shown in Figure 6.3, with the high, middle, and low frequency features attributed to ionic resistance in the pore structure, charge transfer,

and finite diffusion, respectively. In the following discussions, the resistances and impedance spectra shown are all at open circuit, i.e. without the passage of current.

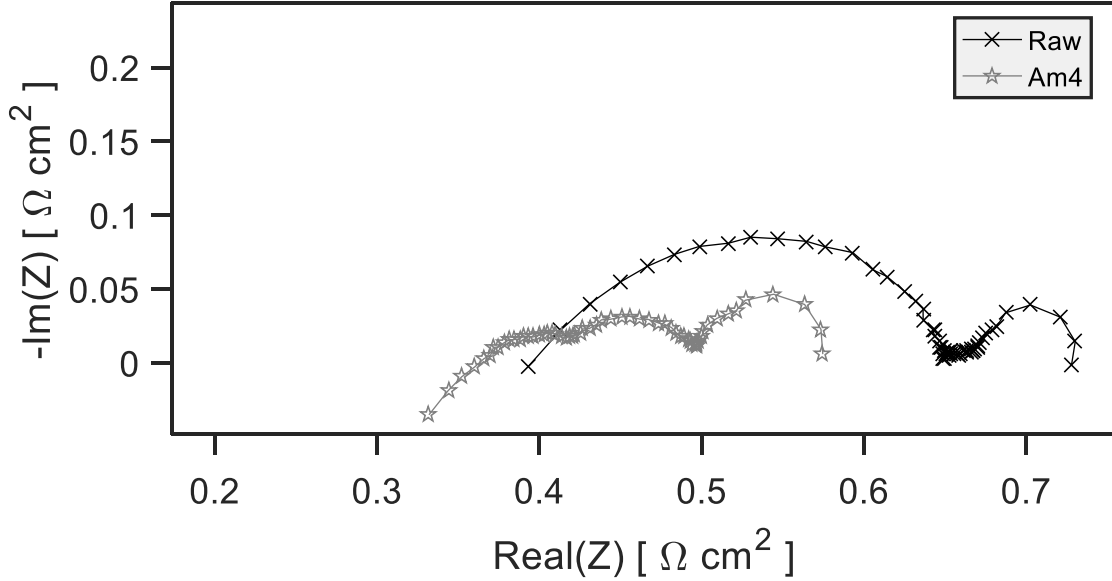


Figure 6.3. Open circuit impedance spectra for untreated and four hour ammonia heat treatment taken at the beginning of the experiment.

Ohmic process

The total ohmic resistance, which is the sum of the series (primarily membrane) and distributed ohmic resistances, is shown for all treatments in Figure 6.4. The four hour ammonia heat treated cell was the lowest at $0.42 \Omega \text{ cm}^2$, and the cells built with hydrothermally treated felt were the highest at $0.54 \Omega \text{ cm}^2$. There was no significant change in the ohmic resistance as a function of time.

The charge transfer resistance plays an indirect role in the distributed ohmic resistance. With facile kinetics, the electrode will support high local current densities with minimal charge transfer/activation polarization. Given that the electronic resistivity of the felt material is an order of magnitude lower than that of the electrolyte solution (0.3 vs $2.48 \Omega \text{ cm}$), the reaction will shift

toward the membrane to find the path of least ohmic resistance. This phenomenon is the origin of the overlap between the charge transfer and distributed ohmic resistances in the impedance spectra.

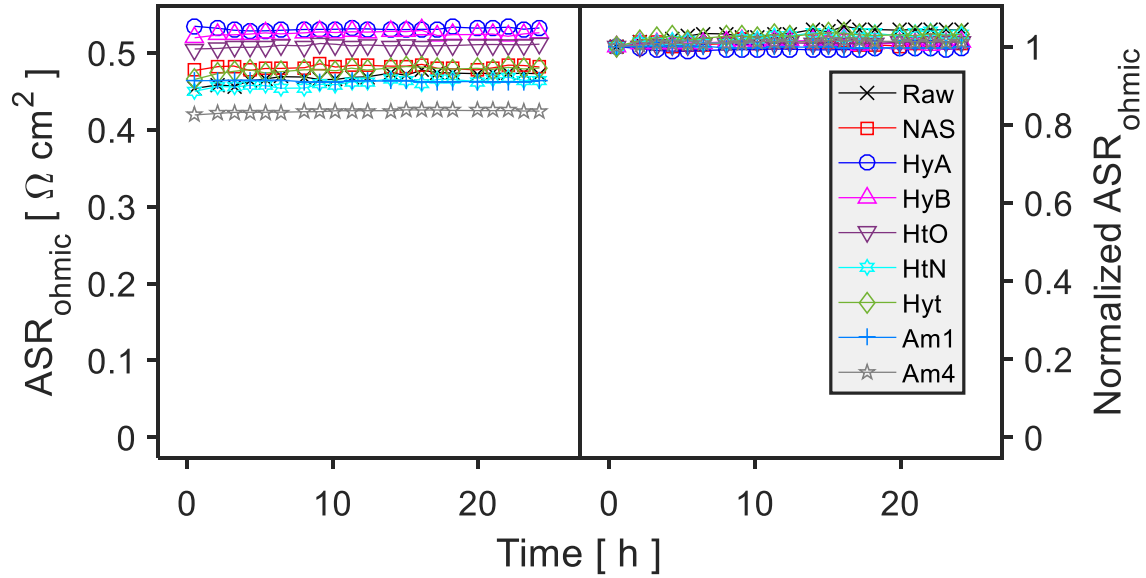


Figure 6.4. Open circuit ohmic resistance as a function of time for all treatments. Left: actual value. Right: normalized to first potentiostatic step for the same treatment.

Charge transfer process

The charge transfer resistances shown in Figure 6.5 varied from $0.2 \Omega \text{ cm}^2$ for the untreated and nitric acid soaked electrodes to $0.06 \Omega \text{ cm}^2$ for the ammonia treated electrodes; thus, treatments can have a strong impact on the charge transfer reaction resistance. The charge transfer resistance as a function of time appears to be stable for all electrode materials, suggesting that the electrode material does not suffer from kinetic deterioration. The charge transfer resistance is dependent on both the surface area and the inherent activity of the electrode

surface. These will be used to explain the relative differences in charge transfer resistance for each of the treatments.

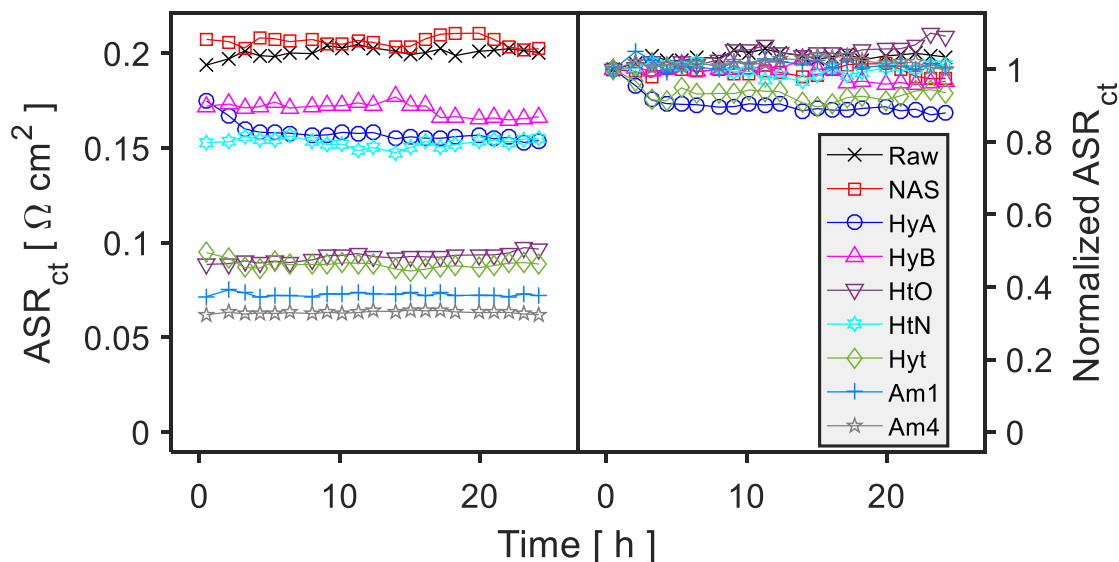


Figure 6.5. Open circuit charge transfer resistance as a function of time for all treatments. Left: actual value. Right: normalized to first potentiostatic step for the same treatment.

The treatments induced large changes in surface area, as shown in Figure 6.6: the untreated, nitric acid soaked, and nitrogen heat treated electrode all had surface areas of ~ 50 - 60 cm^2 ; the mixed hydrothermal/ammonia treatment electrodes had surface areas of 300 cm^2 ; the oxygen heat treated electrodes had surface areas of 450 cm^2 ; the low and high temperature hydrothermal treated electrodes had surface areas of 1000 and 1500 cm^2 , respectively; and both ammonia heat treated electrodes had surface areas of 37000 cm^2 . The origin of the surface area increase for the mid-range improvements was not resolvable by SEM; however, it is possible that the treatments introduced porosity or roughness that is not visible with SEM but may still be

significant.¹⁰⁸ The ammonia heat treatment introduced pores with diameters in excess of 30 nm which were clearly visible with SEM, shown in Figure 6.7.

We have measured capacitance as a proxy for surface area, assuming a fixed specific double-layer capacitance. Different treatments may result in different specific double-layer capacitances; however, these changes are perhaps a factor of two or three, much smaller than the two orders of magnitude difference observed in surface area. Any error in the surface area calculation due to an incorrect specific double-layer capacitance will propagate to the rate constant calculation, i.e. if the double-layer capacitance is underestimated by 50%, the surface area will be underestimated by 50% and the rate constant overestimated by 50%.

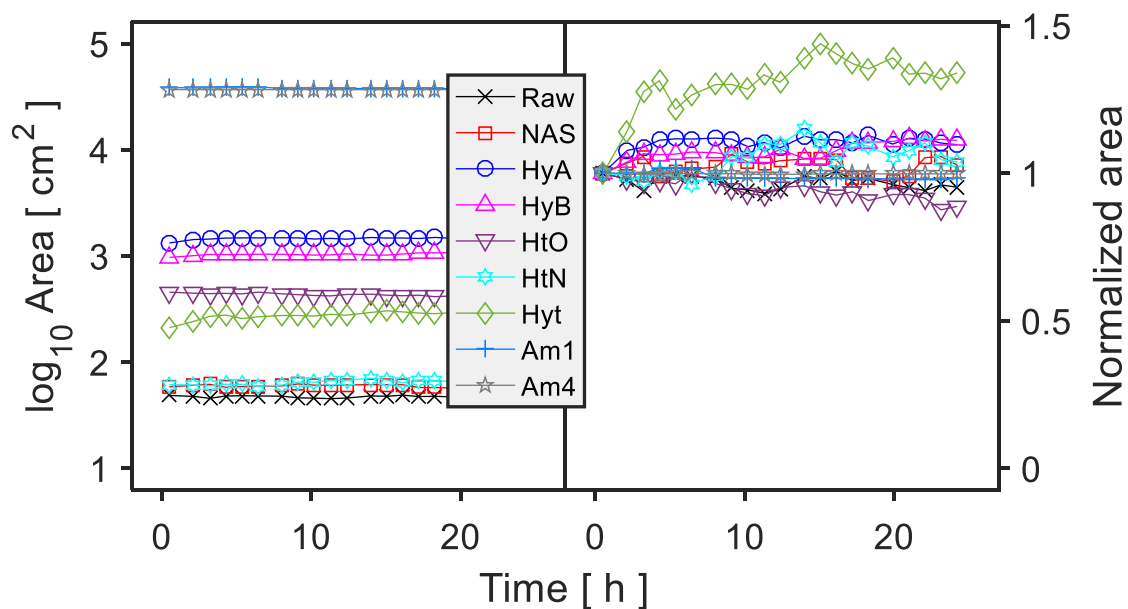


Figure 6.6. Single-electrode surface area. Left: log-scaled area. Right: area normalized to first potentiostatic step for the same treatment.

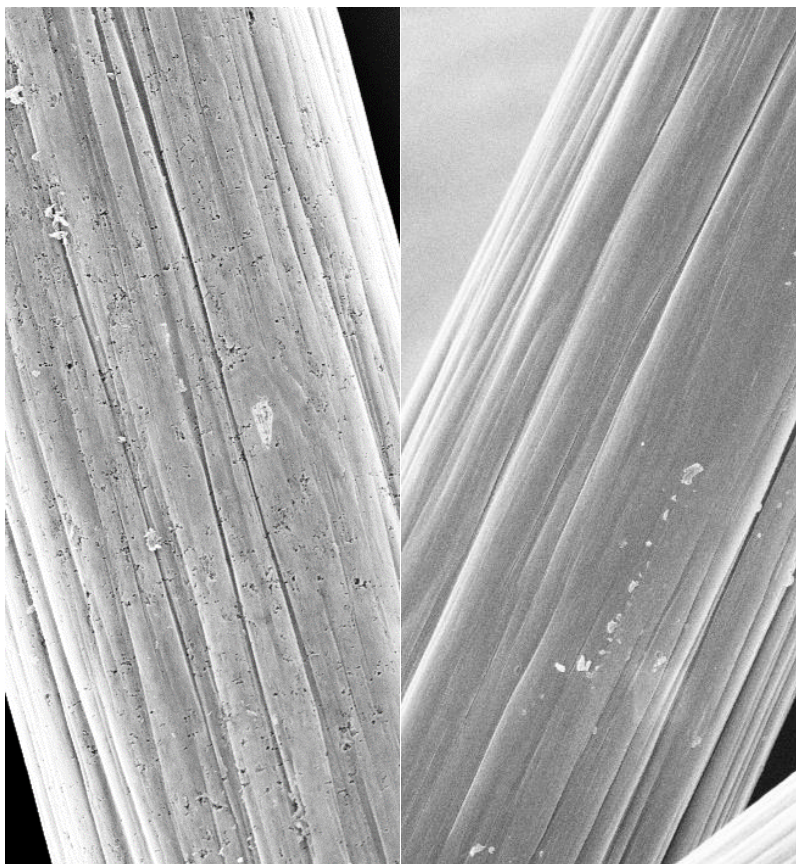


Figure 6.7. SEM images of a fiber from ammonia treated (left) and untreated (right) electrode materials.

The rate constant for each treatment is presented in Figure 6.8. Similar to the electrode area, various treatments induced orders of magnitude differences in the rate constant. Interestingly, the untreated and relatively mild nitric acid soak, along with the nitrogen heat treatment, had the highest rate constant: on the order of $10^{-3} \text{ cm s}^{-1}$. The mixed hydrothermal/ammonia heat treated and oxygen heat treated samples had the next highest relative activity, approximately half an order of magnitude lower than the untreated. Both hydrothermal treatments resulted in a rate constant on the order of $10^{-4} \text{ cm s}^{-1}$, greater than an order of magnitude lower than the untreated. The ammonia heat treatments were yet another order of magnitude lower, approximately $5 \times 10^{-5} \text{ cm s}^{-1}$. The rate constant appeared to be virtually constant as a function of time independent of treatment, suggesting that the positive electrode is not susceptible to significant degradation. This observation is in agreement with that obtained by Derr et al.⁸⁷

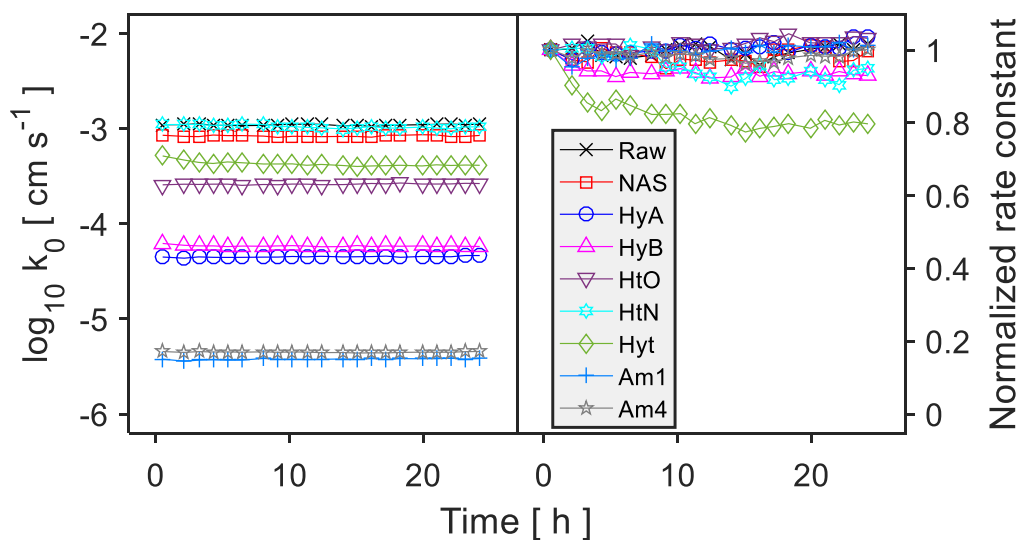


Figure 6.8. Rate constant for each treatment. Left: actual value, log scale. Right: rate constant normalized to first potentiostatic step for the same treatment.

Given that the exchange current and thus the overall charge transfer resistance is determined by the product of the area and rate constant, neither of these factors is independently enough to judge the effects of electrode treatment on kinetic performance. Numerous studies mentioned in Section 1.3.3 have claimed that the mechanism of improved performance for treated carbons used as the positive electrode in VRFBs is due to a change in surface chemistry, neglecting the influence of surface area completely. The electrode treatment results herein show that any improvement in kinetic performance is solely because the surface area has increased, and further, that the inherent activity of the electrode surface is always lower as a result of chemical or thermal treatment. There may be alternative treatments that *do* improve the inherent activity of the surface; however, it appears that efforts to improve surface area may yield more fruitful results.

The finite diffusion resistance is shown in Figure 6.9. All of the non-ammonia heat treated materials were tightly packed around $0.06 \Omega \text{ cm}^2$; the ammonia heat treated materials were centered around 0.08 to $0.09 \Omega \text{ cm}^2$. On average, there was a 1% increase in finite diffusion resistance over the course of a day. The whole cell pressure drop, measured across both electrodes, was approximately 2.8 psi for all treatments and increased by less than 0.5% on average during the course of each experiment, as shown in Figure 6.10. These observed changes are not significant; however, if they continue to increase during operation, performance losses may become appreciable. More work must be done to study the long-term changes. An increased pressure drop and finite diffusion resistance are likely related, given that the pressure drop and effective diffusion coefficients of the vanadium species in the electrolyte both are positively correlated with tortuosity and electrolyte viscosity, and inversely related to porosity.

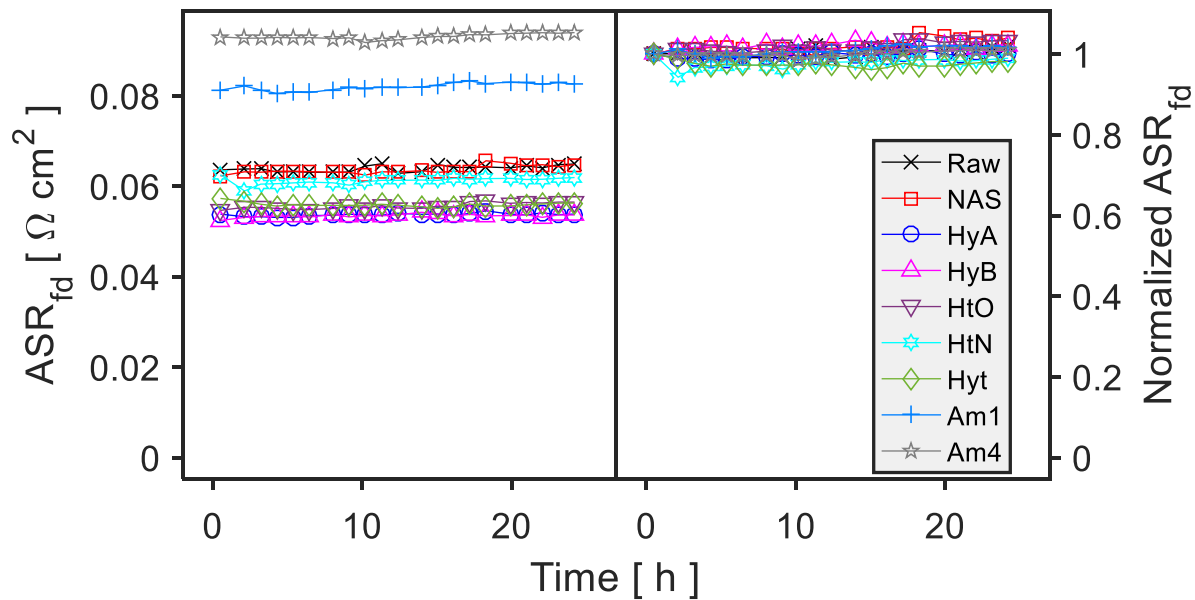


Figure 6.9. Open circuit finite diffusion resistance as a function of time for all treatments. Left: actual value. Right: normalized to first potentiostatic step for the same treatment.

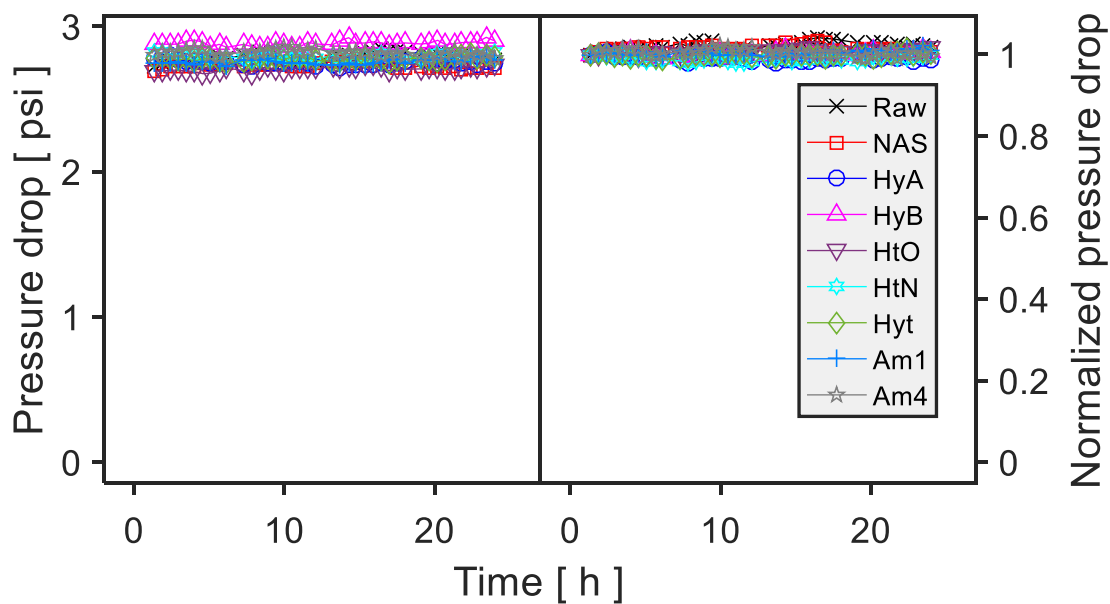


Figure 6.10. Whole-cell pressure drop as a function of time for all treatments. Left: actual value. Right: normalized to first potentiostatic step for the same treatment.

The impedance-resolved polarization curves for the positive electrode are shown in Figure 6.11. From these curves, it is apparent that the ohmic resistance dominates all losses. In particular, the distributed resistance is a significant contributor, similar to the results presented in Figure 5.13 at high concentration. Thus, efforts to improve the positive electrode half-cell performance should focus on decreasing ohmic resistance. Of course, the series resistance cannot be changed as a function of the electrode; it is primarily due to the membrane. Electrode thickness is the other controlling factor and should be decreased. This will have a larger benefit than any sort of kinetic improvement.

6.3.2 Negative electrode

Overall performance

Polarization curves taken at the beginning and end of each experiment are shown in Figure 6.12 for the negative electrode. At a cell overpotential of 200 mV, the first polarization curve for the four hour ammonia heat treatment had the highest current density of 300 mA cm^{-2} ; the untreated had the lowest current density of 30 mA cm^{-2} , with the remaining treatments scattered between the two. Overall, the negative side performs worse than the positive side and is more sensitive to treatment.

The average current measured during each potentiostatic step is shown in Figure 6.13. Unlike the positive side, the negative side shows appreciable declines in performance. The largest decrease in current was 40% for the untreated, nitric acid soaked, and low temperature hydrothermal treatments. The high temperature hydrothermal, oxygen and nitrogen heat treatments, and mixed hydrothermal/ammonia heat treatments also showed declines in the neighborhood of 15 to 25%. Only the two ammonia heat treatments were stable, dropping only 2% in current.

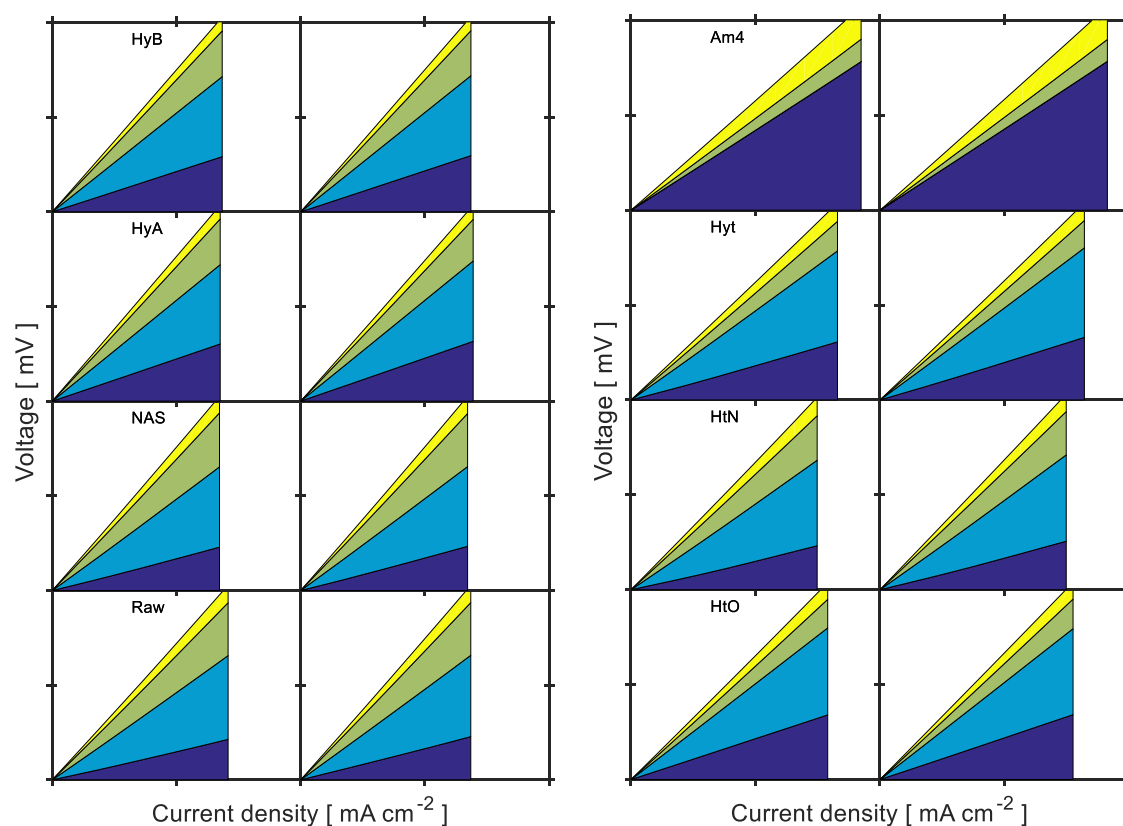


Figure 6.11. Impedance resolved polarization curves for the positive electrode. Scale: 400 mA cm⁻² (x-axis), 200 mV (y-axis). Columns one and three: curve obtained at the beginning of experiment. Columns two and four: curve obtained at the end of experiment. Colors refer to the overpotentials according to the following: dark blue, series ohmic; light blue, distributed ohmic; green, charge transfer; yellow, finite diffusion. Am1 not pictured due to similarity with Am4; Am4 dark blue represents the sum of series and distributed ohmic resistances.

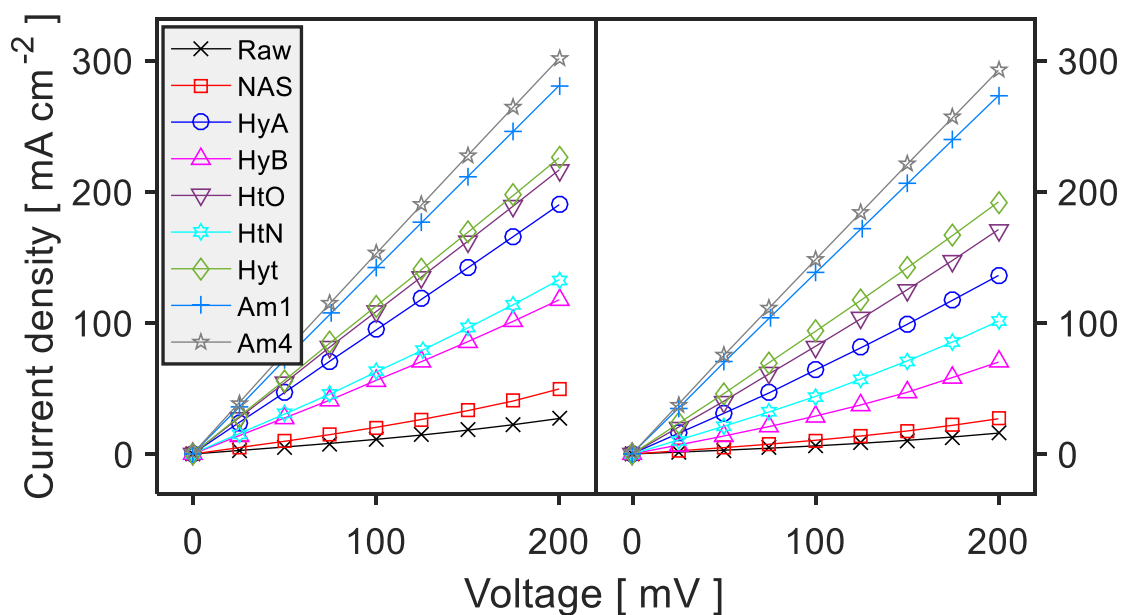


Figure 6.12. Polarization curves obtained at the beginning (left) and end (right) of each experiment. The voltage refers to the total voltage applied across the whole cell.

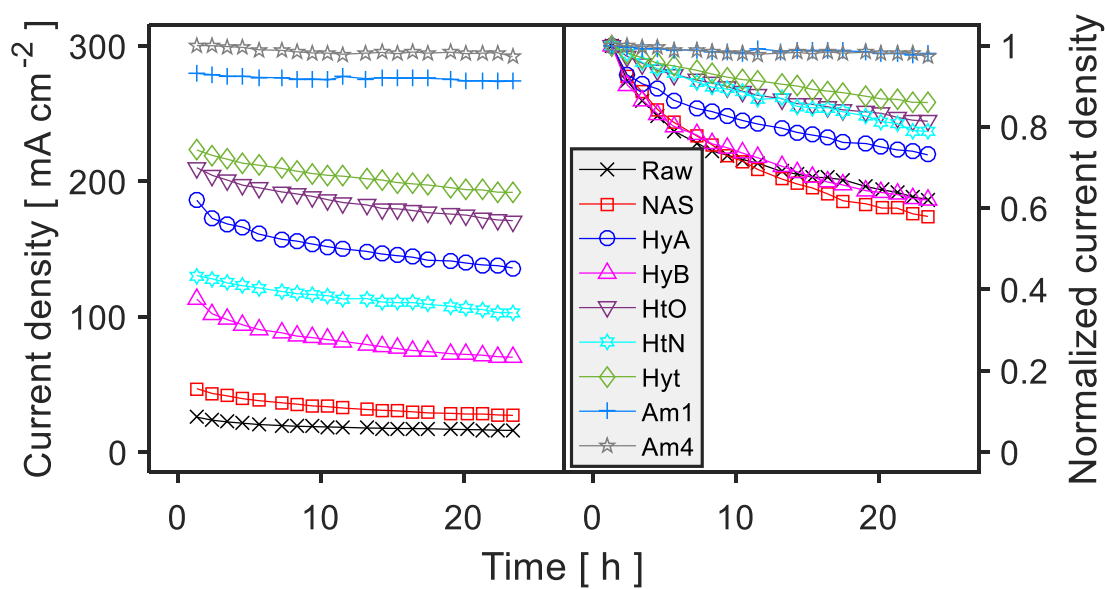


Figure 6.13. Average current measured during each potentiostatic step. Left: actual value. Right: current normalized to first potentiostatic step for the same treatment.

EIS spectra

The open circuit spectra in Figure 6.14 show the wide variation in charge transfer resistance for each treatment. The finite diffusion is always clearly resolved; the charge transfer and ionic resistance features are resolved for those treatments with large charge transfer resistances but begin to overlap in the materials with smaller charge transfer resistances. The ammonia heat treated electrodes are very similar in shape to those observed in the positive electrolyte.

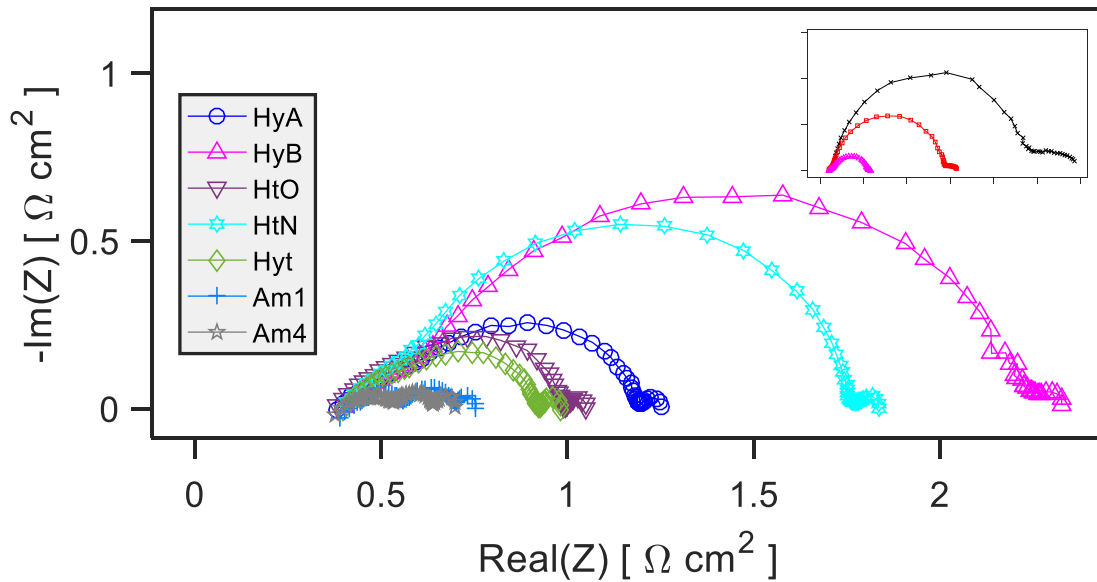


Figure 6.14. Open circuit impedance spectra for all treatments taken at the beginning of the experiment. The inset shows the magnitude of the untreated (black crosses) and nitric acid soaked (red squares) relative to the low temperature hydrothermal (pink triangles).

Ohmic process

Shown in Figure 6.15, the ohmic resistance on the negative side ranged between 0.54 and 0.66 $\Omega \text{ cm}^2$, 20-25% higher than the 0.48 $\Omega \text{ cm}^2$ average ohmic resistance for the positive side. Half of this difference comes from an increase in the series resistance, attributed nearly entirely to the membrane. The remaining difference is due to a higher distributed ohmic resistance. The

resistivity of the negative electrolyte is 5% higher than that of the positive electrolyte; further, the poor kinetics of the negative side drive a more uniform current distribution through the thickness of the electrode. Both of these factors contribute to the higher distributed ohmic resistance.

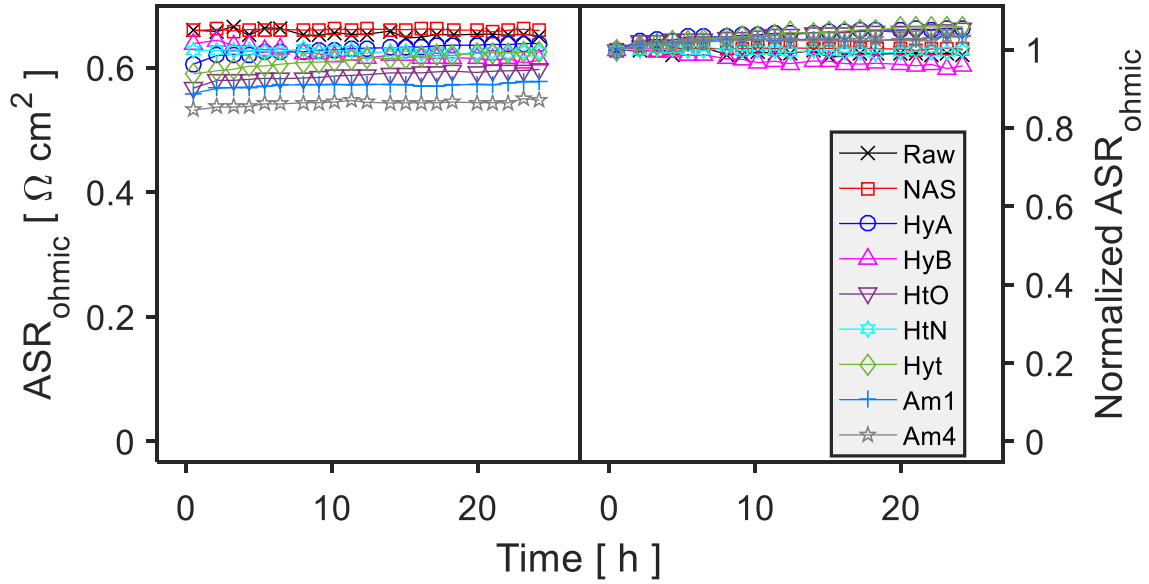


Figure 6.15. Open circuit ohmic resistance as a function of time for all treatments. Left: actual value. Right: normalized to first potentiostatic step for the same treatment.

Charge transfer process

The charge transfer resistance measured at the beginning of the experiment varied from over $7 \Omega \text{ cm}^2$ for the untreated electrode to $0.1 \Omega \text{ cm}^2$ for the ammonia heat treated electrodes; this 70× difference is much larger than the factor of three improvement observed on the positive side. The remaining treatments yielded initial charge transfer resistances of 0.3 (hydrothermal/ammonia mixed), 0.4 (oxygen heat treat), 0.5 (high temperature hydrothermal), 1.0 (nitrogen heat treat, low temperature hydrothermal), and 5.0 (nitric acid soaked) $\Omega \text{ cm}^2$. The

wide range shows that electrode pretreatments have drastically larger effects on the negative electrode kinetics than on the positive side.

Shown in Figure 6.16, the charge transfer resistance showed an increase of 50-150% for all treatments by the end of the experiment with the exception of that for the ammonia heat treated electrodes, which remained relatively constant. The degradation in kinetic performance is largest during the first few hours of the experiment; however, by the end of one day, the rate of change remains significant. These results qualitatively agree with a study performed by Derr et al.,⁸⁷ where an increase in the charge transfer resistance was also found on the negative side. In that study, the charge transfer resistance continued to climb after 10 days of cycling. The effects of such continuous increases in charge transfer resistance are deleterious to battery operation. Given that all treatments tested in this work except for the ammonia heat treatment exhibit the continued increase in charge transfer resistance, it is likely a common issue with most felt-based electrode materials in the literature. The ammonia heat treated felt is thus an excellent material from the perspective of durability, in addition to its top performance compared to the other treatments.

The electrode surface areas calculated for the negative side agreed with those on the positive side to within a factor of ± 2 ; such agreement gives confidence that the impedance-resolved areas are reasonably close to the actual values. However, unlike the positive electrode, the negative side exhibits apparent decreases in surface area of 10-20% for most treatments as shown in Figure 6.17, with the ammonia heat treated felts being the notable stable exception. This apparent decrease in surface area is really a change in the total capacitance of the electrode. The EIS measurements that were taken with sulfuric acid after testing was completed confirm the

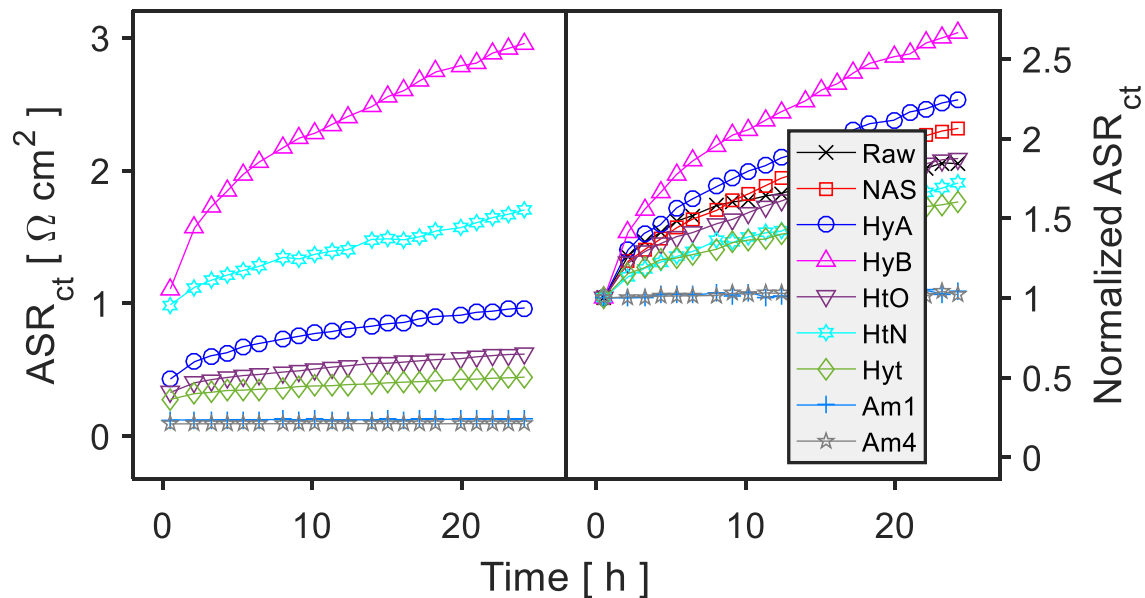


Figure 6.16. Charge transfer resistance as a function of time; untreated and nitric acid soaked are beyond the scale of the left axis. Left: actual value. Right: charge transfer resistance normalized to first potentiostatic step for the same treatment.

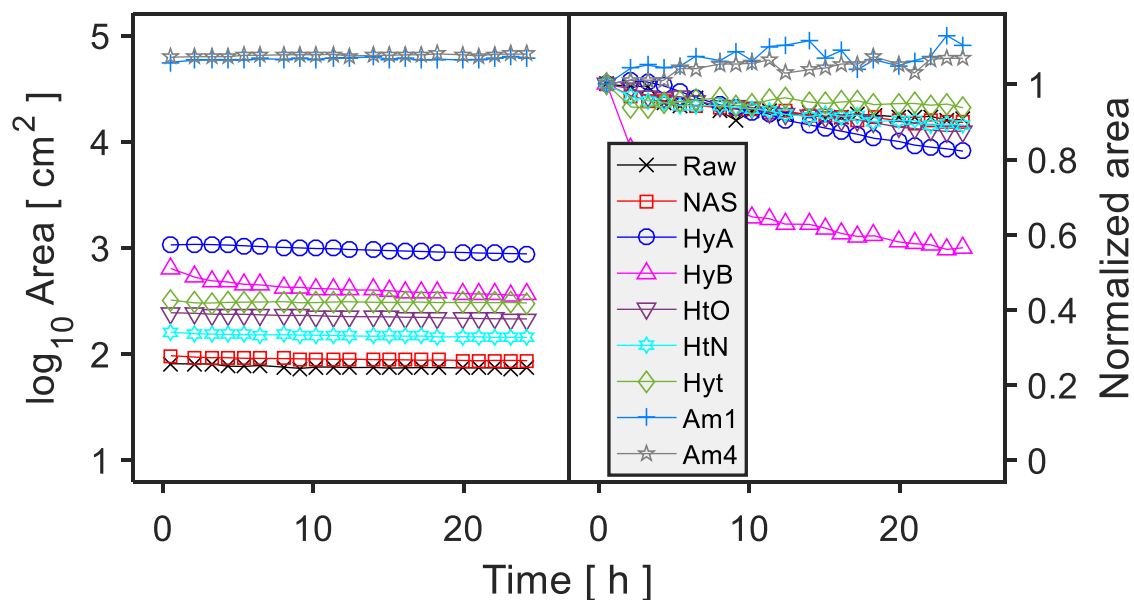


Figure 6.17. Single-electrode surface area. Left: log-scaled value. Right: area normalized to first potentiostatic step for the same treatment.

loss in capacitance. In reality, the loss of capacitance can be due to either a real change in electrochemically active surface area or due to a change in the specific double-layer capacitance as a result of changes on the electrode surface, or a combination of the two. Deconvolution of these phenomena is beyond the scope of this study. Since the capacitance did not change on the positive side, it is reasonable to assume that the specific capacitance had not changed. The assumption is repeated here, i.e. the change is attributed to an actual loss of surface area rather than a change in specific capacitance. Nonetheless, it is entirely possible that the specific capacitance changes on the negative electrode while it remains constant on the positive electrode.

Derr et al. claimed to observe a loss in surface area after looking at the SEM image of a cycled felt, in which it appeared that the surface had “peeled” away from the bulk of the fiber, but there were no capacitance measurements to validate this explanation. SEM images taken of the felts in this work showed no such delamination of the fiber surface or any other morphological change. The change in surface area may be related to de-wetting of the electrode surface. After the materials were removed from the cell post-testing, there were visible changes in the wettability. It is possible that during electrochemical cycling, changes in electrode surface properties induce changes in the wettability and reduce the total wetted surface area.

For the first portion of the rate constant discussion below, all values discussed are the beginning-of-experiment measured value. The rate constant on the negative side, shown in Figure 6.18, was a factor of 60 lower than the corresponding rate constant measured on the positive side for the untreated material, a factor of 30 lower for the nitric acid soaked, and a factor of 20 lower for the nitrogen heat treated. The remaining six treatments also all had lower rate constants on the negative side than the positive, but within factors of two to five. The

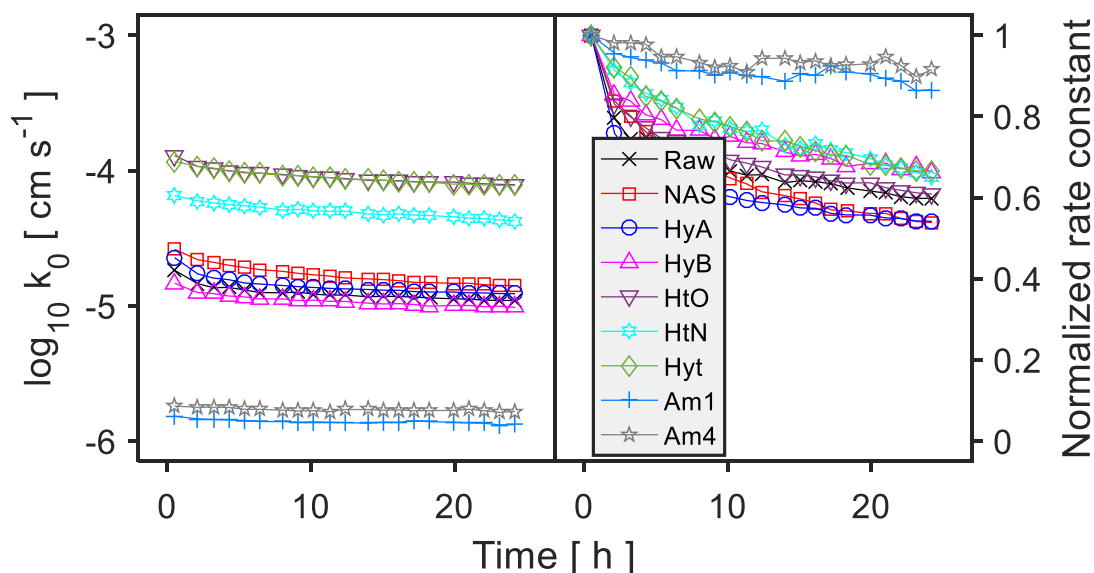


Figure 6.18. Rate constant for each treatment. Left: actual value, log scale. Right: Rate constant normalized to first potentiostatic step for the same treatment.

disparity in the rate constants for the untreated material agrees well with the results of Aaron et al.³⁶ measured on SGL 10AA carbon paper, where the exchange current measured on the positive side was 44× higher than that measured on the negative side.

The rate constant shows the most improvement as a result of heat treatment in oxygen, increasing by a factor of seven. The mixed hydrothermal/ammonia heat treatment was a factor of six improvement over untreated, the nitrogen heat treatment a factor of three, and the hydrothermal treatments and nitric acid soak within 40%. The ammonia heat treatments decimated the rate constant (a ten-fold decrease).

In contrast with the positive side, the negative side exhibits a noticeable and significant loss of activity, between 35 and 50% for all treatments other than the ammonia heat treatment, which had a relatively minor 10% decrease. These changes are best observed in the normalized rate constant portion in Figure 6.18. The 35-50% decrease in activity is greater than the 10-20%

decrease in surface area, suggesting that the surface activity change is the larger driving force for the decrease in charge transfer resistance than the surface area change.

It is again noted that the rate constant calculation is based on the capacitance-derived surface area. If a drop in the specific double-layer capacitance was the true cause of the decreased total capacitance, the calculated area would be higher. The end result would be an overestimation of the measured rate constant, and so the loss of activity shown in Figure 6.18 would be exacerbated. In any case, the loss of activity is both real and significant. The majority of the loss in activity occurs during the first few hours of each experiment, but continues to decline throughout the course of the experiment. Longer-term testing must be carried out to find the timescale of activity loss and establish whether the activity stabilizes or continues to decrease.

Though the apparent rate constant decreased by up to 10% with the ammonia heat treated electrodes, the charge transfer resistance increased by only 1-2%. The apparent increase in surface area balanced the loss of activity. It is possible that the surface area and rate constant changed in opposite directions at the same rate; however, the more likely scenario is that neither is changing much and the measured values shifting are an artifact of the equivalent circuit fit. In any case, the activity of the ammonia heat treated felts is much more stable than that of the other treatments.

The finite diffusion resistance for all treatments is shown in Figure 6.19. Most were in the range of 0.05 to 0.08 $\Omega \text{ cm}^2$; the noticeable exceptions were the untreated (1.65 $\Omega \text{ cm}^2$) and nitric acid soaked (0.45 $\Omega \text{ cm}^2$). The untreated, nitric acid soaked, and low temperature hydrothermal treatment all showed large increases by the end of the experiment; the finite diffusion resistance

more than doubled in all three cases. The remaining six treatments varied from no change (ammonia heat treatments) up to a 30% increase (nitrogen heat treatment). Given that the positive side showed minimal change in finite diffusion resistance, the mechanism for increased diffusion resistance is unlikely to be related to purely mechanical degradation in the electrode structure. De-wetting of the electrode, which decreases the surface area and increases the local current density, is a potential culprit.

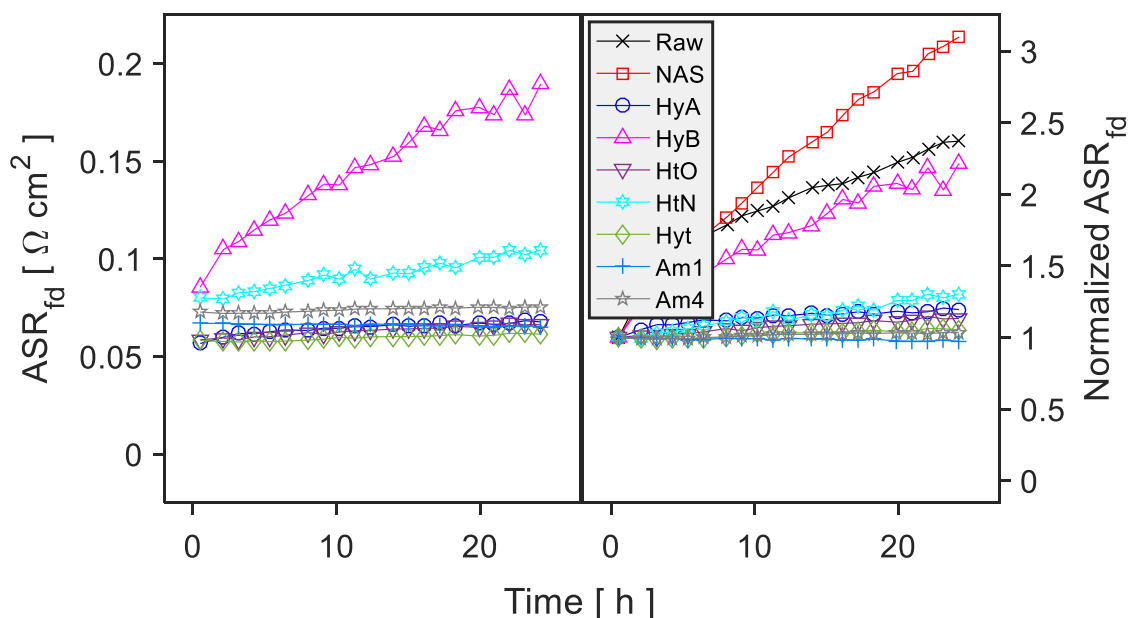


Figure 6.19. Open circuit finite diffusion resistance as a function of time for all treatments; the untreated and nitric acid soak are beyond the scale in the left portion. Left: actual value. Right: normalized to first potentiostatic step for the same treatment.

The whole cell pressure drop, measured across both electrodes, was approximately 2.9 psi for all treatments and showed virtually no change during operation, as indicated in Figure 6.20.

The impedance-resolved polarization curves for the negative side are shown in Figure 6.21. The relatively high performance electrodes – ammonia heat treated, oxygen heat treated,

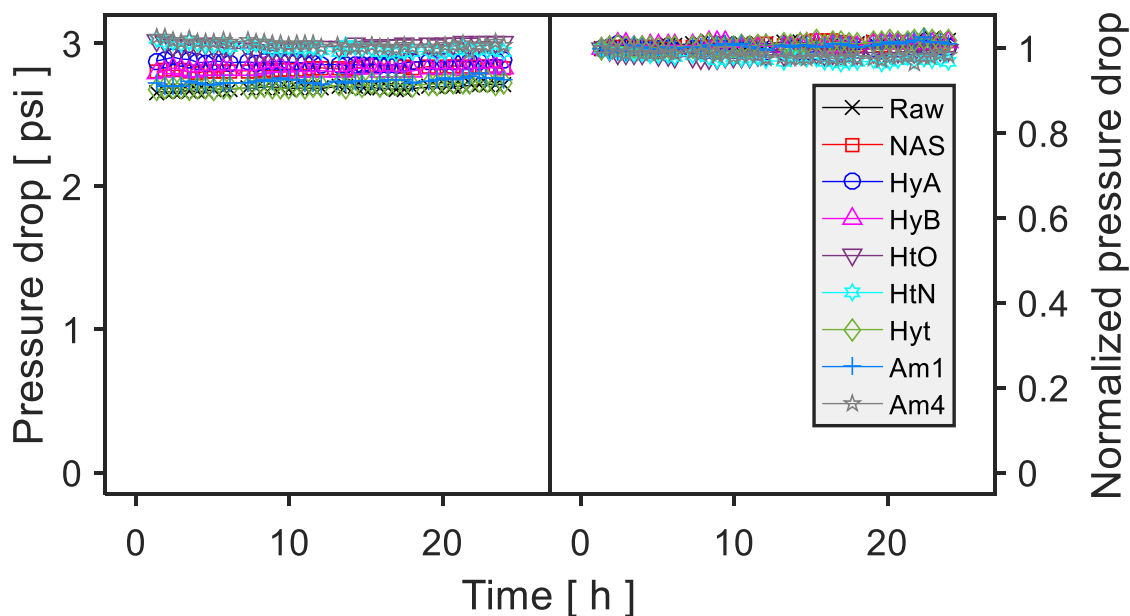


Figure 6.20. Whole-cell pressure drop as a function of time for all treatments. Left: actual value. Right: normalized to first potentiostatic step for the same treatment.

mixed ammonia/hydrothermal, and high temperature hydrothermal treatment – indicate ohmic limitation, again with a large distributed resistance contribution. The poor-performance electrodes are kinetically limited. The decrease in kinetic performance gradually increases the share of kinetic overpotential as a fraction of the total. The open circuit spectra in Figure 6.22 show the increasing charge transfer resistance.

6.3.3 Physicochemical characterization

The results of the XPS and EDS analysis yielded a total oxygen content of 3-6% (elemental composition) for all electrodes. The impact of usage in the battery was minimal, with post-mortem samples falling within a similar range. Measurable quantities of nitrogen were not present in any sample. The type of functionality, observed in the shape of the O1s peak as in Chapter 4, was essentially the same in all electrodes, independent of treatment and electrode polarity. Thus, it appears that, at least for the GFD3 carbon material in this work, oxygen

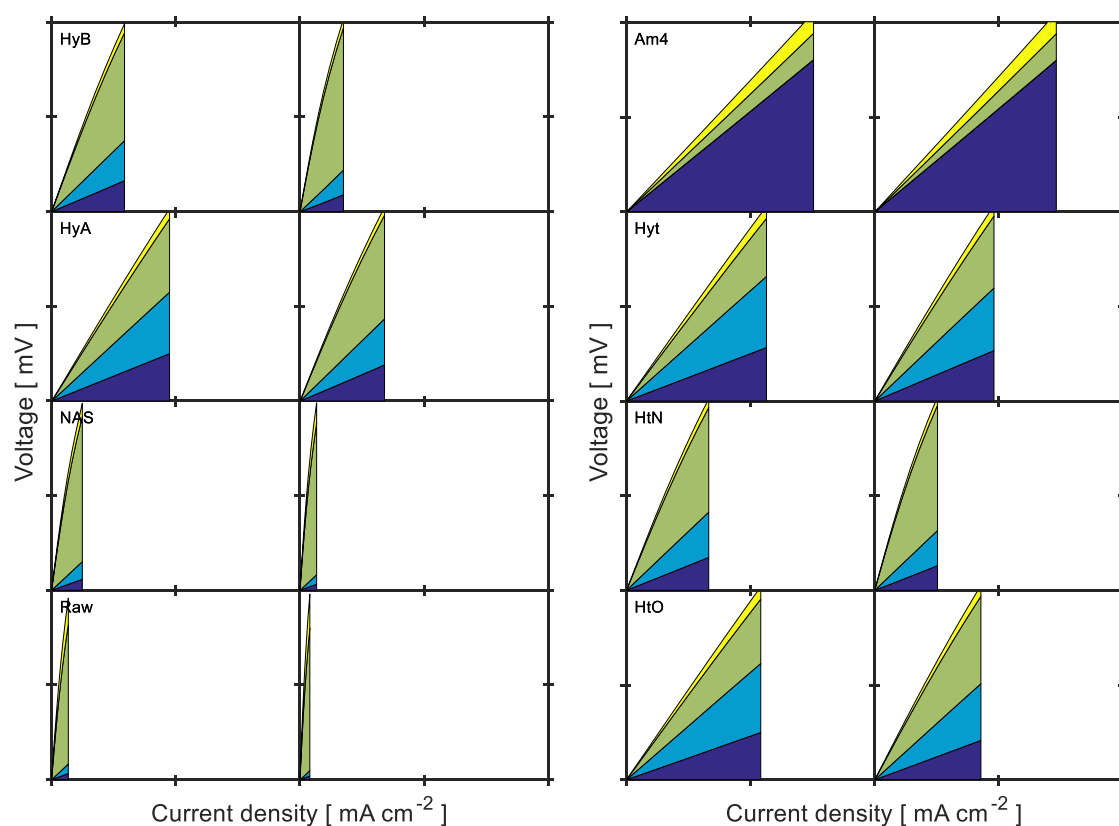


Figure 6.21. Impedance resolved polarization curves for the negative electrode. Scale: 400 mA cm⁻² (x-axis), 200 mV (y-axis). Columns one and three: curve obtained at the beginning of experiment. Columns two and four: curve obtained at the end of experiment. Colors refer to the overpotentials according to the following: dark blue, series ohmic; light blue, distributed ohmic; green, charge transfer; yellow, finite diffusion. Am1 not pictured due to similarity with Am4; Am4 dark blue represents the sum of series and distributed ohmic resistances.

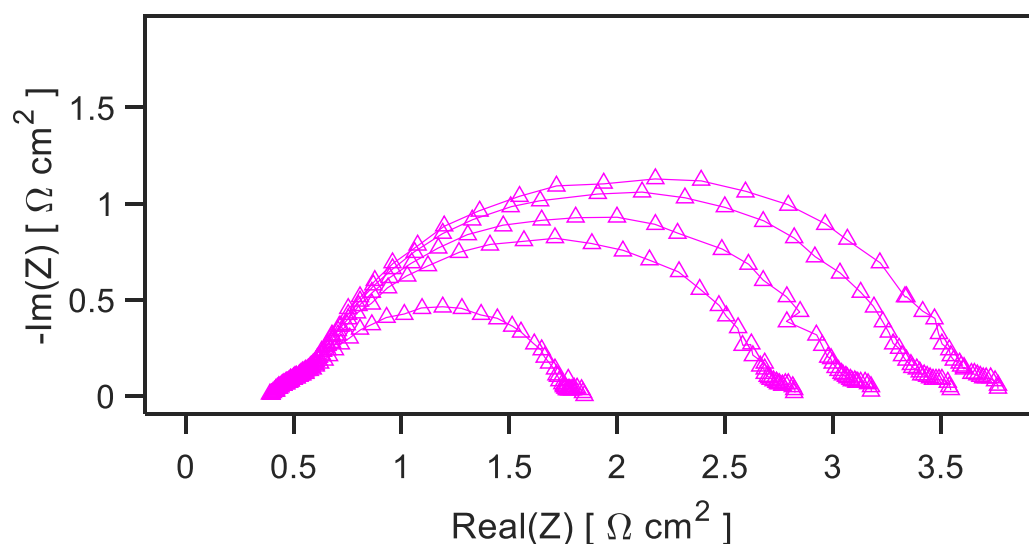


Figure 6.22. Time evolution of impedance spectra for the low temperature hydrothermal treatment. Impedance spectra shown here are evenly spaced by five hour increments. Spectra grow as a function of time.

functional groups play little to no role in affecting the redox kinetics of either half-cell reaction. Fink et al.³⁵ suggested that the presence of oxygen functional groups did nothing to improve the positive half-cell reaction, and may perhaps be detrimental, confirming an earlier study by Roth et al.,⁶⁰ in that study, the authors claimed that a highly graphitic carbon was most desirable for the positive half-cell reaction, i.e. with minimal oxygen functional groups.

The Raman results are shown in Table 6.2. The D:G band ratio and G band position both point to the graphitic character of the carbon according to Ferrari and Robertson.¹⁴⁷ Based on their analysis, the location of the G band for the untreated material suggests that it is primarily nanocrystalline graphite. The hydrothermal treatments and nitric acid soak had similar properties. The heat treatments resulted in lower D:G ratios and a G band shift toward lower wavenumbers; coupled with the sharper peak shapes (smaller widths), the samples may be more ordered, i.e. they are composed of larger graphite crystals. There appears to be little correlation

between the Raman results and the rate constants for both the positive and negative electrodes.

There was little change in the Raman data post-mortem.

Table 6.2. Raman results. D to G band ratio in first column and location of the G band maximum in the second column.

	I_D/I_G	G position (cm⁻¹)	D band width	G band width
Raw	1.33	1595.6	32.0	32.0
NAS	1.38	1597.6	36.7	33.9
HyA	1.40	1595.9	32.0	32.0
HyB	1.39	1595.1	28.9	30.6
HtO	1.28	1594.3	27.6	29.3
HtN	1.25	1592.6	26.2	28.7
Hyt	1.12	1591.9	24.2	27.1
Am1	1.02	1591.8	26.1	28.5
Am4	1.21	1593.1	26.0	27.9

Overall, there appeared to be little correlation between surface functional groups as measured by XPS/EDS and the rate constant. Similarly, Raman results also had little correlation with the rate constant, implying that the graphitic phase of the material did not play a large role in controlling surface activity. It must be noted that Raman spectroscopy penetrates into the bulk of the material and is not surface-sensitive, so the Raman results in this work are not a sufficient negative result to show that the graphitic phase of the material is unimportant; in other words, other techniques sensitive to the surface properties of carb such as near-edge X-ray absorption spectroscopy (NEXAFS) may be useful.⁶⁰ With both XPS/EDS and Raman results, there did not appear to be significant changes in the surface as a function of usage in the battery. Coupled with the fact that the rate constant measured in the negative electrode did change with usage, these results show that these methods alone cannot explain why the negative electrode activity changes.

6.4 Conclusions

The results of this work show first that the symmetric cell impedance method developed in Chapter 5 can be applied successfully to understand the impacts of electrode treatment on performance; further, the evolution of impedance spectra can also explain why performance is changing. The positive electrode exhibited excellent stability with all treatments and benefited only moderately from treatments. The negative electrode performance decayed significantly over the course of one day of operation for all treatments except the ammonia heat treatments, and this change is nearly entirely a consequence of changes in the charge transfer resistance/electrode kinetics. The decline in kinetic performance is driven primarily by a decrease in the inherent activity of the electrode surface, in some cases nearly 50%; losses of 10-20% in the electrochemical surface area as measured by changes in capacitance also occurred.

Surface functional groups could not explain why certain treatments changed electrode activity, nor could they explain the decrease in activity as a function of time for the negative electrode. Thus, for the SGL GFD3 carbon felt used, it appears that surface oxygen functionalities play no role in either the positive or negative electrode reactions. Changes in electrode surface area as a result of treatment played a strong role in affecting kinetics, and it is critical to consider such changes when evaluating the mechanism of improved performance.

Finally, the methods used in this work identified the ammonia heat treatment as one that provides exemplary stability with respect to the negative electrode reaction. Fortunately, this treatment also resulted in the best performance on both the positive and negative half-cells. The primary mode of improvement was due to the orders of magnitude increase in surface area, with the introduction of significant porosity onto the fiber surface.

CHAPTER 7
REVISITING TREATED 10AA CARBON PAPER

Abstract

This article has not been published anywhere, nor will it be, so I did not include a publication statement. This work was presented at the 228th Meeting of the Electrochemical Society in Phoenix, AZ in October 2015. This chapter was authored by Alan M. Pezeshki and Matthew M. Mench.

My primary contribution to this work was experimental design, collection, reduction, and interpretation of data, as well as presentation and composition of the chapter.

7.1 Introduction

This brief chapter revisits the performance degradation in the heat treated 10AA material examined but unexplained in Chapter 4 utilizing an identical impedance method developed in Chapters 5 and 6. The impedance results for the high temperature hydrothermal treatment in Chapter 6 are also presented. The data shown are only for the negative half-cell reaction.

7.2 Results and discussion

The open circuit impedance spectra for the heat treated 10AA material described in Chapters 2 and 4 is shown in Figure 7.1 as a function of time. The entire spectrum is translated to the right slightly, indicating a minor increase in the ohmic resistance in the cell. The low frequency finite diffusion feature shows an additional increase. It is this increase in finite diffusion resistance that causes the decline in cell performance with heat treated 10AA. One may recall that the chemical soaks employed in Chapter 4 resulted in no detrimental effects to electrochemical performance. With the insight from impedance, this result is logical; there is no obvious reason why simply soaking an electrode would alter the morphology of the electrode material, so the performance should not suffer. Further, the loss of performance observed in cell-in-series experiments in Chapter 4 was independent the type of electrochemical stress applied (i.e., overcharge vs. overdischarge). This result suggests that the reason for an increase in mass

transport is independent of the type of electrochemical stress. We hypothesize that the graphitic particles present in 10AA may be dislodged as a result of the flow; these particles may clog portions of the electrode, increasing the mass transport resistance.

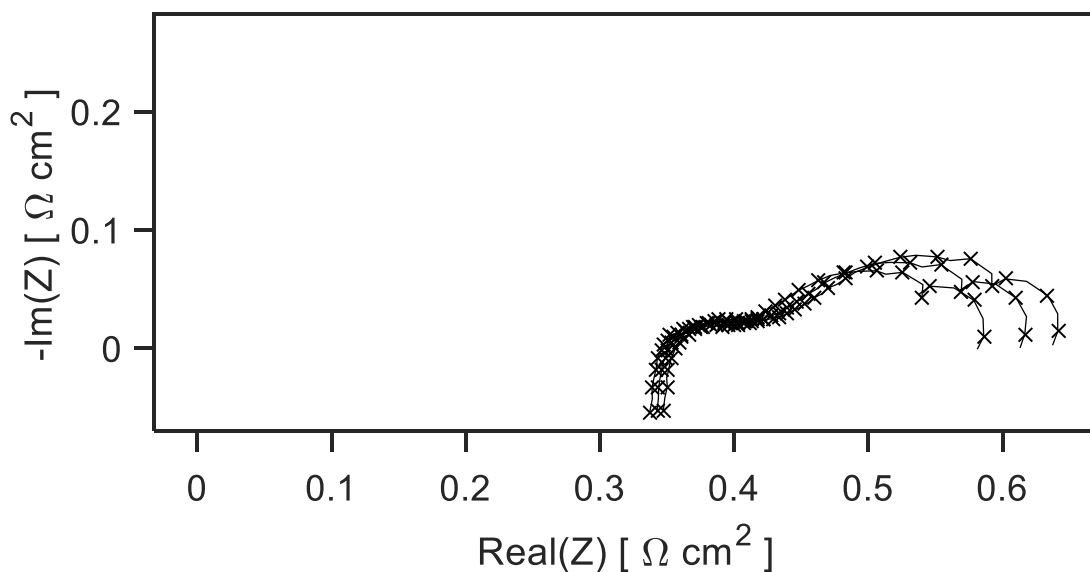


Figure 7.1. Open circuit impedance spectra for heat treated 10AA carbon paper electrodes. Impedance increases as a function of time.

Also notable is the apparent lack of a charge transfer feature, confirming the Chapter 2 conclusion that kinetic overpotential was minimized as a result of the heat treatment. The high to intermediate frequency feature can be attributed to pore geometry effects, as it was replicated when impedance measurements were taken in a sulfuric acid solution.

The high temperature hydrothermally treated 10AA impedance spectra were markedly different from the heat treated 10AA, as well as the nitric acid soaked 10AA shown in Figure 5.3. Perhaps the most interesting feature is the nearly negligible finite diffusion resistance,

estimated to be $< 0.05 \Omega \text{ cm}^2$, a factor of 2 smaller than the $> 0.1 \Omega \text{ cm}^2$ measured for heat treated 10AA and much smaller than the $1 \Omega \text{ cm}^2$ for the nitric acid soaked 10AA electrode in Chapter 5. The large change in finite diffusion resistance is a result of morphological changes; the effluent from the hydrothermal treatment was black with carbon particles, suggesting that the graphitic powder used in 10AA was washed away. This result highlights the fact that impedance can provide comprehensive understanding of treatment effects. The evolution of the impedance spectra shown in Figure 7.2 implies an increase in charge transfer resistance similar to that observed in Chapter 6.

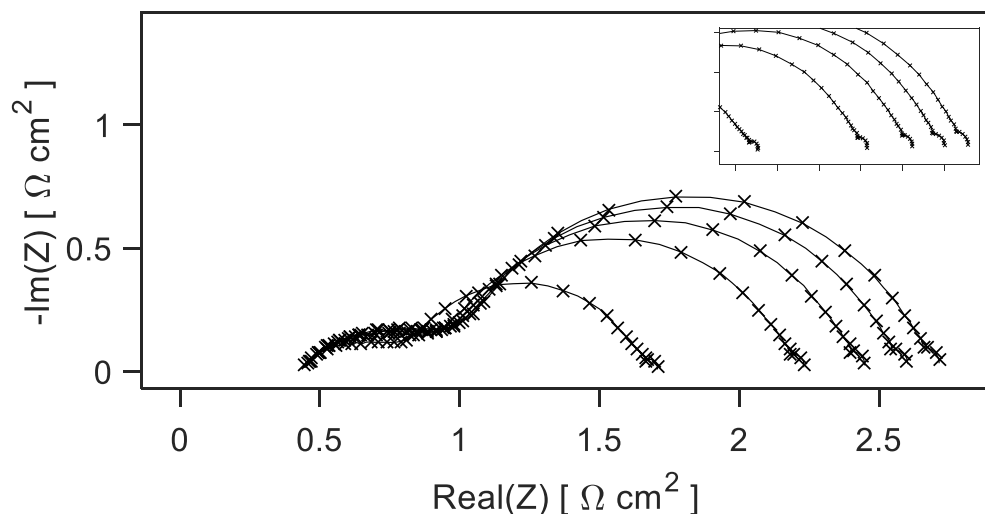


Figure 7.2. Open circuit impedance spectra for high temperature hydrothermally treated 10AA carbon paper electrodes. Impedance increases as a function of time. Inset: finite diffusion feature at low frequency.

7.3 Conclusions

Using impedance, the loss of performance observed in heat treated 10AA in Chapter 4 is shown to be a direct result of increased mass transport resistance; with hydrothermally treated 10AA, the degradation was kinetically-linked, similar to the felt electrodes in Chapter 6. The key

takeaway is that the modes of degradation for felt and paper-based materials can vary as a result of treatment. With knowledge of the degradation mechanism(s), one can begin to intelligently devise methods to rehabilitate performance. The polarity flip method described by Rudolph et al.⁹ would be ineffective for heat treated 10AA because a polarity flip would not unclog the electrode. However, it might be effective for electrodes in which performance degradation is kinetic in origin, especially considering the work by Bourke et al. which showed that electrochemically aging the positive side resulted in a (temporary) kinetic enhancement if the electrode was then used for the negative side and vice versa.¹²

Finally, no treatment applied to the negative side of 10AA electrodes provided stable performance. The ammonia treatment applied to 10AA did not result in significant performance gains, nor did it possess any enhanced stability. Though the heat treated 10AA had higher performance than the ammonia heat treated felt in Chapter 6, the advantage may be temporary when one considers the long timescale of operation for VRFBs.

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CHAPTER 8
**IMPEDANCE-RESOLVED PERFORMANCE CHARACTERIZATION OF A NON-
AQUEOUS FLOW BATTERY**

Abstract

This article has not been published anywhere, nor will it be before I turn in the final version of my ETD, so I did not include a publication statement. This work is a selection from a manuscript in preparation authored by Alan M. Pezeshki, Aman P. Kaur, Zhijiang Tang, S. Modekrutti, Thomas A. Zawodzinski, Gabriel M. Veith, and Susan A. Odom.

My primary contribution to this work was the experimental design, collection, reduction, and interpretation of electrochemical data, and the composition of this portion of the manuscript. Kaur synthesized the redox active materials and assisted in electrochemical data collection. Tang contributed to electrochemical data collection and reduction. Veith assisted in experimental setup.

8.1 Introduction

As previously discussed in Section 1.3.1, there has been a strong push toward the development of alternative redox chemistries, in part due to the high cost of vanadium-based systems and performance issues with other aqueous chemistries. Organic-based molecules in particular present an opportunity for abundant and inexpensive redox-active molecules. Darling and coworkers detailed the engineering considerations for non-aqueous and aqueous-based flow batteries.²⁸ Aqueous systems have a limited voltage window of ~ 1.5 V due to the electrolysis of water, but possess relatively high conductivities in the liquid electrolyte; water is also an inexpensive solvent. Non-aqueous systems can reach much higher voltages, perhaps 4 V, but the solvents are more resistive than their aqueous counterparts and are also more expensive. In this chapter, a step is taken away from vanadium-based batteries to explore the performance of an alternative redox-active molecule, N-EPT in a non-aqueous battery. The redox reaction involves oxidation of EPT to its radical cation, $\text{EPT}^{\bullet+}$ and reduction of the radical cation back to the neutral EPT form. The solvent system, TEABF₄ dissolved in acetonitrile, is one of the

combinations with the highest possible conductivity for non-aqueous systems;¹⁴⁸ therefore, the cell performance in this work is expected to represent an upper bound for non-aqueous RFBs with present-day solvent systems and cell design.

The experiments in this work are designed to reveal information about the EPT redox couple for use in a positive half-cell in a flow battery. The choice of separator, solvent, and supporting electrolyte were chosen to maximize conductivity and reduce ohmic losses through the separator and in the liquid electrolyte and are not necessarily representative of the materials that would be used in a commercially viable flow battery system. Practical material selection involves a separator with smaller pores or an ion-selective membrane to prevent crossover. In this work, because the same redox couple is used on both sides of the battery, crossover is a non-issue. When designing full cells, acetonitrile may not be compatible with the negative redox-active material. More stable solvents will have lower conductivity, reducing cell performance.

8.2 Methods

The test protocol in this work was largely based on the symmetric cell impedance method developed in Chapter 5. The battery architecture in this chapter is very similar to that used with VRFBs in the majority of this dissertation, only differing in the choice of separator material. The flow battery consisted of a 5 cm² active area. Celgard Trisep was used as the separator. SGL GFD3 carbon felt was used as the electrode on both sides of the battery and was compressed to ~70% of its original thickness. The single-channel serpentine graphite flow fields were obtained from Fuel Cell Technologies. Testing was carried out in an argon-purged glovebox. Prior to use, the cell was continuously flushed with acetonitrile to clean the electrode surface. Cell

temperature was controlled at 30 °C during all testing, and flow was provided by a peristaltic pump.

Two separate sets of solution were prepared: one for polarization curve testing and the second for cycling analysis. The polarization curve solution was prepared by dissolving the neutral EPT and radical cation $\text{EPT}^{\bullet+} \text{BF}_4^-$ salts in 80 mL acetonitrile with TEABF_4 as the supporting electrolyte. The molalities of the solutes were 0.051 molal EPT, 0.051 molal $\text{EPT}^{\bullet+} \text{BF}_4^-$, and 1.27 molal TEABF_4 to emulate a 50% SoC solution that would be present on the positive side in a full operating cell. For cycling analysis, two solutions were prepared with 50 mL of acetonitrile: the first with 0.102 molal EPT and 1.27 molal $\text{EPT}^{\bullet+} \text{BF}_4^-$ and the second consisting of 0.102 molal $\text{EPT}^{\bullet+} \text{BF}_4^-$ and 1.27 molal TEABF_4 .

Electrochemical measurement and control were carried out with a Bio-Logic Instruments SP-240 potentiostat with a 4A booster. For all experiments, the cell was operated as a 2-electrode cell; no reference electrode was used. Thus, all overpotentials reported are with respect to the whole cell. During polarization curve measurements, the single solution was pumped in a single hydraulic circuit through both sides of the cell as described in Chapter 5. For the cycling experiment, two separate electrolyte reservoirs were used, and the cell was polarized between +0.45 and -0.45 V at a current density of 100 mA cm^{-2} and flow rate of 50 mL min^{-1} . Cycling continued until the capacity under those voltage limits went to zero.

After cycling, the two solutions used for cycling were mixed together to create a theoretically 50% SoC solution and another set of polarization curves was taken to compare the pre- and post-cycling cell behaviors.

Based on prior symmetric cell polarization curve measurements in Chapter 5, it is reasonable to expect that each half-cell contributes similar amounts of overpotential. The polarization curve behavior is representative of full cell polarization behavior if we were to have a negative solution with a negative redox couple that had analogous kinetic and transport properties as the positive EPT/EPT^{•+} couple.

8.3 Results and discussion

8.3.1 Polarization curves

Shown in Figure 8.1 are the uncorrected and HFR-corrected polarization curves at flow rates of 20 and 50 mL min⁻¹. At a cell overpotential of 200 mV, the maximum current density achieved was 105 mA cm⁻², which is among the highest reported current densities for non-aqueous RFB systems. Assuming that the total cell polarization in this work is representative of the total cell polarization with a negative redox couple, and an open circuit voltage of 3.5 V at 50% SoC, the average charging voltage during a cycling test would be 3.7 V (3.5 V + 200 mV) and the average discharge voltage would be 3.3 V (3.5 V – 200 mV) for a voltage efficiency of 89%¹⁴⁹ at a current density of 105 mA cm⁻². This performance is comparable with the high performance vanadium system described in Chapter 3, where voltage efficiencies of 85% at a current density of 200 mA cm⁻² were reported.¹¹² The concentration of dissolved active species is significantly lower than what would be considered practical. The effect of increasing concentration will be discussed in more detail in the following sections.

The HFR, taken as the intercept of the Nyquist plot with the real axis, is primarily attributed to the ohmic resistance through the separator and was 850 mΩ cm², which is on the higher end of HFR measured for most aqueous flow batteries. At the higher flow rate and the

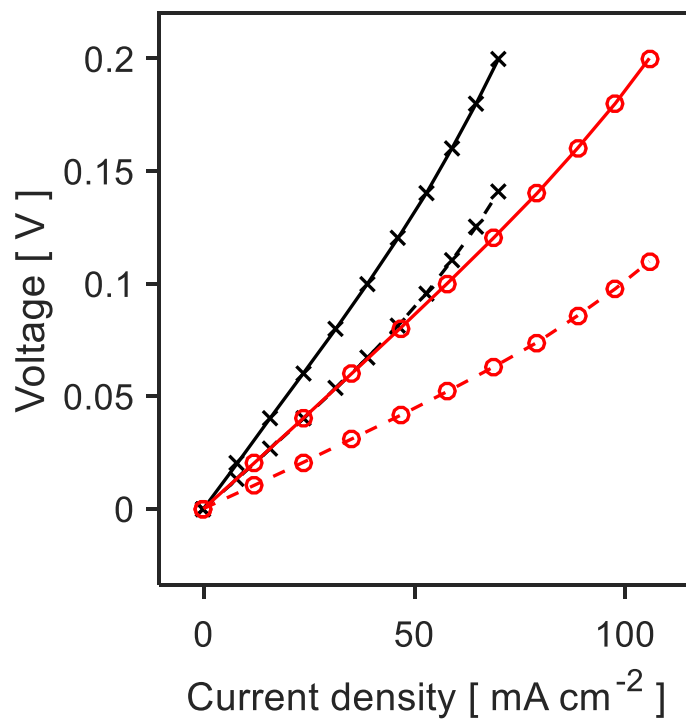


Figure 8.1. Uncorrected (solid lines) and HFR-corrected (dashed lines) polarization curves obtained at 20 mL min⁻¹ (black crosses) and 50 mL min⁻¹ (red circles).

maximum current density of 105 mA cm^{-2} , this translates to an ohmic overpotential of 90 mV, nearly half of the total 200 mV polarization at that current density. Thus, even with an electrolyte solution optimized for conductivity with a relatively low-resistance separator, ohmic resistance is a major limiting factor for the non-aqueous system in this work, and therefore will be a limiting factor for all non-aqueous flow battery chemistries. The development of high conductivity separators will be critical to commercial viability of non-aqueous RFBs.

Comparing the polarization curves at 20 mL min^{-1} and 50 mL min^{-1} , it is clear that increasing flow rate has a significant effect on the total cell overpotential. The flow within the electrode determines the diffusion boundary layer thickness as well as bulk transport of active species throughout the electrode. With higher flow rates, boundary layers are thinner and more uniform transport of active species can occur throughout the electrode, reducing concentration overpotentials. The significant difference in overpotential – 75 mV at a current density of 70 mA cm^{-2} – is an indication that concentration overpotential also plays a strong role in limiting the current density. The impedance spectra, shown in Figure 8.2, confirm that transport processes contribute a large amount to the cell overpotential. At a flow rate of 20 mL min^{-1} , the open circuit finite diffusion resistance is $1800 \text{ m}\Omega \text{ cm}^2$; at 50 mL min^{-1} , the finite diffusion resistance is $725 \text{ m}\Omega \text{ cm}^2$. The open circuit high frequency feature attributable to charge transfer resistance is $\sim 300 \text{ m}\Omega \text{ cm}^2$ under both conditions. Overall, charge transfer is a relatively minor contributor to the overall cell polarization, while ohmic and concentration polarization are of similar magnitude at the higher flow rate. This is in agreement with other non-aqueous RFB studies with organic redox couples, where redox kinetics were typically rapid.

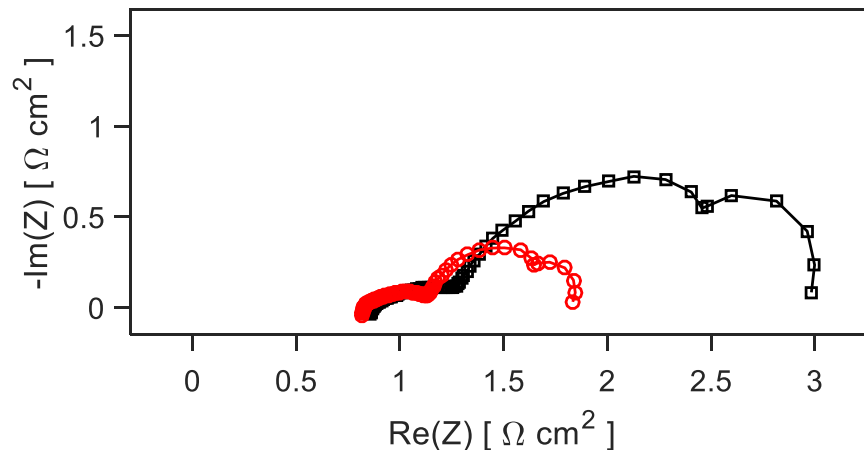


Figure 8.2. Impedance spectra at 20 (black squares) and 50 mL min⁻¹ (red circles).

Practical solutions would contain at least 10× the concentration studied in this work; the expected result would be significantly reduced concentration polarization. However, with organic molecules which are larger than transition metal cations used in aqueous systems, higher concentration may lead to large increases in viscosity. This may reduce the effective diffusion coefficient of the redox active molecules and partially offset the benefit of increased concentration. Further, higher viscosity increases the pressure drop which increases the parasitic pumping losses. Additionally, the solution conductivity may decline as a result of higher redox active molecule concentrations, causing a rise in ohmic resistance across the separator/membrane as well as in the liquid electrolyte solution itself. This tradeoff, also discussed in Chapter 5 for the all-vanadium system, is perhaps an even stronger consideration for non-aqueous and/or organic molecule-based systems.

8.3.2 Cycling

Since the same solution was used on either side of the battery, one cycle physically corresponds to one reservoir being converted from EPT to EPT^{•+}, representing charging in a full

cell; $\text{EPT}^{\bullet+}$ is converted to EPT in the other reservoir, representing discharging in a full cell. The result of one cycle is essentially a flip in the states of the two reservoirs, i.e. while one charges, the other is discharged.

The theoretical capacity of each of the solutions used for cycling is 386 coulombs. The actual capacity of the first cycle was 232.7 coulombs, or 60.3% of the theoretical capacity. The impact of crossover on this artificial cycling experiment cannot explain the discrepancy between the theoretical and actual capacity. To see why, consider that when both reservoirs are at 50% SoC, there is no net change in EPT or $\text{EPT}^{\bullet+}$ concentration as a result of crossover. Assuming that the range of SoC is symmetric about 50% (e.g. 20-80%, 40-60%, etc.), the average SoC in both reservoirs over the cycle is 50%, and so the net crossover of EPT and $\text{EPT}^{\bullet+}$ from one reservoir to the other should be zero. Based on the 60.3% capacity utilization, we would expect that the SoC range in each reservoir would be from 19.85-80.15%. The open circuit voltage after a cycle can be calculated as follows:

$$E_{cell} = E_{R1} - E_{R2} \quad (8.1)$$

$$E_{cell} = \frac{RT}{F} \left(\ln \left(\frac{[\text{EPT}_1^{\bullet+}]}{[\text{EPT}_1]} \right) - \ln \left(\frac{[\text{EPT}_2^{\bullet+}]}{[\text{EPT}_2]} \right) \right) \quad (8.2)$$

$$E_{cell} = \frac{RT}{F} \left(\ln \left(\frac{\text{SoC}_1 [\text{EPT}_{T1}]}{(1-\text{SoC}_1) [\text{EPT}_{T1}]} \right) - \ln \left(\frac{\text{SoC}_2 [\text{EPT}_{T2}]}{(1-\text{SoC}_2) [\text{EPT}_{T2}]} \right) \right) \quad (8.3)$$

$$E_{cell} = \frac{RT}{F} \left(\ln \left(\frac{\text{SoC}_1 (1-\text{SoC}_2)}{(1-\text{SoC}_1) \text{SoC}_2} \right) \right) \quad (8.4)$$

where the subscripts 1 and 2 refer to the two reservoirs and $[\text{EPT}_T]$ refers to the total concentration of EPT in each reservoir. At a temperature of 303 K and with reservoir 1 at 80.15% SoC and reservoir 2 at 19.85% SoC, this expression evaluates to 72.9 mV, which is very

close to the 73.2 mV obtained experimentally after the first cycle. The close agreement between the capacity-predicted open circuit voltage and the actual open circuit voltage corroborates that the net effect of crossover is zero.

Because net crossover during one cycle is zero, the discrepancy between theoretical and actual capacity is due to the significant overpotential experienced by the cell. Given that the open circuit voltage after cycle 1 is 73.2 mV, and the cell voltage at the end of the cycle (with current, immediately before the open circuit step) is 450 mV, the total cell polarization is ~380 mV. The first-cycle HFR was $1 \Omega \text{ cm}^2$, leading to an ohmic overpotential of 100 mV at a current density of 100 mA cm^{-2} . The remaining 280 mV is primarily concentration overpotential according to the polarization curve and impedance analysis above.

Over the first 200 cycles (56 hours), the capacity was relatively stable, with the initial capacity of 232.7 coulombs decreasing to 215.1 coulombs after 200 cycles. After cycle 200, the capacity decreased in a close-to-linear fashion from 215.1 until the battery failed (zero capacity) at 800 cycles as shown in Figure 8.3. A concurrent increase in HFR was also observed, from 1.38 to $2.93 \Omega \text{ cm}^2$ from cycle 200 to 800. The large increase in HFR lines up very closely with the decrease in capacity; therefore, it is likely that the capacity fade is primarily attributable to an increase in ohmic resistance. The cause of the increase is unknown; however, we speculate that it may be due to clogging of the separator pores from precipitation of solute molecules.

8.3.2 Post-cycling polarization curves

The HFR-corrected polarization curves after cycling are shown in Figure 8.4. At low current densities (below 50 mA cm^{-2}), the 50 mL min^{-1} pre- and post-cycling polarization curves nearly overlay, suggesting that the charge transfer polarization has not significantly changed.

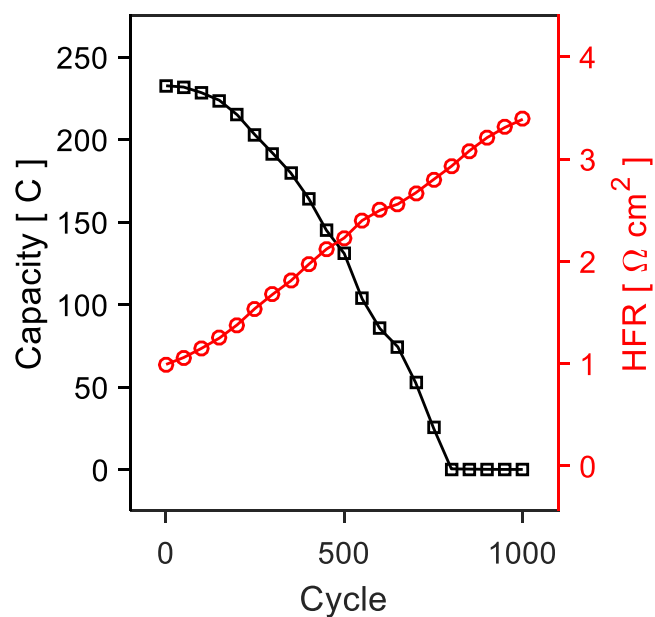


Figure 8.3. Cycling capacity and HFR.

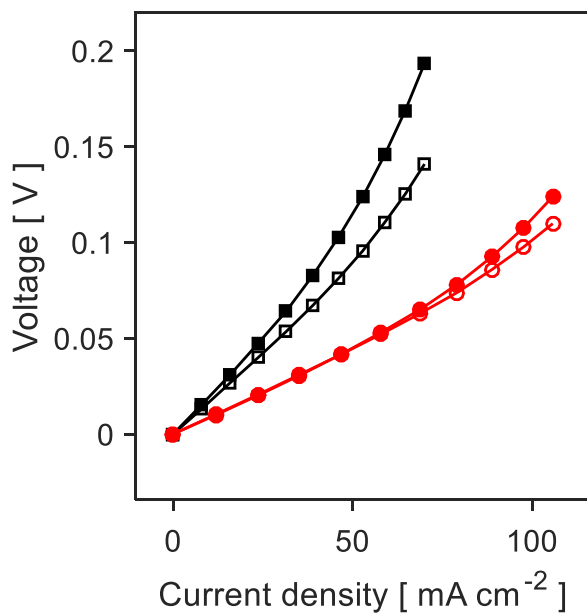


Figure 8.4. HFR-corrected polarization curves before and after cycling. Black open squares: before cycling, 20 mL min⁻¹. Black solid squares: after cycling, 20 mL min⁻¹. Red open circles: before cycling, 50 mL min⁻¹. Red solid circles: after cycling, 50 mL min⁻¹.

However, the HFR-corrected polarization noticeably changed at higher current densities, with a larger increase in overpotential with the 20 mL min⁻¹ curve than the 50 mL min⁻¹ curve. The increased polarization is attributable to increased concentration polarization given that it occurs at higher currents and that the 20 mL min⁻¹ curve exhibited a larger increase in polarization than the 50 mL min⁻¹ curve. Deterioration of either EPT or EPT^{•+} would result in an increase in concentration polarization. Presumably, precipitation/fouling in the porous electrode would decrease the porosity and result in poor electrolyte distribution and increased concentration polarization. More work must be done to identify the specific cause of the apparent change.

8.4 Conclusions

In this chapter, the symmetric cell impedance method developed in Chapter 5 for aqueous VRFBs is shown to be an effective diagnostic tool for non-aqueous systems as well. With the non-aqueous electrolyte composition chosen to maximize conductivity, the ohmic resistance was still a limiting factor for cell performance. In practice, non-aqueous electrolyte solutions with higher redox-active molecule concentration than the ~0.1 M used in this work will have lower conductivity and higher ohmic resistance. Charge transfer resistance was small relative to both ohmic and finite diffusion processes. The finite diffusion resistance was large, but is expected to fall as the active material concentration is increased. However, solution viscosity is positively correlated with concentration, partially offsetting the benefit of increased concentration through inflated pumping losses. Future work involving large organic redox-active molecules must take into account these tradeoffs. The long-term cycling of the EPT / EPT radical cation couple showed an unexplained increase in ohmic resistance that eventually led to the complete failure of battery cycling.

CHAPTER 9
IMPROVED CAPACITY RETENTION IN VANADIUM REDOX FLOW BATTERIES
THROUGH CONCENTRATION ASYMMETRY AND ELECTROCHEMICALLY
STABLE ELECTRODES

Abstract

This article has not been published anywhere, nor will it be before I turn in the final version of my ETD, so I did not include a publication statement. A manuscript will be submitted for publication. This chapter was authored by Alan M. Pezeshki, M. Cyrus Daugherty, and Matthew M. Mench.

My primary contribution to this work was the experimental design, collection, reduction, and interpretation of data, and composition of the manuscript. Daugherty assisted in data collection and reduction.

9.1 Introduction

One major source of capacity fade in vanadium redox flow batteries is due to an imbalance in the crossover rates of V^{2+}/V^{3+} to the positive side and of VO^{2+}/VO_2^+ to the negative side of the electrode. Capacity fade reduces the total amount of energy that can be stored with a fixed amount of vanadium if left unmanaged. Given that the electrolyte accounts for greater than one third of the capital cost of a vanadium redox battery and that vanadium is a large portion of this cost,²⁴ this inefficiency hugely increases the cost of the system. For example, if the battery retains only 75% of its initial capacity, the battery would need 33% more vanadium than if it retained 100% capacity. Methods that mitigate the effects of capacity fade are discussed later in this section.

Described in detail by Knehr et al.^{72,73} and Gandomi et al.,¹⁵⁰ crossover occurs as a result of diffusion, electrostatic potential gradients, and convection (both electro-osmotic and hydraulic). The asymmetry in these processes between the negative and positive electrolyte vanadium species leads to crossover-induced capacity fade. Luo and coworkers showed that in a typical cycling experiment, vanadium accumulates on the positive side of the battery and is depleted on the negative side.⁷

In the work by Luo et al.⁷ it was shown that the total vanadium concentrations on either side of the battery reached equilibrium after 100 cycles. Although vanadium concentrations held steady, capacity fade continued. The authors suggested that a decrease in membrane conductivity increased the cell overpotential and contributed to capacity fade, but did not measure or quantify these changes. It was shown in Chapter 4 that an increase in the cell overpotential, as a result of electrode performance degradation, can contribute significantly to capacity fade,¹³⁵ and others have observed a similar phenomenon.⁸⁷ In Chapter 6, it was shown that carbon felts, both untreated and treated by various means of oxidation, suffer from a loss of activity over time. Therefore, observations of capacity fade in the literature are likely electrode degradation-induced in addition to the commonly assumed crossover-induced fade.

Observations of “stable performance” made while capacity fade continues to occur are not sufficient to declare an electrode material as “durable” or “stable”. To the best of the author’s knowledge, no electrode material presented in the literature has shown stable electrochemical performance verified by means other than cycling. The use of intermittent polarization curves during cycling as demonstrated in Chapter 4 constitutes a reasonable measure of electrode degradation (or lack thereof). The identification of a truly stable electrode material could eliminate degradation-induced capacity fade altogether. In Chapter 6, the high temperature ammonia treatment on SGL GFD3 carbon felt was identified as a material that did not suffer from deactivation in either half-cell; coupled with its excellent cell performance, the ammonia-treated felt is one such candidate material to show good cycling performance with minimal degradation-induced capacity fade.

As opposed to electrode-induced capacity fade, crossover-induced capacity fade can be mitigated using established methods such as electrochemical rebalancing with external electrolysis cells or chemical rebalancing with oxidizing or reducing agents.^{136,137,151} Solution remixing, in which some portion or the entire positive and negative electrolytes are mixed and divided into equal volumes to restore equal vanadium concentrations on both sides of the battery, is another known method.^{7,136,137} These methods involve active control systems to detect and mitigate capacity imbalances. Electrochemical rebalancing and remixing both require energy to restore a balanced state of charge. Further, electrochemical rebalancing will also include additional cost of the electrolysis cell. Chemical rebalancing incurs the cost of consumable chemicals. These active methods are reactionary measures to mitigate capacity fade after it has occurred. Because the driving forces for net crossover remain, capacity fade will reoccur; therefore, costs associated with solution reconditioning will be repeated and ongoing. Passive methods that proactively prevent or minimize crossover-induced capacity fade are desirable because they would reduce system complexity and either prevent or minimize the need for active rebalancing.

Though it is unclear which driving force (e.g. diffusion, migration, or convection) draws V^{2+}/V^{3+} to the positive side, this driving force eventually equalizes in both directions, as the concentration in either half-cell reaches a steady-state value. Agar et al. proposed the use of asymmetric charge and discharge currents to alter convective crossover and investigated the potential of this method with a computational model.⁹² However, they found that increasing the charging current relative to the discharging current was necessary to reduce capacity fade. This mode of operation is undesirable in that an increased charging current will limit the total capacity

of the battery; an increased overpotential will result in reaching the voltage cutoff at a lower SoC. Additionally, as grid operation dictates the operating current, it is unlikely that such a method could ever be useful in practical operation.

In this chapter, an alternative method is presented in which asymmetric concentrations are used to alter the net crossover rate and reduce crossover-induced capacity fade. Using decreased vanadium concentration on the negative side, the steady-state capacity retention was greatly improved relative to using equal concentrations on either side of the battery. The strategy employed herein is specific to the cell design (i.e. membrane, flow fields, and electrodes), cycling profile (i.e. constant current cycling at a 300 mA cm^{-2}), and operating conditions (i.e. temperature and flow rate). In a true grid-connected energy storage application, the cycling profile is more complex, with variable charge/discharge currents. A utility seeking to minimize crossover-induced capacity fade could apply computational modeling to select the optimal concentration asymmetry. The computational model must account for all modes of crossover and would use the expected average load profile as an input.

9.2 Methods

In this chapter, a single 5 cm^2 battery with a Nafion 212 membrane, rectangular flow-through flow fields (described in Chapter 5), and carbon felt (SGL GFD3) electrodes was tested. The felt electrodes were heat treated for 4 h at $900 \text{ }^\circ\text{C}$ in flowing gaseous ammonia as described in Chapter 6. For all testing, the cell temperature was controlled at $30 \text{ }^\circ\text{C}$, and a flow rate of 50 mL min^{-1} was provided by a dual-channel peristaltic pump. Electrolyte solutions with varying vanadium concentrations were prepared by dissolving VO_2SO_4 in sulfuric acid, followed by filtration to remove impurities. A separate cell was used to charge the initial solutions to V^{2+} and

VO_2^+ , after which half of the positive electrolyte was removed to have equal amounts of total vanadium in either side. All cycling experiments were carried out at 300 mA cm^{-2} . The charge and discharge voltage cutoffs were 1.7 V and 0.6 V, respectively. Polarization curves were taken periodically with a solution comprised of 1.5 M vanadium / 4.5 M total sulfate concentration coulometrically tuned to 50% SoC. During the polarization curve experiments, electrochemical impedance spectroscopy was performed to measure the HFR of the Nyquist plot as a proxy for the ohmic resistance of the cell. Based on the results from Chapter 5, the HFR captures the entirety of the membrane resistance and a portion of the distributed resistance through the thickness of the electrode.

9.3 Results and discussion

The first set of cycling experiments used equal 1.5 M vanadium concentrations on either side of the battery to establish a baseline for capacity fade. Periodic remixing was carried out to deconvolute crossover-induced and degradation-induced capacity fade. Polarization curves were taken with 50% SoC solutions to measure the cell performance degradation independent of solution.

To demonstrate the impact of concentration asymmetry on capacity fade, the second set of cycling experiments began with 1.5 M vanadium on the positive side and 0.9 M vanadium on the negative side. After a steady state capacity was reached, 3 M sulfuric acid was added to the negative side to further alter the concentration asymmetry relative to the initial 1.5 and 0.9 M concentrations.

9.3.1 Symmetric concentration

The first cycling experiment was performed with 50 mL of 1.5 M vanadium solution on either side of the battery, hereafter referred to as the “symmetric concentration” case. Prior to cycling, a set of charge and discharge polarization curves was taken to measure the cell performance under reproducible conditions. The first cycle capacity was 1.65 Ah, declining to 0.95 Ah after one week of cycling (93 cycles). The electrolyte was reconditioned by mixing the positive and negative solutions and then dividing the mixed solution into two equal volumes, thereby restoring the initial 1.5 M vanadium concentrations. The solutions were then tuned coulometrically to 50% SoC for a second set of polarization curves. As shown in Figure 9.1, the HFR-corrected charge and discharge polarization curves showed a slight increase in overpotential from the pristine to the 1-week cycled cell, suggesting some electrode degradation/deactivation had occurred. At a current density of 200 mA cm^{-2} , the increase in HFR-corrected overpotential was 4 mV. This is much smaller than the 25 mV observed with the heat treated 10AA carbon paper electrodes in Chapter 4. After the polarization curves were taken, cycling was resumed with the reconditioned electrolyte. The discharge capacity of the first cycle post-reconditioning was 1.54 Ah, or 94% of the first cycle with fresh electrolyte. The 6% difference is attributed to the increase in cell overpotential as measured with the polarization curve.

The cell was cycled for an additional two weeks (249 cycles, or cycles 94-343); at the end of these two weeks, a stable capacity of 0.72 Ah was reached, as shown in Figure 9.2. The steady capacity indicates that the driving forces for crossover had equilibrated and that the vanadium concentrations in either half-cell were at a steady state. The vanadium concentration in the positive half-cell cycling solution was estimated by discharging to 0% SoC and recharging

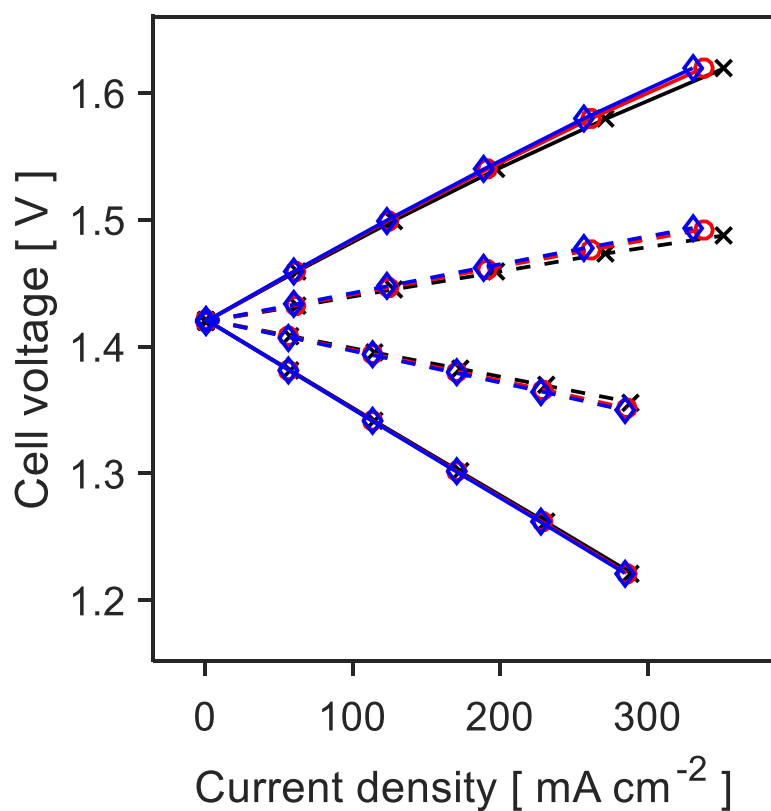


Figure 9.1. Uncorrected and HFR-corrected charge and discharge polarization curves obtained with coulometrically tuned 50% SoC electrolyte. Solid lines: uncorrected voltage. Dashed lines: HFR-corrected. Black crosses: curves obtained before any cycling. Red circles: curves obtained after 1 week / 93 cycles. Blue diamonds: curves obtained after 3 weeks / 343 cycles.

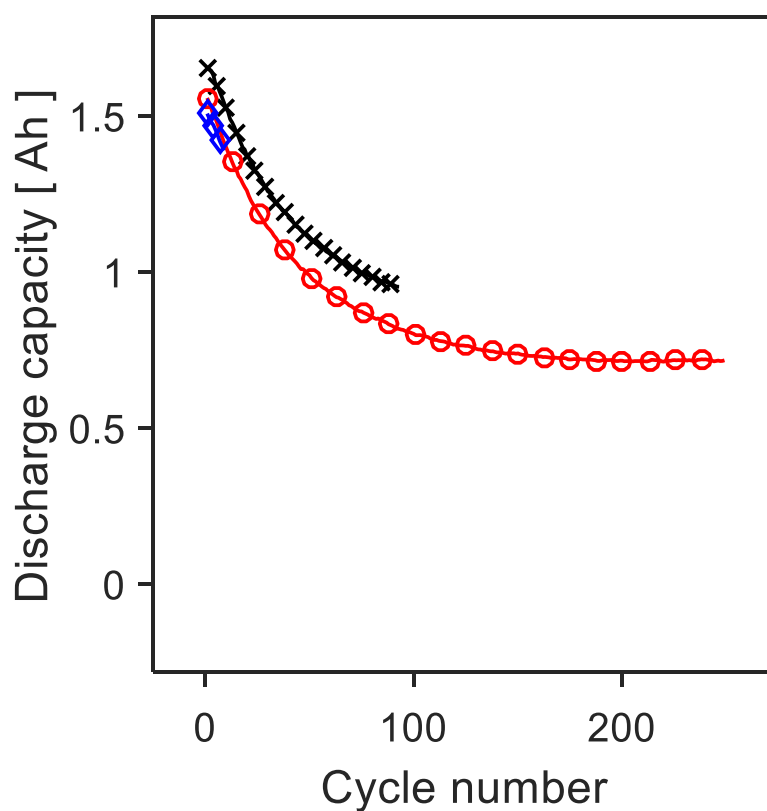


Figure 9.2. Symmetric concentration capacity fade. Black crosses: discharge capacity during first week of cycling (93 cycles). Red circles: discharge capacity for the 249 cycles after remixing at the end of the first 93 cycles (cycles 94-343). This portion of cycling lasted two weeks, after which the third set of polarization curves was taken (blue diamonds in Figure 9.1). Blue diamonds: discharge capacity for the nine cycles after the second remixing.

to 100% SoC with a separate excess negative electrolyte solution. Similarly, the negative half-cell cycling solution vanadium concentration was estimated by discharging to 0% SoC and recharging to 100% SoC with a separate excess positive electrolyte solution. The steady-state positive and negative solution concentrations were ~ 1.9 M and ~ 1.1 M total vanadium. These relative concentrations agree with those measured by Luo et al. with a Nafion 115 membrane.⁷

The solution was then reconditioned with remixing to restore the 1.5 M vanadium concentrations in both sides and tuned to 50% SoC as described above. The charge and discharge polarization curves measured at 50% SoC showed a 2 mV increase in HFR-corrected cell overpotential at 200 mA cm^{-2} from the end of week one polarization curves to the end of week three. The 2 mV increase over weeks two to three compared to the 4 mV increase over week one suggests that the rate of electrode degradation decelerated. Cycling was again resumed for one day (nine cycles) with the reconditioned electrolyte. The discharge capacity immediately after this second remixing was 1.51 Ah, i.e. 98% of the capacity after the first electrolyte reconditioning step. Thus, additional electrode degradation during cycles 94-343 contributed only 2% to capacity fade, while the remaining 51% was from crossover. The rate of capacity fade after initial cell build as well as the subsequent capacity fade after the first and second electrolyte reconditioning steps was reproducible.

9.3.2 Asymmetric concentration

The electrolyte solutions were then removed from the cell and replaced with fresh 50 mL of 1.5 M total vanadium on the positive side and 83.3 mL of 0.9 M total vanadium on the negative side. The volumes were chosen to ensure that the total molar quantity of vanadium was equal on both sides. This experiment is hereafter referred to as the “asymmetric concentration”

case. The cell was not rebuilt between the symmetric and asymmetric experiments, so any electrode degradation is cumulative. The cycle 1 capacity during asymmetric cycling was 1.50 Ah. Similar to the symmetric concentration experiments described above, the capacity declined as shown in Figure 9.3; however, the steady-state value of 1.07 Ah (obtained after ~2 weeks and 204 cycles) was significantly higher than the 0.72 Ah in the symmetric concentration case. The fact that capacity fade still occurred means that the 1.5 M positive/0.9 M negative initial vanadium concentration still has a net driving force for vanadium crossover from one side to the other. The observed half-cell potentials suggest that the net transport of vanadium was still from the negative to positive side. However, the lower rate of capacity fade and higher steady-state capacity confirm that lowering the vanadium concentration on the negative side relative to the positive can partially mitigate capacity fade. In principle, with knowledge of all crossover mechanisms, one could predict the concentration asymmetry that would result in no capacity fade. Again, the charge/discharge profiles and other operating conditions will influence the driving forces for net crossover and thus alter the optimal concentration asymmetry.

9.3.3 Secondary dilution

After the asymmetric concentration cycling experiment reached a stable capacity, 17 mL of deaerated 3 M sulfuric acid was added to the negative electrolyte. The steady-state result achieved with this second dilution corresponds to an asymmetric concentration cycling experiment with 50 mL of 1.5 M vanadium on the positive side and 100 mL of 0.75 M vanadium on the negative side. The additional dilution of the negative side was expected to draw vanadium back to the negative side. The first cycle immediately after the second dilution step had an expected small drop in capacity. When the vanadium concentration is decreased, the charge

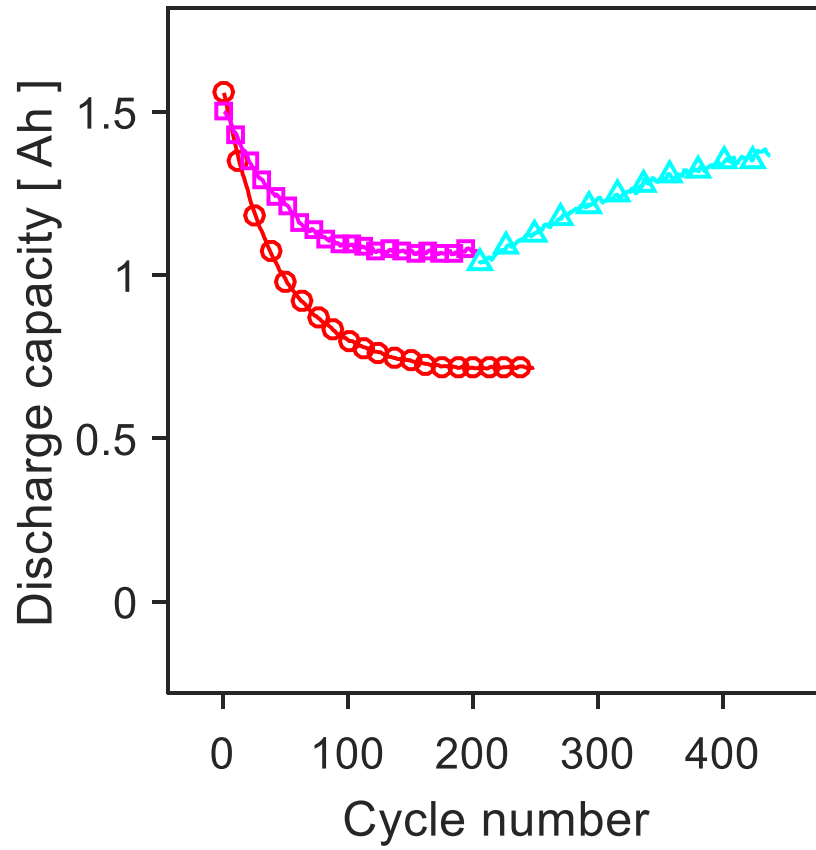


Figure 9.3. Asymmetric concentration discharge capacity with symmetric case for comparison. Red circles: cycles 94-343 of the symmetric cycling for comparison. Magenta squares: discharge capacity for the first two weeks of asymmetric concentration cycling (204 cycles). Cyan triangles: discharge capacity during cycling after 3 M sulfuric acid was added to the negative side.

transfer and mass transport overpotentials increase, which means the charge voltage reaches the cut-off voltage at a lower SoC. However, 234 cycles after the second dilution, the capacity recovered to over 1.38 Ah or 92% higher than the 0.72 Ah steady state capacity obtained with the symmetric concentration experiment.

9.3.4 Cycling efficiencies

The coulombic efficiency (CE) was relatively constant over the course of cycling, shown in Figure 9.4. During the symmetric concentration case, the cycle 1 CE was 96.3%, rising to 97.3% after ~120 cycles. The first cycle CE was again 96.3% after the electrolyte reconditioning, and after ~120 cycles again reached 97.3%, where it remained stable until the experiment was concluded. During the asymmetric concentration case, the CE began at 96.7% and reached 97.3% within 10 cycles. After the capacity stabilized, the CE had also stabilized at 97.9%. After the second dilution step, the CE slightly increased to 98.1%, where it remained stable. Thus, the concentration asymmetry had a marginally beneficial effect on the CE.

The voltage efficiency (VE) during the symmetric concentration case was 75.5% during cycle 1, dropping to 72.2% for cycle 93. Some portion of this drop was due to the electrode degradation increasing the cell overpotential, measured with the polarization curves. The remaining drop in VE can be attributed to crossover. As discussed in Chapter 5, charge transfer and finite diffusion overpotentials are inversely related to vanadium concentration. As the vanadium is depleted on the negative side as a result of crossover, the charge transfer and finite diffusion overpotentials in the negative half-cell increase. After reconditioning the electrolyte, the symmetric concentration VE recovered to 74.4%. Thus, ~1% of the drop in VE can be attributed to electrode degradation, and the remaining 2% can be attributed to crossover-induced

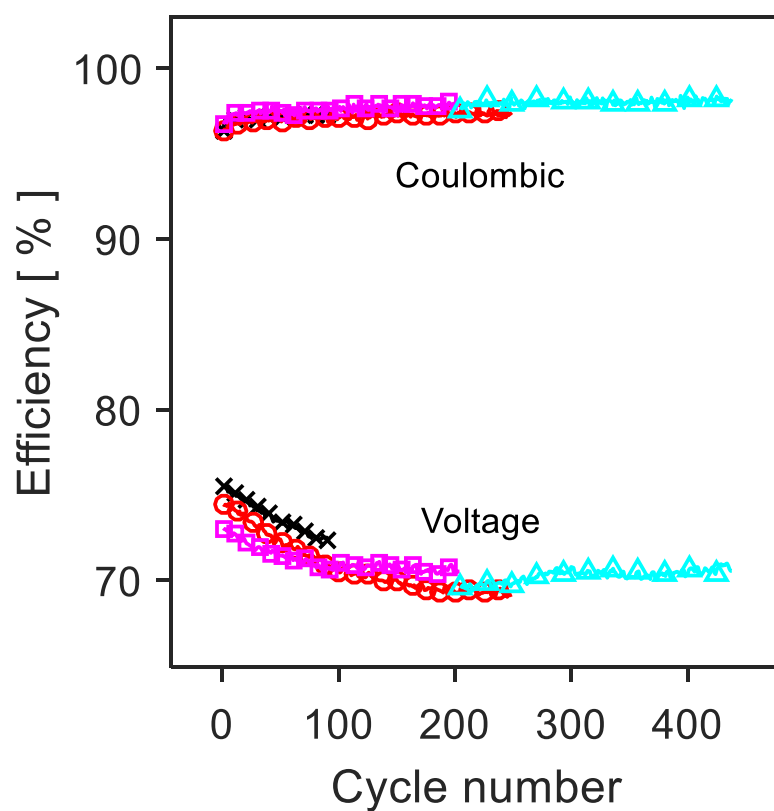


Figure 9.4. Coulombic and voltage efficiencies during cycling. Black crosses: symmetric concentration, cycles 1-93. Red circles: symmetric concentration, cycles 94-343. Magenta squares: asymmetric concentration, cycles 1-204. Cyan triangles: asymmetric concentration after second dilution.

concentration changes on the negative side. As crossover progressed during cycles 94-343 of the symmetric concentration case, the VE dropped from 74.4% to stabilize around 69.2%.

The VE for cycle 1 during the asymmetric concentration case was 73.0%. This is lower than the VE during cycle 1 for the symmetric concentration case because the lower concentration on the negative half-cell increases the overpotential. Over 204 cycles, the VE dropped to 70.6%, again due to additional depletion of vanadium in the negative half-cell. When the second dilution step was performed, the VE further decreased to 69.5%; however, as vanadium returned to the negative side, the VE increased back to 70.7%. Overall, the asymmetric concentration appears to have an initially detrimental effect on VE; however, if one allows both cases to reach steady state capacity, the asymmetric concentration has a marginally higher VE than the symmetric concentration case.

9.4 Conclusions

In this work, we demonstrate the successful use of concentration asymmetry to proactively, yet passively, reduce crossover-induced capacity fade. The CE and VE were also maintained, even slightly improved in the asymmetric over the symmetric case based on the steady-state values. In an experiment in which equal concentrations were used on both sides of the battery, the steady-state discharge capacity faded to 0.72 Ah or 47% of the 1.54 Ah first-cycle capacity, only 2% of which can be attributed to electrode degradation with the balance reasonably attributed to vanadium cross-over. Using asymmetric concentrations, the steady-state discharge capacity was 1.07 Ah or 69% of the first-cycle capacity. Further dilution of the negative half-cell increased the capacity to 1.38 Ah or 92% of the first-cycle asymmetric capacity. The steady-state coulombic efficiency marginally improved with asymmetric

concentration to 98.1% compared to 97.3% with the symmetric concentration. The steady-state voltage efficiency was also higher with the asymmetric concentration case, 70.7% compared to 69.2% with the symmetric concentration. Additionally, the stable 70.7% VE achieved with a cycling current of 300 mA cm^{-2} is among the highest reported in the literature.

The cost associated with asymmetric concentration is due to the larger volume of water and sulfuric acid required to dilute the negative electrolyte, as well as the larger tank size required. Given the low cost of water and sulfuric acid and assuming tank size does not add significantly to cost for a stationary application, the asymmetric concentration method may be useful for grid-scale applications. Even if concentration asymmetry does not completely eliminate capacity fade under dynamic operating conditions, operators could still employ the strategy to slow capacity fade in order to reduce the frequency (and thus reoccurring cost) of active electrolyte maintenance programs described in Section 9.1.

The asymmetric concentration method is specific to cell design (membrane, electrode, flow field) and operating conditions (load profile, temperature, and flow rate) and is simply one strategy to reduce capacity fade. The optimal concentration/volume asymmetry to prevent or greatly reduce capacity fade is highly dependent on the load profile. A known average load profile, coupled with a computational model that can predict species crossover, could be used to suggest an optimal concentration asymmetry. Demonstration of this capability is left for future work.

CHAPTER 10 CONCLUSION

10.1 Summary of state of the art

Low cost, reliable energy storage is a prerequisite for significant grid penetration of renewables. The redox flow battery is one of many energy storage technologies in development today, but improved cell performance is needed in order to reduce costs associated with the stack. Alternative chemistries present an opportunity to decrease the cost of electrolyte systems. Long-term stable system performance is a prerequisite for grid deployment. The state of the art in the all-vanadium redox battery has made great strides since Mench, Zawodzinski, and coworkers developed a modified cell design in 2011 based on 10AA carbon paper electrodes.¹⁰⁴ A recent report demonstrated efficiencies over 80% at the very high current density of 400 mA cm⁻² through modification of the 10AA material.¹⁵²

The adoption of improved electrode materials has in some ways outpaced the diagnostic tools used to understand the mechanisms of improved performance. Despite studies that emphasize the importance of quantifying surface area and the weakness of CV in measuring kinetic parameters in the porous electrodes characteristic of flow batteries,^{35,42,62} recently published works, e.g. Reference 153, still fail to account for changes in surface area when interpreting the impact of electrode modification on performance and rely upon cyclic voltammetry to quantify changes in kinetics. Impedance spectroscopy is the most sophisticated electrochemical technique for resolving ohmic, charge transfer, and finite diffusion processes. Sun, Delnick, and coworkers were the first to demonstrate the full capability of EIS in measuring all three processes;⁶⁹ prior to their work, no study had shown a capability of measuring a finite diffusion/mass transport resistance with flowing electrolyte. In that study, the authors adopted

the macrohomogeneous porous impedance model developed by Paasch, Micka, and Gersdorf¹⁵⁴ to fit their data. Petek et al. applied a similar model to study slurry electrodes.⁷⁰ Others have applied EIS to measure charge transfer resistance and extract kinetic parameters, notably Stimming and coworkers^{35,42} among others. To the best of the author's knowledge, all impedance studies specifically applied to VRFBs other than the work by Sun et al. rely upon simple equivalent circuit fitting.

Measurement and understanding of degradation in the literature are sparse; cycling experiments exhibit the symptoms of performance loss but do not provide the *why*. Impedance spectroscopy is an excellent tool for the study of performance loss, as it is non-destructive and can be carried out on an operating battery, but is sensitive to solution composition. Derr et al. applied EIS to study degradation in a typical VRFB cycling experiment,⁸⁷ but the spectra were taken at the end of charge and discharge cycling steps. Crossover over time affects the composition of the electrolyte at these endpoints, so the changes in performance in their work are due to both changes in the electrode material properties as well as electrolyte composition. Accelerated stress tests have not been designed specifically for RFBs. Knowledge of degradation mechanisms can guide the design of such tests to ensure that the accelerated stress tests age the electrode in a realistic manner.

10.2 Summary of work

Chapters 2 and 3 in this dissertation are primarily concerned with enhancing cell performance. In Chapter 2, significant performance benefits were realized through enriched oxygen heat treatment of the SGL 10AA carbon paper electrode material, with a demonstrated energy efficiency of 76% at the relatively high current density of 200 mA cm^{-2} compared to the

63% for untreated 10AA. Chapter 3 demonstrated further improvement in energy efficiency using Diels Alder poly(phenylene) membranes, with energy efficiencies of 85% at 200 mA cm⁻².

In Chapter 4, the focus shifted toward understanding the durability of the high performance heat treated 10AA electrode developed in Chapter 2. In this work, we quantify the contribution of electrode degradation to capacity fade, a first in the literature. The impact of crossover and increased ohmic resistance were also deconvoluted. To the best of the author's knowledge, this work also was the first to measure polarization curves with a fixed electrolyte composition before and after cycling, allowing quantitative measurement of the change in electrode performance without crossover-induced composition changes influencing the measurement. These approaches have since been reproduced elsewhere.⁸⁷

In this chapter, the cell-in-series method was also developed, allowing the study of a single steady-state flow battery operational point, i.e. at a fixed SoC and current. This is a significant contribution because it enables one to study how a given condition affects electrode performance without the confounding effects of SoC changes and alternating current characteristic of cycling experiments. For example, with the cell-in-series, one could carry out a parametric study in which a cell is held at a fixed SoC and current or voltage. Combined with electrochemical performance diagnostics such as polarization curves or EIS, this type of study might indicate under which conditions electrode degradation is most severe. With this information, operating guidelines could be developed to improve the lifetime of redox flow batteries. The cell-in-series method at extreme high and low voltages accelerated the increase in electrode overpotential seven-fold when compared to the rate of electrode overpotential increase in a typical cycling experiment; thus, the cell-in-series under certain conditions can also be used

as an accelerated stress test. The demonstration of an accelerated stress test is among the first in the literature.

In Chapter 5, one of the limitations in EIS analysis of RFBs mentioned by Sun et al.⁶⁹ was addressed; namely, the deleterious effect of pulsation from peristaltic pumps on the measurement of a finite diffusion resistance at low frequency. A simple pulse dampener effectively dampens the pulsations, allowing the measurement of finite diffusion resistances even with peristaltic pumps, circumventing the inconvenience of the gravity siphon and allowing EIS measurements with operationally relevant flow rates (i.e. much higher than the 1.5 mL min^{-1} with the gravity siphon). By using a symmetric cell configuration, it was possible to do hours-long experiments without changes in solution composition. The method was applied to study the impact of flow field design and total vanadium concentration on cell performance.

The macrohomogeneous electrode impedance model developed by Sun et al.⁶⁹ was successfully used to fit the impedance data, enabling a physical-based understanding, rather than relying on simple equivalent circuit models. The limiting process for 10AA carbon paper was controlled by both kinetics and diffusion, while GFD3 carbon felt was primarily kinetically limited. At high vanadium concentration, ohmic resistance was a significant factor, contributing nearly half of the total cell overpotential with both 10AA and GFD3. The thickness of the felt resulted in a significant distributed ohmic resistance; in 10AA, the ohmic resistance was dominated by the membrane. This chapter demonstrated the broad applicability of EIS to study RFB systems.

The most significant output of this dissertation is in Chapter 6, where the symmetric cell/pulse-dampener/impedance method developed in Chapter 5 was applied to study a series of

nine variations of the commercially available SGL GFD3 material. Each material was tested over the course of a day to evaluate the initial degradation phenomena. Application of this method in conjunction with the macrohomogeneous porous electrode model allowed unequivocal analysis of the influence of each treatment on cell performance and the associated degradation.

The positive electrode was shown to be very stable, with nearly negligible changes in performance over the first day of operation. The calculated electrode surface area and activity were essentially constant. Moderate performance gains were observed as a result of treatment, from 270 mA cm^{-2} to 370 mA cm^{-2} at a total cell overpotential of 200 mV.

On the negative side of the battery, treatment increased the current at a total overpotential of 200 mV from a minimum of 30 mA cm^{-2} to 300 mA cm^{-2} with the best-case treatment. A significant loss in the inherent activity of the surface – between 35 and 50% in a single day – occurred with all but two of the applied treatments. This loss in activity was the main driver for the observed 50-150% increases in charge transfer resistance; a loss in surface area of 10-20% on average contributed to a lesser degree. With the SGL GFD3 carbon felt, the change in charge transfer resistance accounted for nearly all changes in the observed cell performance. Analysis of the electrode surface showed no correlation between the electrode activity and surface functional groups, challenging the conventional wisdom that oxygen functional groups are the mechanism for improved performance when treatments are applied to electrode materials used on the negative side of the battery.

The ammonia heat treatment showed exemplary performance with respect to both the positive and negative couple in the VRFB, with the highest demonstrated current at a given overpotential when compared to the other treatments in Chapter 6. The treatment induced visible

pores on the order of 30 nm on the electrode surface and a massive 300-fold increase in surface area. Further, and perhaps more significantly, the felt showed virtually no performance degradation when deployed as the negative electrode; this is especially significant considering the large losses in performance that occurred in just one day with the other treatments.

Darling first suggested the use of a symmetric cell to perform steady-state durability tests;¹⁰¹ to the author's knowledge, the results in Chapter 6 are among the first applications of the method for this purpose. Combining the symmetric cell technique with the impedance analysis from Chapter 5, this study is a solid framework for how one can unambiguously evaluate electrode performance as a function of time. In contrast, any method that involves cycling in a full cell configuration will be complicated by crossover and changes in SoC over the course of the experiment. The exceptionally good fits with the macrohomogeneous porous electrode impedance model allow extraction of useful parameters such as surface area and rate constants. This model is particularly useful in situations where simple equivalent circuit fitting is insufficient to model data, namely, when the pore structure contributes significantly to the impedance spectra as was the case with carbon felt.

With the impedance methods developed in Chapter 6, performance degradation in the heat treated 10AA material was revealed to be a mass transport-related issue in Chapter 7, contrasting with the charge transfer dominated degradation in felts. This result is to the author's knowledge the first reported experimental evidence of degradation induced by an increase in mass transport resistance. Though polarization curve analysis combined with variation of flow rate might have yielded similar conclusions, the impedance-resolved method provides compelling evidence. The overall conclusion of this chapter is that the degradation mechanism

can differ between felt and paper-based electrodes. Impedance allows one to have confidence in the identification of such degradation phenomena.

Chapter 8 saw a brief foray into non-aqueous flow batteries. Therein, the symmetric cell impedance approach from Chapter 5 was applied yet again to study the limiting processes for an organic redox-active molecule. Though solvent/supporting salt/separator choices were made to maximize conductivity, ohmic resistance was still significant. Concentration polarization was also a strongly limiting factor. Rapid kinetics were observed in agreement with other kinetic studies of organic-based redox-active molecules. The ability of impedance with the symmetric cell to measure these limiting processes without the use of a reference electrode demonstrates the utility of the approach, that is, it extends beyond vanadium and can in theory be applied to any liquid-phase half-cell reaction. A pseudo-cycling experiment was carried out to evaluate the stability of the redox-active molecule, but battery failure due to an increase in ohmic resistance cut the experiment short.

In Chapter 9, the ammonia heat treated felt material was cycled in a full cell configuration to verify that the stability observed in the Chapter 6 symmetric cell testing would carry over. Indeed, the very minimal electrode performance degradation observed using the method of intermittent polarization curves first demonstrated in Chapter 4 confirms the expected stability. At a current density of 200 mA cm^{-2} , the ammonia heat treated felt exhibited a 6 mV increase over three weeks, much less than the 10 mV seen over one week with enriched oxygen heat treated 10AA in Chapter 4. The degradation, minimal as it was, decelerated through the course of the cycling experiment, with 4 mV of the 6 mV increase occurring during the first week of operating and only 2 mV occurring from the end of the first week to the end of the third

week of cycling. It is stressed here that the changes in overpotential measured with the polarization curves were obtained with a known and fixed SoC solution, rather than measured from changes in the voltage profiles during cycling. Voltage profiles from cycling are influenced heavily by crossover and needlessly overcomplicate the analysis.

In addition to demonstrating the stability of the ammonia heat treatment in carbon felt, we proposed and tested a passive method to minimize crossover-induced capacity fade in VRFBs. The method is based on using asymmetric concentrations on the positive and negative sides of the battery to counter the driving forces for net diffusion of vanadium from the negative to the positive side. In the baseline symmetric concentration case, crossover-induced capacity fade was approximately 50% of the cycle 1 capacity. Using asymmetric concentrations with the exact same cell and membrane, capacity retention was on the order of 90% with no active control required. This can simplify operation and reduce maintenance costs associated with rebalancing electrolyte.

The ultimate voltage efficiency of $\sim 71\%$ at a current density of 300 mA cm^{-2} in the asymmetric concentration is among the highest reported in the literature and the observation of stable performance is backed by the impedance results in Chapter 6, lending credence to the observation.

10.3 Recommendations

The results of this dissertation provide ample opportunities for future exploration. The symmetric cell impedance method in particular is a robust method for evaluating cell performance; its use is recommended when one would like to understand drivers of cell performance.

10.3.1 Aging protocols

The symmetric cell impedance method used to evaluate beginning-of-life performance and durability in VRFBs used flat potential holds, alternated every 30 minutes, to simulate cycling stress. Laboratory cycling experiments are carried out at constant current with fixed voltage cutoffs to terminate charge and discharge steps. In practice, flow batteries on the grid experience dynamic load conditions with potentially large transient changes, a far cry for the well-controlled experiments in the laboratory. A prototypical dynamic load profile should be developed for laboratory use to compare the rate of degradation for transient loads to the rate of degradation in controlled constant-current full cell cycling or potentiostatic symmetric cell cycling. If no change is observed, perhaps the well-controlled laboratory experiments of the current day are sufficient; if not, it is imperative to implement dynamic load testing when evaluating material durability. The symmetric cell configuration could still be useful, provided that one takes care to avoid side reactions on either half of the cell. There also exists the possibility for combining the symmetric cell and cell-in-series methods to design more elaborate degradation experiments. The cell-in-series is just one way to artificially accelerate performance loss; other methods that can further accelerate performance loss would provide additional utility.

The beginning-of-life tests in Chapter 6 that evaluated degradation over the course of one day still showed significant rates of performance loss by the end of the experiment. Longer-term experiments should be carried out to identify the timescale of degradation. If one were to continue using the symmetric cell configuration, it would be advisable to periodically refresh the solution to ensure that side reactions do not influence the solution composition over time.

10.3.2 Fundamental kinetic/material property studies

Some fundamental issues were raised, particularly in Chapter 6. For example, it would be extremely useful if a method were developed to either measure the specific double-layer capacitance of a porous carbon electrode material or to give experimental-based limits for how much the capacitance might change as a result of treatment and/or exposure to cell cycling.

We found no relationship between surface functionality with XPS/EDS and rate constant. Other methods, such as NEXAFS, that probe surface-specific properties may be able to provide a connection between rate constant and a physicochemical property of the surface. This property could be measured pre and post-cell operation to see if it can be correlated to the decrease in inherent surface activity on the negative side. If such a property and correlation can be obtained, the question of what aspect of the negative electrode half-cell reaction specifically causes that physicochemical property to change would remain. If that question were answered, it would in theory be possible to intelligently design electrode materials to be resistant to such forms of performance degradation. Given the apparent stability of the ammonia heat treated felt, it may be a particularly useful model material to study what physicochemical parameters are important and which are not from the perspective of stability.

10.3.3 In situ remediation of performance loss

As discussed in Section 7.3, knowledge of degradation mechanisms can suggest ways of rehabilitating cell performance. The polarity flip method⁹ could be studied in the symmetric cell configuration by periodically changing the electrolyte solution from negative to positive and vice versa. The timescale of degradation might suggest optimal polarity flip intervals; on the other hand, the results of such an experiment may show that polarity flip is an ineffective method after repeated use.

Other ways of regenerating cell performance are also possible. For example, if a loss of wetted surface area is a suspected mode of kinetic decline, one could attempt to re-wet the electrode by introducing a vanadium-free sulfuric acid solution into the cell and applying voltage. Electrochemical cycling in sulfuric acid might also reactivate the electrode surface.

10.3.4 Identification of degradation-inducing operating conditions

In Chapter 4, heat treated 10AA performance declined equally under aggressive charging and discharging conditions, leading to the conclusion that degradation was independent of charge/discharge condition. However, it was later found that the loss in performance was transport-related. In kinetically controlled materials like GFD3 felt, aggressive charge or aggressive discharge conditions may have differing impacts on electrode properties and performance. Application of the cell-in-series method could provide such insights.

10.3.5 Additional studies with ammonia heat treated felt material

Though the felt appears to be stable, more work must be done to verify its stability under a wider variety and perhaps harsher set of operating conditions; the cell-in-series method is one possible way to stress test the material.

The ammonia heat treated felt could not be fitted to the macrohomogeneous porous electrode model used in Chapter 5; additional modeling work could provide a better understanding of the impedance spectrum and thus the performance.

Optimization of the ammonia heat treatment could also be carried out, as the treatment parameters chosen in this work were simply chosen for convenience.

10.3.6 Impedance model development and application

The impedance model used in Chapters 5 and 6 fit the open circuit data well. However, the model relies upon a “geometric factor” that is meant to account for the distribution of concentration and porosity throughout the electrode. This factor is not physically grounded and is used as a matter of convenience to fit the data (note that this factor is only used to fit the finite diffusion portion of the spectrum, and that the fit was only used to approximate the finite diffusion resistance; no conclusions were drawn based on the geometric factor). The model also does not explicitly account for the convective flow that occurs in the flow battery. The addition of convection-derived mass transport coefficients, e.g. those in References 64 and 68, might be useful additions to the model.

The model in the original work also had expressions for predicting the impedance with applied overpotential. One of these expressions had an unresolved term; solving this term could permit one to use the model more fully. The equations only had provisions to account for the overpotential at the electrode/electrolyte interface, i.e. the charge transfer polarization; addition of concentration overpotential terms that occur across the boundary layer might extend the usefulness of the model. These types of model additions could be validated with the experimental data from Chapter 5.

10.3.7 Impedance model application to cell optimization and alternative chemistry evaluation

Given the exceptional ability of the impedance model to fit the data under a wide variety of conditions – with altered cell architecture in Chapter 5 and modified electrode materials in Chapter 6 – the results of a parametric study with the impedance model would be convincing. The parametric study could systematically vary the rate constant, surface area, electrode

thickness, and electronic and ionic resistivities, among others, to predict the sensitivity of cell performance to a variety of material properties. Such a parametric study would provide researchers with the best avenue for continued cell optimization. The parametric study by Kok et al. is a good example of such a parametric study.⁶⁸ The ammonia fuel was ohmic-limited; conceivably, one could reduce ohmic resistance by simply reducing electrode thickness. However, the loss in surface area would result in increased charge transfer and finite diffusion resistances; the model could suggest optimal thicknesses to minimize the total overall resistance.

Additionally, one could predict the best possible cell performance with alternative chemistries by measuring certain physical properties such as ionic resistivity *ex situ*, and then using carefully tailored experiments like those in Chapter 5 to obtain other relevant parameters such as rate constants. If the best-case predictions based on physical parameters show excessive resistances, it would suggest that the chemistry may not be practical.

10.3.8 Concentration asymmetry

As discussed in Chapter 9, the concentration asymmetry was an effective means for passively improving capacity retention. However, it was carried out for well-controlled laboratory conditions. It remains to be seen if the method can be useful in maintaining balanced electrolyte solutions under dynamic load conditions. Ideally, a computational model that accounts for all modes of crossover would be the best way to identify the optimal concentration asymmetry for a given representative dynamic load. Such a model may be difficult to implement given the wealth of parameters required. In this case, empirical experimental methods to find an optimal concentration asymmetry with a representative load profile could be beneficial.

10.3.9 Reference electrode considerations

As shown in Chapter 5, the use of a reference electrode to measure half-cell impedance resulted in distorted spectra. Clever cell/experimental design could perhaps remove the distortion and relax some of the assumptions required for the whole cell symmetric cell impedance analysis in this work.

10.4 Overall conclusions and outlook

The overarching goal of this thesis was to develop insights into performance and durability in redox flow batteries. An accelerated stress test was developed that can be used to screen material durability. This work highlighted the need for additional diagnostics to understand the changes in performance. The state of the art in impedance spectroscopy for redox flow batteries was improved, allowing measurement of finite diffusion resistance in a reasonable timeframe with typical flow rates. With this method, the effects of treatment on beginning-of-life performance and durability were successfully evaluated for a series of treatments applied to SGL GFD3 carbon felt. Changes in kinetic performance were linked primarily to a decrease in the inherent kinetic activity of the surface; surface area losses contributed to a lesser extent. In SGL 10AA carbon paper, the degradation mechanisms similarly included loss of kinetic performance in some cases; mass transport resistance increase was also present. Surface oxygen functionalities were not identified as the relevant physicochemical parameter driving the observed rate constants. The impedance-resolved screening identified the ammonia heat treated carbon felt material as the most stable; a long-term cycling experiment conclusively verified this result.

This dissertation demonstrates a robust methodology for evaluating electrode and cell performance in redox flow batteries. The tools herein advance state of the art methods for

measuring performance and degradation, demonstrating how to quantify and resolve ohmic, charge transfer, and finite diffusion processes. Successful application of these tools will guide intelligent cell design to optimize performance and lifetime, ultimately leading to decreased cost for redox flow batteries as a grid-scale energy storage solution.

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