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Engineering Ionomer Materials for Addressing Ohmic Resistances in Electrochemical Desalination and Waste Heat Recovery

Varada Menon Palakkal
Louisiana State University and Agricultural and Mechanical College

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ENGINEERING IONOMER MATERIALS FOR ADDRESSING OHMIC RESISTANCES IN ELECTROCHEMICAL DESALINATION AND WASTE HEAT RECOVERY

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Gordon A. and Mary Cain Department of Chemical Engineering

by

Varada Menon Palakkal
B.S., National Institute of Technology, Calicut, India, 2015
August 2020
Dedicated to my Ammamma
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<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>MCDI</td>
<td>Membrane Capacitive Deionization</td>
</tr>
<tr>
<td>RW-EDI</td>
<td>Resin-Wafer Electrodeionization</td>
</tr>
<tr>
<td>RO</td>
<td>Reverse Osmosis</td>
</tr>
<tr>
<td>AFB</td>
<td>Ammonia Flow Battery</td>
</tr>
<tr>
<td>TRAB</td>
<td>Thermally Regenerative Ammonia Battery</td>
</tr>
<tr>
<td>TRB</td>
<td>Thermally Regenerative Battery</td>
</tr>
<tr>
<td>ASR</td>
<td>Area Specific Resistance</td>
</tr>
<tr>
<td>IEM</td>
<td>Ion-Exchange Membrane</td>
</tr>
<tr>
<td>AEM</td>
<td>Anion-Exchange Membrane</td>
</tr>
<tr>
<td>CEM</td>
<td>Cation-Exchange Membrane</td>
</tr>
<tr>
<td>TEG</td>
<td>Thermoelectric Generator</td>
</tr>
<tr>
<td>RW</td>
<td>Resin Wafer</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical Impedance Spectroscopy</td>
</tr>
<tr>
<td>DI</td>
<td>Deionized</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>TDS</td>
<td>Total Dissolved Salts</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>ASAR</td>
<td>Average Salt Adsorption Rate</td>
</tr>
<tr>
<td>ENAS</td>
<td>Energy Normalized to Adsorbed Salt</td>
</tr>
<tr>
<td>FLVS</td>
<td>Free-Liquid-Void-Space</td>
</tr>
<tr>
<td>IEC</td>
<td>Ion-Exchange Capacity</td>
</tr>
<tr>
<td>TEC</td>
<td>Thermo-Electrochemical Cell</td>
</tr>
<tr>
<td>RFB</td>
<td>Redox flow battery</td>
</tr>
<tr>
<td>-----------</td>
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</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive X-ray spectroscopy</td>
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Abstract

Water scarcity and energy availability present important challenges that need to be addressed in the coming centuries. In the front of water technologies, desalting brackish water is of extreme importance for thermal electric power plants, chemical manufacturing plants, and other industrial operations that treat and reuse their water utilities. Membrane capacitive deionization (MCDI) is an energy efficient desalination technique that has drawn attention from commercial entities. Most material research studies on MCDI focus on enhancing electrode performance while little emphasis is given to rationale design of ion-exchange membranes (IEMs). In this work, the ionic conductivity, permselectivity, and thickness for three different IEM chemistries (polyaliphatic, poly (arylene ether), and perfluorinated) were correlated to MCDI performance attributes. A 5-10-fold reduction in area specific resistance (ASR), with unconventional perfluorinated and poly (arylene ether) IEMs reduced the energy expended per ion removed in MCDI by a factor of two, compared to conventional electrodialysis IEMs. For further advancement in energy efficiency of operation, ohmic resistance of the spacer channel needs to be addressed for which, ion-exchange resins bound by a polymeric binder termed resin wafers were explored. A new class of ion-exchange resin wafers (RWs) fabricated with ion-conductive binders were developed that exhibit exceptional ionic conductivities - a 3-5-fold improvement over conventional RWs containing a non-ionic polyethylene binder. Incorporation into a resin-wafer electrodeionization stack (RW-EDI) resulted in an increased desalination rate and reduced energy expenditure. Overall, this work demonstrates that ohmic resistances can be substantially curtailed with ionomer binder RWs at dilute salt concentrations.
With respect to energy, thermally regenerative ammonia flow batteries (TRBs) are an emerging platform for extracting electrical energy from low-grade waste heat (T < 130 °C). Previous TRB demonstrations suffered from poor heat to electrical energy conversion efficiency when benchmarked against state-of-the-art thermoelectric generators. This work reports the highest power density to date for a TRB (280 W m\(^{-2}\) at 55 °C) with a 5.7× improvement in power density over conventional designs and thermal efficiency (\(\eta_{\text{th}}\)) values as high as 2.99 % and 37.9 % relative to the Carnot efficiency (\(\eta_{\text{th}/C}\)). The gains made in TRB performance was ascribed to the zero gap design and deploying a low-resistant, inexpensive anion exchange membrane (AEM) separator and implementing a copper ion selective ionomer coating on the copper mesh electrodes. The improved TRB power density and the use of a low-cost materials represent significant milestones in low-grade waste heat recovery using electrochemical platforms.
Chapter 1. Introduction

1.1 Significance and background

Two of the most pressing challenges facing humanity today are the lack of water resources available for drinking, agriculture, and energy production and developing and deploying energy technologies that curtail climate disruption.1,2 Addressing both problems are paramount for a sustainable planet facing a growing population demanding a higher standard of living. In particular, proliferation of technologies capable of generating potable water and water adequate for cultivating agriculture and producing energy will be immediately needed over the next decade.3,4 Although harvesting large quantities of energy without detriment to the earth’s atmosphere or environment is perhaps a more important global problem, society contains sufficient amounts of fossil fuel resources to power the planet for several hundred years. Unlike the vast reserves of fossil fuels, 0.3% of the water resources available on earth are acceptable for drinking, agriculture, and energy production. Furthermore, on-going climate disruption has led to more frequent extreme weather events leading to draughts causing water resources in some geographical areas to be scarce. Meeting the water challenge head on requires further development of technologies (or invention of new technologies) capable of desalinating, decontaminating, and purifying salt-water bodies and wastewater resources with low energy footprint at a reasonable cost for society.

The intertwined relationship between water and energy has led to the coined term the ‘water-energy nexus’. Energy production involves water usage, whereas freshwater production requires energy usage. Due to this interdependency, problems in one sector manifests as problems in the other as well.1 One of the major source of freshwater withdrawals (40% in the US,1 as of 2014) are for meeting the cooling requirements in thermoelectric power plants.
Figure 1.1. Water scarcity and abundant availability of seawater and brackish waters as potential water resources. Source: https://www.worldwildlife.org/threats/water-scarcity, https://water.usgs.gov/ogw/gwrm/saltwater/salt.html

One approach to meeting the energy requirements of treating cooling water in this sector is to tap into low-grade waste heat generated in the energy sector, its storage into chemical energy that can be converted to electrical energy when required.

This Dissertation focuses on addressing ohmic resistances known to hamper the efficiency of electrochemical unit operations used for clean water production and low-grade waste heat recovery. The work will show that significant reductions in ohmic resistances through better conducting materials and thinner solid-state polymer electrolytes can lead to improvements in energy efficiency of electrochemical platforms used in treating water and harvesting energy. However, the reduction in ohmic resistances is not necessarily commensurate with improvement in unit operation efficiency. In addition to deploying low-resistant ion-exchange membranes, the Dissertation shows the importance of addressing spacer channel resistances by incorporating porous ionic conductors or implementing zero-gap cell designs. Further, ionomer coatings on
electrodes can also play a role in augmenting the performance of electrochemical device platforms by enhancing reaction kinetics and improving mass transfer of reactants. Hence, new materials with improved functional properties offer a pathway for better device performance, but gains in device efficiency can be limited without characterizing how the materials perform in the device using in-situ diagnostic techniques such as electrochemical impedance spectroscopy. This Dissertation will investigates the electrochemical properties of ion-exchange membranes, resins, and coatings. The first chapter presents the limitations of electrochemical deionization and some of the challenges posed by ohmic resistances followed by introducing electrochemical platforms for waste heat recovery and the challenges associated with that platform in the context of ohmic resistances.

1.1.1 Electrochemical unit operations for deionization

From the perspective of saline solutions, the permissible total dissolved salt (TDS) content for drinking is 500 ppm. Although, health specialists contend that the ideal drinking water should contain TDS values of 50 ppm or less. The ideal water quality required for agriculture (e.g., to grow salt sensitive crops) is 450 ppm or less. Salt tolerant crops can tolerate irrigation water having conductivity values around 2000 ppm TDS.

Several technologies are available for desalination and they include reverse osmosis (RO), double distillation, electrodialysis (ED), electrodeionization (EDI), multistage flash distillation (MSF), multi-effect distillation (MED), and mechanical vapor compression (MVC). RO and MSF makeup 90% of technologies used in water desalination plants worldwide. Membrane based processes include RO, ED, and EDI and RO has seen greater adoption (86%) in comparison to ED/EDI (14%). Both RO and ED/EDI are mature water treatment technologies with a strong track record for desalinating seawater (i.e., water with TDS values of 35,000 ppm).
Figure 1.2. Current operational desalination technologies, a) Membrane distillation, b) Electrodialysis, c) Multi-stage flash distillation, d) Reverse osmosis.


The popularity behind the selection of RO for desalinating seawater stems from its modularity and its high energy efficiency realized through several decades of membrane research and development. ED, on the other hand, desalinates water using electrical energy rather than mechanical energy. Because the dissolved ionic species are removed from the feed water in contrast to the removal of water from the water-ion mixture as in RO, they have the potential to offer greater feed recovery and better energy efficiency. EDI works in the same principle as that of ED, except that the diluent compartment contains a mixed-bed ion-exchange resin bed that binds the ions of the feed solution while also supplementing the conductivity of the water in the
dilute compartment. However, for low concentration regime like brackish water streams, typically found in estuaries or brackish fossil aquifers that contain a lower TDS content (5000 ppm or less), electrochemical methods of separations like CDI/ MCDI have shown to more robust, cost-effective and energy-efficient.

Capacitive deionization (CDI) and membrane capacitive deionization (MCDI – a variant of CDI) are electrochemical energy efficient desalination process capable of desalinating seawater and brackish water. In particular, MCDI is a low-energy input technology for purifying water from saline bodies at the lower end of the salinity regime in brackish water. For example, MCDI has shown an overall energy consumption of 0.26 kWh m$^{-3}$ for 10 mM reduction in salinity (when energy recovery is factored in) which is lower than the energy consumed during a commercial RO process plant, 2.9-3.7 kWh/m$^3$. Hence, MCDI is an attractive desalination technology with a low energy footprint. Both CDI and MCDI function by application of an electric field gradient across an aqueous solution flowing pass oppositely charged porous electrodes that adsorb dissolved salts – i.e., anions and cations. The difference between CDI and MCDI is that the former does not contain ion-exchange membranes while the latter does. MCDI is found to be more charge efficient due to the selective nature of the IEMs, prevents energy loss due to co-ion adsorption. The IEMs play a pivot role as ion-selective layers improving charge efficiency of the ion adsorption process onto the porous electrodes.

MCDI is an upcoming technology, and opportunities exist to improve the performance and energy efficiency through materials innovation. Numerous reports and research groups have focused on new electrode materials to boost the performance of CDI and MCDI, but less headway has been made with regard to ion-exchange membrane materials or spacer channel materials which account for the highest proportion of resistance in the cell, geared towards MCDI. Hence, there is
an immediate need for more membrane and spacer channel related research aimed at MCDI, since they contribute to the highest resistance within the MCDI cell. High performance materials for IEMs and spacer channel enable improvement in the desalination performance and reduce energy losses that stem from ohmic resistances from these components, in addition to continued research in different electrode designs - for instance graphitic carbon, carbon sponges, flowable carbon electrodes, carbon nano tube based electrodes etc., to improve upon this technology.

In an attempt to explore alternative spacer material which is ion-conductive in nature, established solutions for spacer channel resistance problem were examined which occurs in a similar electrochemical based separation process, electrodialysis. The current inefficiencies arising from dilute feed concentrations in ED, due to the high resistance in the feed (or diluate) chamber, were addressed by using ion-exchange resins in the feed compartment in the format of a wafer where ion-exchange resin beads were held together by a polymeric binder like polyethylene. The resin wafer (RW) as a porous medium in the feed compartment aids ion-transport towards the corresponding ion-exchange membranes.\textsuperscript{20} RW-EDI, which is a modification to an ED/EDI configuration, features a RW in its standard design.\textsuperscript{20}

1.1.2 Electrochemical devices for waste heat recovery

Low grade waste heat (temperature < 130 °C), is an untapped energy resource, which is generated in considerable amounts from industrial facilities, thermal power plants, solar and geothermal sources. It approximately equates to half of the present energy demand (2.9×10\textsuperscript{13} kWh in 2013) in the United States (US)\textsuperscript{21} and a bulk of this waste heat is not recovered. Harvesting of low-grade waste heat into electrical power has drawn popularity due to its vast potential and availability at locations where electrical power is needed. A thermal-electrical energy conversion technology which has made most headway in harvesting low-grade waste heat, is based upon solid-state
thermoelectric generators (TEGs) that uses $p$- and $n$-type semiconductor materials. However, this technology lacks economic feasibility for large scale productions due to its high costs and lack of capacity for energy storage.\textsuperscript{22,23} Furthermore, the brittle nature of solid-state TEGs due to their usage of semiconductor materials and non-modularity of this technology makes them unattractive for large-scale waste heat recovery and energy storage\textsuperscript{24,25}. Liquid-based thermally regenerative batteries (TRBs) offer an alternative approach for thermal energy conversion, which is potentially cheaper and scalable\textsuperscript{26,27} over TEGs. Furthermore, TRBs have energy storage capabilities upon conversion from waste heat while TEGs do not. Typically, in TRBs, different redox couples, such as metal ions complexed with amines (e.g., $[\text{Cu(NH}_3\text{)}_4]^{2+}/\text{Cu}$ and $\text{Cu(II)/Cu}$), are used to directly produce a cell voltage between two electrodes. There has been a substantial progress recently, in the development of TRBs. Some notable examples include: i) copper-ammonia ($\text{Cu-NH}_3$) redox chemistries; ii.) bimetallic type redox couple based on $\text{Cu(II)/Cu}$ and zinc-ammonia ($\text{Zn(NH}_3\text{)}_4^{2+}/\text{Zn}$)\textsuperscript{27} and iii.) Cu-ethylenediamine.\textsuperscript{28} However, only marginal improvement have been made by these TRB systems in terms of the power density and thermal-electrical conversion efficiencies.

Figure 1.3. Current waste heat harvesting technologies- a) Thermal electric generators,\textsuperscript{29} b) Thermo-electrochemical cells, aqueous ferri/ferrocyanide redox couple ($\text{Fe(CN)}_6^{3-}/\text{Fe(CN)}_6^{4-}$).\textsuperscript{30}
1.2 Ion-exchange materials

The ion-exchange process is reversible and stoichiometric in nature, in which one species displaces another ionic species in the medium. The exchanger usually constitutes an open network structure, made of either organic or inorganic materials, that transports the ions and allows it to pass through it.\textsuperscript{31} Ion-exchange process is one of the most commonly employed techniques for water treatment and separations in sectors such as – food processing, synthesis of chemicals, pharmaceuticals manufacture, mining, agriculture etc.\textsuperscript{32,33} The most earliest application of ion-exchange has been observed for water softening and water demineralization processes for industrial usage. It was also used for recovery of certain species from effluent streams before they were discarded or recirculated.\textsuperscript{34} This process occurs mainly through the utilization of a synthetic material, called ion exchangers, which acts as a sorbent, to adsorb the desired ions.\textsuperscript{35} Traditionally used ion-exchangers are in the format of ion-exchange membranes, ion-exchange resins and ionomer binders in separations and energy applications. The advantages of adopting an ion exchange method is the simplicity of equipment, easy operation, versatility of applications, ability to tailor the material according to the application required. They have been taken advantage for their properties of ionic conductivity and ionic selectivity in batteries,\textsuperscript{36–38} in separation processes,\textsuperscript{13,39} as an ion-conductive binder for electrically conductive electrodes in fuel cell membrane electrode assemblies (MEAs).\textsuperscript{40,41} This Dissertation explores the applications of polymeric ion-exchangers in the format of ion-exchange membranes, resins and ionomer binders made from organic materials for electrochemical based separation processes - membrane capacitive deionization (MCDI) and resin-wafer electrodeionization (RW-EDI) and in the field of energy storage, in thermally regenerative copper-ammonia flow batteries (TRB). It reports a detailed study of the influence of ion-exchange materials’ ionic conductivity on the energy-efficiency of the said electrochemical applications.
1.2.1 Polymeric ion-exchange membranes

Commercial application of ion-exchange membranes emerged in the beginning due to its role in saline water desalination, and now has found broader application in various industrial processes, like wastewater treatment, drinking water treatment, organic acid removal etc., and energy storage and conversion. Ion exchange membranes (IEMs) for aqueous applications are predominantly polymeric materials containing tethered ionic groups to the polymer backbone. The tethered ionic moiety has an oppositely charged counterion to satisfy iso-neutrality conditions. IEMs can be generally classified into cation exchange membranes (CEMs) and anion exchange membranes (AEMs). Membranes with tethered negatively charged (e.g., sulfonate) groups are designated CEMs. Conversely, tethered positively charged (e.g., quaternary ammoniums) groups are defined as AEMs. These membranes, owing to their high electrical conductivity and ability to selectively permeate certain ions, while maintaining optimal desired properties such as mechanical stability, hydrophilicity, thermal stability etc. are of high potential to serve as separators and ionic conductors. The role of IEMs in electrochemical based separation processes like ED, EDI, RW-EDI and CDI/MCDI is dependent upon the application requirements and basic principle of operation. For example, in MCDI, the polymeric IEMs are incorporated within the cell to prevent co-ion adsorption to the electrodes, improving the charge efficiency of the process by 49.2% over CDI. The ion-exchange membranes are typically 90 to 100% selective and also assist in a faster rate of ion desorption during discharge. During desorption, there also lies a tendency for ions to move to the oppositely charged electrode instead of exiting through the concentrated brine stream. However, the presence of the oppositely charged ion-exchange membranes positioned in front of the electrodes reject the ions into the concentrated brine stream through Donnan exclusion. Thereby, the discharge process in MCDI avoids instances of incomplete electrode regeneration.
and reduction of adsorption capacity of electrodes that leads to a gradual loss in device Faradaic efficiency. Additionally, the presence of membranes prevents any direct contact of the feed water with the electrodes eliminating the potential for electrode scaling. In summary, MCDI drastically minimizes co-ion adsorption on the electrodes providing greater utilization of the electrical current for separating ions from saline bodies.

On the contrary, in RW-EDI, the alternating series of AEM and CEM in the stack serve as separators of the diluted stream and concentrate stream, by accepting or rejecting the ions in the compartment.\textsuperscript{20,45} These membranes require adequate mechanical strength to serve as separators in comparison to the ion-exchange layers required in MCDI. However, optimization of membrane conductivity only offers marginal improvements in energy efficiency of EDI operation, as the spacer channel resistance increases ohmic losses in the EDI setup.

Ion-exchange membranes are recently being used in batteries for medium and large scale energy storage applications, particularly for redox-flow batteries.\textsuperscript{33} The membrane which functions as a separator is a vital component in these energy storage systems responsible for battery performance and determines the economic viability of the system.\textsuperscript{36,46} The TRB system utilizes an AEM in a which separates the anodic and cathodic compartments in the cell, preventing crossover of active cationic redox species thereby mitigating self-discharge of the battery.\textsuperscript{47,48} The anion-selective nature of the AEM permits only anion conduction (which is the nitrate and hydroxide ions) between the electrolyte chambers to balance the internal charge transfer between the electrolyte chambers. The primary role of the AEM is to minimize self-discharge in the battery by inhibiting cation transfer such as the ammonium ion and the copper (II) amine complex from the anolyte to the catholyte. The transfer of hydroxide ions from the anolyte chamber which is alkaline in pH (pH~10) to the catholyte chamber which is acidic (pH~2.6) favors the conversion of
ammonium to ammonia, shifting the acid-base equilibria. This implies undesirable consumption of chemicals, instead of electrochemical consumption of the copper, affecting the functioning of the TRB. Previous reports have shown that the electrical energy production in the TRB gets limited due to substantial self-discharge while using commercially available AEMs like Selemion™.47,49,50 Consequently, there is a requirement to explore better performing AEM materials that exhibits high ionic conductivity and prevents battery self-discharge.

1.2.2 Resins/resin wafers

Resin wafers (RWs) are porous materials in which ion-exchange resin particles are immobilized in a wafer format. The RW constitutes a mixture of CER and AER bound by a thermoplastic polymer binder like polyethylene (PE) where the ion-exchange resin beads function to supplement ionic conductivity across the RW, while the PE binder holds the resin beads stationary. These were developed by Argonne National Laboratory 39 as spacer materials for EDI by the substitution of the packed bed compartment of loose ion-exchange resin particles which is traditionally used in an EDI setup. The presence of these resins augments the ionic conductivity of the diluate chamber of EDI. As a result, it lowers the ohmic resistances in the feed compartment, making the EDI stack more thermodynamically efficient for ion removal in the more challenging dilute concentration regime. However, the utilization of loose resin beads fosters inconsistent process performance, stack leakage, and disruption of bulk liquid flow. Moreover, the loose particle bed in EDI requires routine maintenance.18,39,51 Hence, RWs were developed and the modified EDI stack named as RW-EDI demonstrated significant advantages over conventional EDI in terms of the rate of removal of ions from liquids, energy efficiency, and process stability and consistency.39,52 To this present date, no significant material innovation has occurred for RW materials. Although the RW has exhibited successfully in ameliorating the ionic conductivity of the diluate liquid compartment
and facilitating ion removal by ion-exchange,\textsuperscript{39} the presence of the non-conductive binder in the RW limits energy efficiency gains in EDI.\textsuperscript{53} The non-conductive binder impedes pathways for ion-exchange and ion transport between the liquid and resin beads leading to larger ohmic resistances in the diluate compartment that compromises EDI energy efficiency. To obtain optimal performance of the resin wafers, an ion-conductive substitute for polyethylene was explored that enhances the ionic conductivity and ion-transport performance of the material. From initial studies, these ionomer binders maintain the porosity and desirable mechanical integrity of the wafers. However, long-term stability studies are essential to determine their performance longevity. The minor drawbacks of ion-exchange materials in separation processes is that ion-exchange membranes and resins can be costly and they have stability concerns (e.g., fouling) that compromises the cells longevity and the resins and membranes themselves offer an additional electrical and flow resistance term to the cell. In other words, cell lifetime is often dictated by the lifetime of these ion-exchange materials

\subsection*{1.2.3 Bipolar junctions}

For RW-EDI, the role of ion-exchange resins, besides the function of augmenting the ionic conductivity of the diluate compartment in RW-EDI, is to self-regenerate via water splitting at the bipolar junction sites in the RW. These bipolar junctions are formed at the interface where the AERs come into contact with CERs. The tethered, oppositely charge ionic moieties at this interface lead to an abrupt p-n type junction that splits water under an applied electric field.\textsuperscript{54-58} The electric field drives water-dissociation forming hydronium (H$_3$O$^+$) and hydroxide (OH$^-$) ion that carry the current flow in the unit, under dilute conditions. From a theoretical perspective, ineffective water-splitting in the ion-exchange resins may hinder deionization and current efficiency of EDI and a non-conductive binder like PE would not only derail the ionic conductivity of the RW but would
also jeopardize the population of bipolar junction regions needed for water-splitting. Hence, ion-conductive binders as replacement would not only improve the overall ionic conductivity of the wafer material but also produce larger number of effective bipolar junction sites within the material, facilitating efficient water splitting.

1.2.4 Electrode coatings/thin film ionomers

Ionomer materials or ion-conductive polymers have been extensively utilized in electrochemical devices that employ solid-electrolytes for energy conversion and separations such as polymer-electrolyte fuel cells, alkaline fuel cells, redox flow batteries and electrolyzers. These ionomers as coating on electrode surfaces facilitate selective transport of ions and/or fluids. The desirable properties of the thin film coating are dependent upon their function in an application. For example, in fuel cells, ionomers as thin films to promote transport of ionic and gaseous species to the catalyst. Due to their confined thicknesses (<100 nm) in a heterogeneous electrode structure, properties of ionomer are substantially different from the bulk (membrane) and influenced by ionic and interfacial interactions. Subsequently, the chemistry of these ionomers influences the kinetics of the electrode reaction and device performance thereof.

Notably, TRABs are known to suffer from poor Faradaic efficiency due to parasitic site reactions that involve Cu oxidation with hydroxide ions and oxygen species. As a result, the reported anodic Faradaic efficiencies for the cell are typically less than 40%. Herein, it was initially hypothesized that cation selective ionomer coating on the Cu mesh electrodes may mitigate interaction of hydroxide anions and dissolved oxygen during Cu oxidation.
1.3 Electrochemical platforms where ohmic resistances are addressed

1.3.1 MCDI

A MCDI cell consists of two porous, electron conducting electrodes where each electrode is sandwiched between a current collector and an ion-exchange membrane. The current collectors are the outer layers while the oppositely charged ion-exchange membranes face each other in the MCDI cell. A spacer unit, typically made of a thin dielectric material on the order of 100 μm thick, separates the ion-exchange membranes so liquid solution can flow through the cell and also prevents electrode shorting. The MCDI cell contains machined inlet(s) that delivers the salt water into the spacer channel and an outlet that allows the water to exit the cell. The current collectors in the MCDI are connected to an electrical power control source (e.g., a potentiostat/galvanostat) to apply electrical potential or a constant current during cell operation. The product stream emanating from the MCDI module is analyzed using an in-line conductivity probe and pH probe. Figure 1.4 provides a schematic of MCDI operation.

![Figure 1.4. Schematic of membrane capacitive deionization cell design](image)

During MCDI operation, a constant voltage or constant current is applied on the current collectors which drives cations and anions towards the respective oppositely charged electrodes through ion-selective membranes and are stored in the electrochemical double layer of the porous electrodes.
A typical electrical potential difference applied ranges from 0.8V-1.2V. The upper potential value is set to minimize or mitigate faradaic reactions such as carbon oxidation, water electrolysis etc.\textsuperscript{4,13} Faradaic reactions, reduce desalination efficiency of the system as the electron are used to drive the faradaic reaction instead of salt removal. Once the electrodes become saturated with ions in the electrochemical double layer during the charging step, the polarity of the electrodes are reversed in order to desorb the ions and release them back into solution leading to a concentrated brine that emanates from the cell during the discharge step. During this discharge step, part of the electrical energy used for the charging step can be recovered and can be applied subsequently (e.g, by storage in an adjacent battery) to remove salt from the feed solution. The energy recovery steps uniquely position MCDI to be an attractive, low energy footprint water desalination technology that is not only capable of producing potable water but also water quality acceptable for industrial applications that include energy production, agricultural requirements, pharmaceutical and semiconductor manufacturing.

1.3.2 RW-EDI

A conventional RW-EDI stack is similar to that of an EDI stack because both devices utilize the same basic structure consisting of two electrodes that are separated by a stack of alternating liquid compartments, which are partitioned by alternating cation and anion exchange membranes and the diluate feed stream packed with ion-exchange resins (in wafer format for RW-EDI and loose resin beads in EDI). Bipolar membranes are installed at the ends close to the electrodes, which isolate the electrode rinse solution from the process fluid.\textsuperscript{52} The operation process involves the application of an electric field which drives the transport of ions towards their respective, oppositely-charged electrode, while circulating the concentrate and feed streams continuously through their respective compartments in the stack. Consequently, ionic species are continuously
removed from the diluate/ the feed stream chamber and transferred into the adjacent concentrate chambers. Figure 1.5a- 1.5b shows the schematic of a RW-EDI stack and a resin wafer respectively.

![Diagram of RW-EDI stack and resin wafer](image)

Figure 1.5. a) Schematic representation of a RW-EDI single cell setup; b) Schematic of a mixed resin wafer with anion-exchange resins (green) and cation-exchange resins (blue) held by a binder (yellow).

RW-EDI differs from ED because its traditional design features a resin wafer constituting cation-exchange and anion-exchange resin particles held together by a polymeric binder like polyethylene in the diluate liquid chamber. The resins in the wafer augment the ionic conductivity of dilute aqueous solutions in the diluate chamber of EDI. Its modular design and flexible operating parameters (e.g., adjustment of the cell’s operating voltage or current) make it uniquely versatile to carry-out a wide-range of ionic separations for various applications. The incorporation of a resin wafer in place of loose ion-exchange resin beads, ensures consistent process performance and stability. Additionally, due to the ease of handling these wafers, they require less maintenance.

1.3.3 TRBs

TRBs were developed as a new approach for harvesting waste heat and conversion into electricity based on the oxidation and reduction of electrodes. A chemical potential difference between two
electrodes is induced by addition of a ligand to one electrolyte that forms a metal-amine complex with it. The anode undergoes oxidative dissolution as this potential gets discharged and the cathode undergoes reduction and deposition of the metal. Post discharge, the ligand from the anolyte side can be separated using distillation and added onto the other electrode for the next discharge cycle.\textsuperscript{47,48,50}

The ammonia-copper redox flow batteries, a type of TRB, designated as Thermally-regenerative ammonia flow batteries (TRABs), developed as a relatively new approach for low-grade waste heat energy recovery.\textsuperscript{26,28,29,47,48,59,60} The TRB combined with a distillation unit, transforms low-grade waste heat to chemical energy in the form of concentrated ammonia and stores it, making available for discharge as electrical energy when required. Both electrodes of the TRAB are composed of inexpensive copper (Cu) meshes, immersed in aqueous copper nitrate salt solutions separated by an anion exchange membrane (AEM). Ammonia (NH\textsubscript{3}), added as the ligand into the anolyte, results in generation of a potential difference between the Cu electrodes. During discharging, the Cu anode gets oxidized and undergoes dissolution, forming a Cu\textsuperscript{2+} amine complex, while Cu\textsuperscript{2+} gets reduced and deposited on the cathode. Post discharge, NH\textsubscript{3} is distilled using low-grade waste heat and is transferred to the compartment (previously the catholyte) that did not contain NH\textsubscript{3}. Hence, the labeling of the chambers are switched. Subsequently, the Cu\textsuperscript{2+} in the catholyte (previous anolyte) gets redeposited onto the electrode, while the copper in the anolyte (previous catholyte) gets oxidized. The regenerative dissolution/deposition cycle of the electrodes prevents the Cu electrodes from being sacrificial, and allows storage of low-grade waste heat energy using NH\textsubscript{3} solutions. A schematic of a typical TRAB setup is shown in Figure 1.6.

The output power density and the thermal-electrical conversion efficiencies are the performance parameters for the basis of evaluation of the TRAB. Few of the issues that hinders
the performance of TRAB are: i.) low thermal to electrical conversion efficiency; ii) poor anodic Faradaic efficiency due to parasitic reactions; and iii) the instability of electrodes over multiple cycles, due to lack of balance of gain and loss of copper on the electrodes.

**1.4 Conclusions**

Ion-exchange materials play an important role in electrochemical based separation processes and design of thermo-electrochemical cells for waste heat recovery. Their favorable properties like ionic conductivity, permselectivity (selective uptake of ions) etc. provide plethora of opportunities in tailoring them in the format of membranes, adhesives or ionomer binders, and electrode coatings for specific electrochemical applications. This chapter elucidated the significance of ion-exchange materials and the role they play as ion-exchange membranes in MCDI, ionomer binders in resin wafers for RW-EDI and ionomer electrode coatings and AEMs in TRABs. The challenges associated with improving device performance by lowering ohmic overpotential of components in

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Figure 1.6. Schematic representation of a copper-ammonia based thermally regenerative flow battery setup with an integrated distillation unit.
electrochemical based separation techniques and waste heat recovery devices can be done by application of high-performance ion-conductive materials. Hence, there is a need for a materials-based research and development is pivotal for further improvements in device performance.
Chapter 2. Theory

2.1 Research objective

The goal of this dissertation is to provide a detailed investigation on the application of selective ion-exchange materials with low area specific resistance and their influence in addressing ohmic overpotentials in electrochemical based desalination processes like membrane capacitive deionization and resin-wafer electrodeionization as well as waste heat recovery technologies like TRABs. These ion-exchange materials were synthesized by performing functionalization reactions on commercially available polymers and transformed into membranes, ionomer binders and coatings. Their properties were measured and correlated to device performance for separations (desalination) in 2 electrochemical platforms: i.) ion-exchange membranes in MCDI and ionomer binder resin wafers in RW-EDI and ii.) thermoelectrochemical cells featuring AEM and cation-exchange coated electrodes in TRABs.

The specific objective for each electrochemical system is stated as follows:

Objective 1: Exploring alternative ion-exchange membranes that are thinner and highly conductive to reduce ohmic overpotential contributions in MCDI and TRABs

Objective 2: Fabricating ion-conductive binders for designing resin wafers with enhanced ion-transport properties as spacer materials for deionization in MCDI and EDI

Objective 3: Deploying a zero-gap design and cation-exchange coated electrodes, coupled with a low resistant AEM to advance high power density TRABs

2.2 Significance of ionic conductivity in electrochemical devices

Ion-exchange membranes are vital material components for a plethora of electrochemical applications in energy storage and conversion (e.g., fuel cells, water electrolysis, redox flow batteries) and water desalination (e.g., electrodialysis). These membranes, owing to their high ionic conductivity, electron insulation, and ability to selectively permeate certain ions, while
maintaining optimal desired properties such as mechanical stability, hydrophilicity, thermal stability etc. are of high potential to serve as separators and/or electrolytes for electrochemical cells. Like all processes, concerted efforts are being made to optimize their efficiency in the domains of conductivity, permselectivity, better mechanical and chemical properties etc. To do so, it is essential for the fundamental understanding of chemical and physical nature of ion exchange materials and their interaction with the external solution. Further, it is important to identify the parameters that are decisive in the transport of solute and solvent molecules through the materials. An important parameter of ion-conductive materials is their ionic conductivity, as this in turn impacts ohmic overpotentials and device energy efficiency.

The polarization (i.e., steady-state current – voltage relationship) of any electrochemical device that compromises energy efficiency arises from overpotential sources that deviate the cell from the equilibrium potential. These overpotential sources include the surface overpotential, the ohmic overpotential and the concentration overpotential. The surface overpotential refers to the dissipative losses that arises due to the activation barrier resistances for the electrochemical reaction. The ohmic overpotential entails resistance to ionic or electronic current. The concentration overpotential term accounts for the potential difference caused due to the concentration gradients in the electrodes and supporting electrolyte.

\[
E(i) = E^o + \eta_{s,a}(i) - \eta_{s,c}(i) + \eta_{c,a}(i) - \eta_{c,c}(i) + \eta_{ohm}(i) <2.1>
\]

Where \(E\) denotes the overall cell potential, \(E^o\) denotes the standard cell potential, \(\eta_{s,a}\) denotes the surface overpotential from the anode side and the \(\eta_{sc}\) denotes the contribution from the cathode, \(\eta_{c,a}\) denotes the concentration overpotential from the anode side and \(\eta_{c,c}\) is the cathode side contribution. \(\eta_{ohm}\) is the ohmic overpotential. \(E\) and the \(\eta_i\) values are a function of the current values in the cell.
For an electrodeionization based separation techniques like MCDI or RW-EDI, the ohmic overpotential dominates device performance. For instance, there are no formal charge-transfer reactions in MCDI and the current is operated at low values and thus limiting currents are not present. The ohmic overpotential can be described by equation 2.2 which is analogous to ohm’s law ($V = I \cdot R$).

$$\eta_{ohm} = i \cdot ASR$$  

<2.2>

The area specific resistance (ASR) is the thickness of the electrolyte divided by the conductivity.

$$ASR = \frac{d}{\kappa}$$  

<2.3>

Reducing the ohmic overpotential term can be achieved by lowering the ASR. Decreasing the ASR is possible through a reduction in the thickness of the electrolyte and/or improving the ionic conductivity through the electrolyte. The ionic conductivity in electrolytes (liquid/solid – also sometimes referred to as the electrical conductivity of the electrolyte despite it being electron insulating) occurs by the transport of ions, unlike electrons in metal conductors.

For any electrolyte, the electrical current passing through it under the influence of an electrical potential gradient, is proportional to the concentration of ions in the solution, the stoichiometric coefficients for the ions, valence of the ions and its ionic mobility in the medium.

The net flux of species from Faraday’s laws of electrolysis can be represented as:

$$i = \sum_l z_l F N_l$$  

<2.4>

Where $N_l$ is the molar flux, $N_l = J_l + C_l \nu_l$, $J_l$ denotes the diffusive flux term, and $C_l \nu_l$ denotes the convective flux term.

The general form for any diffusive flux can be represented as:

$$J_l = \sum_k L_{lk} X_k$$  

<2.5>

Where $J_l$ denotes the flux, $L_{lk}$ is the constant of proportionality, $X_k$ denotes the driving force.
For Fick’s first law, \( J_i = D_i C_i d_i \), where the driving force \( d_i \), chemical potential gradient or the electrochemical potential gradient.

\[
\eta_i = \mu_i + z_i F \phi 
\]

Where \( \mu_i \) is the chemical potential gradient.

\[
\mu_i = \mu_i^0 + RT \ln \alpha_i = \mu_i^0 + RT \ln Y_i C_i
\]

Assuming transport in the \( x \)-direction alone and no bulk fluid flow/convection (i.e., \( N_i = J_i \))

\[
J_{i,x} = D_i C_i \left( \frac{1}{RT} \frac{dn_i}{dx} \right) = D_i C_i \left[ \left( \frac{d \ln Y_i}{d C_i} + \frac{1}{C_i} \right) \frac{d C_i}{dx} + \frac{z_i F d \phi}{RT dx} \right]
\]

Assuming solution ideality, and substituting equation 2.8 in 2.4,

\[
i_x = F^2 \sum_i \frac{z_i^2 D_i C_i}{RT} \left[ \frac{RT}{z_i FC_i} \frac{d C_i}{dx} + \frac{d \phi}{dx} \right]
\]

Hence, conductivity \( \kappa = \frac{1}{R} = F^2 \sum_i \frac{z_i^2 D_i C_i}{RT} \)  

In order to understand the ion-transport mechanism within these solid electrolytes, three established ion-transport models are discussed in the next sections: i.) Nernst-Planck model, ii.) Stefan-Maxwell model, and iii.) the Dusty-fluid model.

### 2.2.1 Nernst-Planck’s model

The Nernst Planck relation is useful in determining the transport mechanism in ion-exchange materials. It is applicable for ideal solutions and based on the assumption that cations and anions migrate independently in the solution and membrane matrix. \(^4\) Ion-transport dictates the feasibility of the ion mobility across the membranes which translates into device energy efficiency. The two factors that would govern ion mobility would be kinetic and thermodynamic which would signify the driving forces in order to overcome the resistance to ionic mobility across the membrane. \(^12\) In order to establish a relation between the thermodynamic and kinetic parameters
that would describe the ionic mobility in an ion-exchange membrane, an extended version of the Nernst-Planck equation is used.

\[ \eta_i = \mu_i + z_i F \varphi = \mu^o_i + V_i p + RT \ln a_i + z_i F \varphi \]  \hspace{1cm} <2.11>

where \( \eta \) gives the electrochemical potential, \( \mu \) is the chemical potential, \( V \) is the partial molar volume, \( p \) is the hydrostatic pressure, \( z \) is the valence, \( F \) is the Faraday constant, \( R \) is the gas constant and \( T \) is the absolute temperature, where \( i \) refers to the component and \( o \) to the standard state.

The electrochemical potential gradient which is the major driving force for motion of ions through the ion-exchange membranes. The three modes of mass transport that are considered in the extended Nernst-Planck equation. They include diffusion, migration and convection. For MCDI, migration and diffusion are the dominant modes of transport during deionization (i.e., removal of ions perpendicular to the fluid flow).

### 2.2.2 Stefan-Maxwell’s model

The drawback of the Nernst–Planck approach is that it assumes the solution to be ideal and disregards contribution of ion-ion interactions. However, the model developed by Maxwell–Stefan includes the interaction of different components and the non-ideal nature of the solution is taken into consideration, besides water-transport via solvent-ion interactions.\(^{12,44,61}\)

The Stefan-Maxwell approach for ionic transport is based on the assumption that the driving forces acting on an ionic component \( i \), which is in constant flux is equal to the sum of the friction forces between the ion ‘i’ and the rest of the components in the system.\(^{62}\)

\[ C_{Total} X_i (RT \frac{d \ln a_i}{dx} + z_i F \frac{d \varphi}{dx}) = \sum_j \frac{RT}{D_{ij}} (X_i N_j - X_j N_i) \]  \hspace{1cm} <2.12>
Where X denotes the mole fraction, C is the concentration, a denotes the activity, z denotes the valence, F is the Faraday’s constant, φ denotes the electrical potential, R is the universal gas constant, T denotes the temperature, D denotes the Stefan-Maxwell diffusion coefficient and N denotes the molar flux of the species. Subscripts i and j refer to the individual components (ions/solvent molecules). This generalized equation 2.12 can be written in terms of concentration, as depicted in equation 2.13.

\[
\frac{dc_i}{dx} + \frac{z_i C_i F}{RT} \frac{d\phi}{dx} = \sum_{j \neq i} \frac{1}{C_{Total} D_{ij}} (C_j N_j - C_i N_i)
\]

2.2.3 Dusty-fluid model

The dusty-fluid model was developed for describing gas phase flow through a porous media. There are 4 independent mechanisms through which gas transport occurs within a porous media. The first being Knudsen diffusion, where the gas pressure is low resulting in collisions between the walls of the pores and the molecules dominating. The second mechanism is viscous flow, where the molecular interactions dominate. The third mechanism is continuum diffusion, where molecule-molecule interactions dominate, and the fourth mechanism is through surface diffusion.\(^{62,63}\) For describing ionic transport through a membrane, an extended version of the generalized Stefan-Maxwell equations can be used to develop a Dusty-fluid model, where the membrane backbone and the attached side chains (functional groups like -CH2N+(CH3)3 in AEMs) are considered as ‘dust’ in the model. The assumptions made for the model are: i) the dust species are fixed, such that their velocity with respect to the frame of reference is 0. ii) the dust species are distributed evenly in concentration, i.e., \(\frac{dC_M}{dx} = 0\), where M denotes the membrane. iii) the molecular weight of the dust approaches infinity relative to the mobile ions.\(^{62}\)
The impact of the membrane structure is accounted for by approximations based on empirical correlations like a Bruggeman correlation. The Bruggeman correlation \(((\varepsilon - \varepsilon_o)^q)\) relates the phase volume fraction and the exponent aimed at correcting the membrane complex structure.

\[
\sigma = (\varepsilon - \varepsilon_o)^q D_{12} \frac{k^2}{RT(1+\delta)} C
\]

\(\sigma\) is the ionic conductivity, \(\varepsilon\) is the volume fraction of water in the membrane, \(\varepsilon_o\) is the volume fraction of water in the membrane at the percolation limit, and \(q = 1.5\) is the Bruggeman constant.

The diffusion and structural correction terms are condensed into a fitting parameter that factors the diffusivity between the mobile species and the membrane which is \(\delta\).

### 2.3 Equivalent Circuit modeling using Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is a useful tool to characterize an electrochemical system by application of an electrical perturbation. Through the Nyquist plot which plots the real part of impedance measured vs the imaginary part of electrical impedance, obtained from EIS, an electric circuit model can be used to represent the behavior of the system. For example, the traditional electrochemical interface which can be a planar electron conducting electrode interfaced with an ion-conducting electrolyte and an electrochemical reaction occurring on the electrode surface. The electrochemical behavior of this interface can be described in the format of an electric circuit - like a simple Randle’s model which incorporates three elements. i) equivalent series resistance (ESR) which includes the sum of resistances from the electrode, electrolyte, and electrical contacts, in series to a parallel connection of ii) double layer capacitance \(C_d\) and iii) a charge transfer resistance \(R_{ct}\). \(R_{ct}\) constitutes all Faradaic reactions occurring on the electrode’s surface and \(C\) represents the non-Faradaic charge storage. However, this simple model does not effectively describe porous electrodes. To develop a model for describing porous electrodes, representative of porous carbon electrodes in MCDI, a transmission line theory is adopted,
wherein, highly porous electrodes are differentiated into two parts — the base electrode and the porous portion. The gradual inflow of ions into a pore can be described using transmission lines as shown by Figure 2.1. The model consists of several elements connected in parallel and series.

![Figure 2.1. Schematic of a generic transmission line model with elements along the electrode pore.](image)

$L$ denotes the length of the transmission line or the depth of the pore. A series of repeating impedance elements represent the transmission line along the pore. $\chi_1$ is the impedance of the electrolyte within the pore, $\chi_2$ is the impedance of the porous electrode’s solid phase.

### 2.4 Bipolar junction

The advantages of EDI over ED is the higher ionic conductivity of the diluate compartment rendered due to the presence of ion-exchange resins. The resins aids in faster electromigration of ionic species from the feed water to the IEMs. Moreover, the resins can be electrochemically regenerated without the use of chemicals. Regeneration occurs through water splitting in the bipolar junctions formed at the interface where the cation-exchange moieties (in the CERs) come into contact with the anion-exchange moieties (in AERs). The oppositely charged tethered ionic moieties in proximity at this interface leads to an abrupt p-n type junction that dissociates water under an applied electric field.$^{54-58}$ When the diluate compartment is under dilute conditions, the
applied electric field shifts the reaction towards the formation of hydronium ($\text{H}_3\text{O}^+$) and hydroxide ($\text{OH}^-$) ions that carry on the current flow in the unit. The evidence for water-splitting in the ion-exchange resin bed in EDI is observed from the pH changes in the effluent stream and measurement of the device’s current efficiency.\textsuperscript{64}

![Diagram](https://example.com/diagram.png)

Figure 2.2. Schematic figure showing the different types of bipolar junctions formed within a resin wafer (type b applicable only to ion-conductive binders)

The mechanism for water splitting in such electro-membrane processes are poorly understood. The Second Wein effect is the theory that is used to explain water splitting in bipolar membranes which is extended for bipolar junction sites in resin wafers.\textsuperscript{64,65} It confirms that the forward rate constant of water dissociation is promoted by the electric field strength of the depletion layer. Similar to bipolar membranes, the immobile anionic moieties in the CER create an electric field electrostatically opposing diffusion of additional $\text{H}^+$ from the CER to the CER-AER junction, as depicted in Figure 2.2. The mobile $\text{OH}^-$ within the AER continuously diffuses to the AER-CER junction until the fixed cationic charges opposes the diffusion of additional $\text{OH}^-$ by generating an
opposite field. At steady-state, the flux of ions due to diffusion towards the interface equals the flux of ions due to migration in both CERs and AERs.$^{56}$

\[ J_{H^+} (\text{diffusion}) + J_{H^+} (\text{migration}) = 0 \]  \hspace{1cm} <2.15>

\[ J_{OH^-} (\text{diffusion}) + J_{OH^-} (\text{migration}) = 0 \]  \hspace{1cm} <2.16>

Due to the fixed charges on either side of the interface, an electric field, E, is produced by the resulting a potential difference between the two materials. The potential gradient \( \phi(x) \), is opposite to that of the electric field produced, \( E(x) \).$^{56}$ A relation at steady state, between the activity of the mobile ions and the electric field can be obtained by derivation using equation 2.15,

\[ J_{H^+} (\text{net}) = 0 = q[\mu_{H^+} a_{H^+} E(x) - D_{H^+} \left( \frac{da_{H^+}}{dx} \right)] \]  \hspace{1cm} <2.17>

where \( q \) is the elementary charge, \( \mu_{H^+} \) is the proton mobility, \( a_{H^+} \) is the activity of the protons, and \( D_{H^+} \) is the proton diffusivity. Substituting the Einstein relationship \( \frac{\mu_{H^+}}{D_{H^+}} = q/kT \), where \( k \) is the Boltzmann constant and \( T \) is the temperature.

\[-\left( \frac{q}{kT} \right) \left( \frac{d \phi(x)}{dx} \right) = \left( \frac{1}{a_{H^+}} \right) \left( \frac{da_{H^+}}{dx} \right) \]  \hspace{1cm} <2.18>

where \( \phi(x) \) is the potential within the ion-exchange material as a function of the distance \( x \) going from the cation-exchange site to the anion-exchange site. Integrating of equation 2.18 from the bulk of the cation-exchange material , \( \phi^{CE} \), to the bulk of the anion-exchange material, \( \phi^{AE} \), and the proton activity from the bulk of the cation-exchange material, \( a_{H^+}^{CE} \), to the bulk of the AE, \( a_{H^+}^{AE} \), yields equation 2.19

\[ E_j = ( \phi^{AE} - \phi^{CE} ) \left( \frac{kT}{q} \right) \ln(\frac{a_{H^+}^{CE}}{a_{H^+}^{AE}}) \]  \hspace{1cm} <2.19>

\[ E_j = ( \phi^{AE} - \phi^{CE} ) \left( \frac{RT}{F} \right) \ln(\frac{a_{H^+}^{CE}}{a_{H^+}^{AE}}) \]  \hspace{1cm} <2.20>
Where \( E_j \) is the contact potential between the anion-exchange material, \( \varphi_{AE} \), and cation-exchange material \( \varphi_{PE} \) and \( R \) is the ideal gas constant. The hydroxide and protons are assumed to be in equilibrium everywhere, \( K_w = a_{H^+}a_{OH^-} \) which yields

\[
E_j = (\varphi_{AE} - \varphi_{CE}) \left(\frac{RT}{F}\right) \ln(a_{H^+}a_{OH^-}) - \frac{RT}{F} \ln K_w \tag{2.21}
\]

If the activity of the protons and hydroxide were each at unity, then the interface potential would be 0.83 V.

### 2.5 Butler-Volmer equation

The Butler-Volmer equation relates the surface overpotential \( \eta_s \) to the rate of electrode reaction:

\[
i = i_o \left[ \exp \left( \frac{\alpha_a F}{RT} \eta_s \right) - \exp \left( -\frac{\alpha_c F}{RT} \eta_s \right) \right] \tag{2.22}
\]

The first term in equation 2.18 gives the anodic reaction whereas the second term determines the cathodic reaction rate. The net reaction rate is given by the difference between the two. \( i_o \) corresponds to the exchange current density which is representative of the reaction rate constant as described in chemical kinetics. The net direction of the reaction depends upon the sign of the surface overpotential. The terms \( \alpha_a \) and \( \alpha_c \) are the apparent transfer coefficients that relates to how the reaction direction favors in response to an applied potential.

Depending on the surface overpotential, the overall rate can be given by:

\[
i = i_o \exp \left( \frac{\alpha_a F}{RT} \eta_s \right) \text{ for } \alpha_a F \eta_s \gg RT \text{ or,} \tag{2.23}
\]

\[
i = -i_o \exp \left( -\frac{\alpha_c F}{RT} \eta_s \right) \text{ for } \alpha_c F \eta_s \ll -RT \tag{2.24}
\]

A special case of the Butler-Volmer equation is the Tafel equation which depicts the surface overpotential in terms of the logarithm of current density, as shown in equation 2.25.

For large cathodic current densities, taking log on both sides of equation 2.24,
\[
\log|i| = 2.303 \log{i_o} - \left(\frac{\alpha_c F}{RT} \eta_S\right) \Rightarrow \eta_S = \frac{2.303RT}{\alpha_c F} \log{i_o} - \frac{2.303RT}{\alpha_c F} \log|i| <2.25>
\]

The Tafel slope is given by \(\frac{2.303RT}{\alpha_c F}\). The Tafel slope is an indicator of reaction rate kinetics, the lower the value, the faster the electrode reaction rate kinetics.

### 2.6 Pourbaix diagram

The Pourbaix diagram is a plot of the potential vs pH (E_H-pH diagram) that depicts all possible stable phases of an aqueous electrochemical system. The copper Pourbaix diagram was used to determine the stable phases of Cu in the anolyte and catholyte used in the TRABs.

![Pourbaix Diagram](image)

Figure 2.3. Pourbaix diagrams of 0.2 M copper in (a) water and (b) 3 M NH_3 solution (simulated using Geochemist’s Workbench).

The copper Pourbaix diagrams shown in Figure 2.3 a and b, show that copper precipitates depending on the pH and the composition of the electrolyte. The copper precipitation into Cu(OH)_2 which is a parasitic reaction in the anode, can be regulated by adjusting the solution composition and the pH. Cu(OH)_2 precipitate formation occurs as shown in equation 2.26.

\[
\text{Cu(NH}_3\text{)}_4^{2+} + 4\text{H}_2\text{O} \rightarrow \text{Cu(OH)}_2(\text{s})\downarrow + 2\text{NH}_3\cdot\text{H}_2\text{O} + 2\text{NH}_4^+ <2.26>
\]
2.7 Conclusions

The theoretical concepts explained in Chapter 2 were used in the dissertation for the following purposes:

i) Understanding the ionic transport within ion-exchange membranes to understand the ion-exchange membrane properties and to conduct a systematic study on their influence on membrane capacitive deionization

ii) Developing a modified Bisquert open model with transmission lines for determining the sources of impedance in the MCDI setup

iii) Developing ionomer binders for resin wafers that show improved performance by faster ionic transport in the porous networks and understanding the mechanism of regeneration by water splitting in the bipolar junctions of resin wafers

iv) Studying the cathode kinetics by measuring the Tafel slope and exchange current density in TRABs and determining the influence of electrode coatings on cathode kinetics

v) Deducing the source of parasitic reactions within the anode in TRABs using the copper Pourbaix diagram.
Chapter 3. Experimental Methods

3.1. Introduction

This chapter discusses the experimental methods used to carry out the research disseminated in this dissertation. The chapter includes the materials used to conduct desalination experiments in MCDI and RW-EDI modules and battery discharge experiments for TRBs, synthesize ion-exchange polymer electrolytes, and to fabricate membranes, resin wafer, and electrode coatings given in section 3.2. Further, the procedure for materials synthesis and characterization, device operation is given in sections 3.3-3.5.

3.2. Materials

Commercially available activated carbon cloths (i.e., porous carbon electrodes) were washed in 1 M nitric acid at 95 °C and used as carbon electrodes (from Kuraray, Japan) and the electrodes were separated using a nylon net spacer (200 μm thickness, Sefar NITEX). Grafoil™ sheets from Graftech International were used as current collectors (10 cm x 10 cm). Commercially available Tokuyama AMX (i.e., AEM) and CMX (i.e., CEM) membranes (thickness of AMX = 140 μm, CMX= 140 μm) were used in this study. Nafion™ 211 (thickness 25.4 μm, Ion Power, Inc.) was the CEM for the perfluorinated IEM tests. The perfluorinated AEM (thickness of 25 μm, sourced from the National Renewable Energy Laboratory (NREL)) was prepared from the sulfonyl fluoride form of perfluorosulfonic acid membrane precursors made by 3M. The sulfonated poly(ether ether ketone) (SPEEK) CEM and the quaternary benzyl ammonium chloride poly(2,6-dimethyl 1,4-phenylene oxide) (QAPPO) AEM were synthesized in house (details in section 3.1.2). The polymers poly(ether ether ketone) (PEEK) was obtained from VICTREX and poly(2,6-dimethyl,1,4-phenylene) oxide (PPO) was sourced from Polysciences, Inc. Commercially available cation-exchange resins (Purolite, PFC100E (IEC=1.9 eq L⁻¹), density = 1.27 g cm⁻³) and anion-exchanges resins (Purolite, PFA400 (IEC=1.3 eq L⁻¹), density= 1.07 g cm⁻³) were used in
the resin wafer (RW) preparation. The cation-exchange resins consisted of sulfonated sodium polystyrene crosslinked with divinylbenzene. The anion-exchange resins were composed of quaternary benzyl trimethylammonium chloride polystyrene crosslinked with divinylbenzene. The chloromethylation and amination reactions for preparation of the quaternary ammonium polysulfone (QAPSf) is given in section 3.3.1. Udel® polysulfone pellets (PSf) were attained from Acros Organics, and the polymer had an average molecular weight of 60,000 g mol⁻¹. Chemicals such as: 97% sulfuric acid (H₂SO₄), sodium chloride (NaCl), 99.8% chloroform (CH₃Cl), 95% paraformaldehyde, 98% chlorotrimethylsilane, 99% stannic chloride (SnCl₄), 98% N-methyl pyrrolidine, 99% N-methyl pyrrolidone (NMP), 99.96% deuterated dimethylsulfoxide (d₆-DMSO), and 99.6% deuterated chloroform (CDCl₃), 28-30 % ammonium hydroxide in water (NH₄OH, ACS grade), and copper (II) nitrate trihydrate (Cu(NO₃)₂·3H₂O) were attained from VWR or Sigma-Aldrich and used as is. Trimethylamine (40 wt% in aqueous solution) and copper (Cu) gauze (50 mesh woven from 0.23 mm diameter wire) were obtained from Alfa Aesar. Commercially available cation-, anion-, and bipolar membranes were used for the RW-EDI stack measurements (at Argonne National Laboratory) and were obtained from Ameridia (Neosepta CMX, AMX, and BP; ASTOM Corporation, Tokyo, Japan). Poly(styrene-block-(ethylene-random-butylene)-block-styrene) (SEBS, Mw ~118,000). All chemicals were used as is. Deionized water (DI H₂O, 18.2 MΩ, < 20 ppb TOC) was produced at the time of a particular synthesis or experiment with a Milli-Q Millipore Elix 10.

3.3 For MCDI Study

3.3.1 Preparation and characterization of ion-exchange membranes

SPEEK was prepared by first dissolving PEEK in concentrated sulfuric acid (10 wt% PEEK in 98 % pure sulfuric acid) and mixing the solution for 72 hours at room temperature. The
polymer was precipitated in an ice-cold bath and repeatedly washed and filtered until the pH of the washing water was 7. A 5 wt% SPEEK solution in n-methyl pyrrolidone (NMP) was prepared and the solution was drop casted on to a 15 cm x 15 cm glass plate placed on a leveled surface in an oven. The oven temperature was then set to 70 °C and the solvent was evaporated over 24 hours. The membrane on the glass plate was immersed in deionized water to remove it and the resulting thickness of the membrane, after drying, was 24 μm.

To make QAPPO AEMs, free radical bromination was performed on PPO. A 7 wt% solution of PPO in chlorobenzene was prepared and n-bromosuccinimide was mixed into the dissolved PPO solution (0.7 moles to each mole of PPO repeat units). After heating the solution to 115 °C, azobisisobutyronitrile (AIBN), a free radical initiator (2 wt% to the amount of PPO dissolved), was added. The reaction was carried out for 12 hours prior to precipitation in methanol. The filtered polymer was redissolved in chloroform and precipitated in methanol to remove unwanted impurities. The polymer formed was dried under vacuum at room temperature for 24 hours to remove residual solvents. A 5 wt% solution of brominated PPO (BrPPO) in NMP was prepared. To the resulting solution, trimethylamine (TMA, 40 wt% in water) was added to the dissolved BrPPO in the molar ratio of 3:1 (TMA to bromomethyl groups as determined from $^1$H NMR as shown in Figure A.1. in the Appendix). The resulting mixture was allowed to react overnight at 40 °C. The aminated polymer solution was then drop casted on to a leveled 15 cm x 15 cm glass plate in an oven at 70 °C to form QAPPO membranes with bromide counterions.

The SPEEK CEM and QAPPO AEMs were ion-exchanged to the sodium and chloride counterion forms, respectively, before testing in MCDI and characterization. Ion-exchange of SPEEK to the sodium ion form was performed by immersing the membrane in 1 M sodium hydroxide (NaOH) solution for 24 hours followed by excess rinsing and immersing in deionized
water to remove the excess salt. QAPPO was ion-exchanged to the chloride form by immersing the membrane in 1 M sodium chloride (NaCl) solution and following the same rinse procedure to remove excess ions. Figures 3.1 shows the reaction mechanism for SPEEEK and QAPPO synthesis and Figure 3.2 shows the chemical structures for the perfluorinated AEM and Nafion CEM.

3.3.2. Electrochemical Impedance Spectroscopy

Hybrid *in-situ* EIS was performed with a Gamry Reference 3000 potentiostat/galvanostat to analyze current distribution resistances in the MCDI cell with different IEMs. This electroanalytical technique was used to apply a background direct current of 0 mA, 20 mA, or 40 mA with a 2 mA perturbation current and ten data points were collected every decade in the frequency range of 100,000 Hz to 0.1 Hz. The individual resistance components within the MCDI
were identified and values extracted from the Nyquist plots using an electric circuit equivalent (ECE) model.

![Chemical structures of a.) Nafion™ 211 CEM in Na⁺ form and b.) perfluorinated AEM in Cl⁻ form](image)

Figure 3.2. Chemical structures of a.) Nafion™ 211 CEM in Na⁺ form and b.) perfluorinated AEM in Cl⁻ form

### 3.3.3 Measurement of membrane properties

The IEMs properties were characterized in terms of thickness, ionic conductivity, permselectivity and area specific resistance (ASR). Membrane thickness was measured using a micrometer. The ionic conductivity of these IEMs (in Na⁺ form for CEMs and Cl⁻ form for AEMs) was measured in deionized water, 250 ppm NaCl solution, and a 540 ppm NaCl solution. A four-point platinum cell was used to measure ionic conductivity (κ) of the IEMs. EIS was collected in the frequency range 100,000 Hz to 0.01 Hz with ten data points per decade and an alternating current perturbation of 1 mA. Equation 3.1 was used to determine the ionic conductivity of the IEMs. The membrane resistance values from EIS experiments were determined from the Bode plots at phase angle values of 0°.

Equation 3.2 gives the area specific resistance from ionic conductivity of the membrane and its thickness. Permselectivity of the membranes was calculated from the transference number

37
(Ti) of the membranes, where the transference numbers were determined by measuring the IEMs’ junction potential when partitioning two liquid solutions of different concentrations (0.1 M NaCl and 0.001 M NaCl solutions).\textsuperscript{44,67} Using two silver/silver chloride reference electrodes, the membrane potential was recorded. Equation 3.3 relates membrane potential to counterion transference number. Equations 3.4 and 3.5 were used to determine membrane permselectivity from transference number of the counterion. The ideal permselectivity for an IEM is 1.

\[ \kappa = \frac{d}{L \cdot W \cdot R} \quad <3.1> \]

\(d = \) distance between the electrodes where the potential drop is measured

\(L = \) membrane thickness

\(W = \) width of the membrane thickness in the 4 point probe

\(R = \) membrane resistance

\[ ASR = \frac{L}{\kappa} \quad <3.2> \]

\[ E = \frac{RT}{2F} [T_{\text{counter}} \ln \frac{a_{\text{counter}}^{\text{conc}}}{a_{\text{counter}}^{\text{diff}}} - T_{\text{co}} \ln \frac{a_{\text{co}}^{\text{conc}}}{a_{\text{co}}^{\text{diff}}}] \quad <3.3> \]

\[ \phi_{\text{CEM}} = \frac{T_{\text{CEM}, \text{c}}}{T_{\text{c}}} \quad <3.4> \]

\[ \phi_{\text{AEM}} = \frac{T_{\text{AEM}, \text{a}}}{T_{\text{c}}} \quad <3.5> \]

\(T_{\text{counter}}\) and \(T_{\text{co}}\) = the transport number of the corresponding counterion and co-ion of IEM type

\(\phi = \) the permselectivity of the membrane

\(T_{\text{a}}\) or \(T_{\text{c}}\) = transport number for anion (a) and cation (c).

3.3.4 MCDI cell setup and experiments

The MCDI unit cell was operated in a single flow through cell that consisted of a pair of Grafoil\textsuperscript{TM} current collectors, carbon electrodes, IEMs (one AEM and one CEM), and a nylon spacer. Figure 3.3a shows the arrangement of the materials in the single flow through cell, while Figure 3.3b is a picture of the home-built MCDI setup. A feed solution of synthetically prepared NaCl solutions (250 ppm or 540 ppm) was pumped into the MCDI unit cell using a peristaltic...
pump at the rate of 10 mL min\(^{-1}\). The salt water feed was not deaerated and hence it was assumed to be saturated with oxygen (note: the dissolved oxygen concentration was approximately 8.1 mg L\(^{-1}\) – data from the literature).\(^{58}\) The effluent steam from the unit cell was monitored in terms of total dissolved salt (TDS) concentration and pH using a conductivity and pH probe placed in line of the exit stream. The charging durations were kept constant for each set of IEMs tested in the MCDI unit to ensure that the same amount of charge was supplied to the MCDI unit with different IEMs and allow for uniform testing protocol. Table 3.1 lists the class of IEM chemistries evaluated for MCDI. Note: Positive electrode and negative electrode designations used throughout this document correspond to charge mode for MCDI (i.e., removal of salt from water).

The MCDI experiments were conducted with two different salt concentrations of NaCl: 250 ppm and 540 ppm. The first set of experiments operated the MCDI cell under constant current mode at 0.5 mA cm\(^{-2}\) for 250 ppm feed inlet concentration. The second set of experiments was carried out at 0.9 mA cm\(^{-2}\) for 540 ppm. The two set of experiments with 250 ppm and 540 ppm feeds had a charging cycle duration of 2 and 2.5 minutes respectively. The cell was discharged at the same current density value magnitude, but in negative polarity. The cell was discharged until the corresponding cell voltage reached zero indicating complete discharge. A constant current operation was selected for MCDI experiments because of the ability to control the effluent salt concentration in this mode.\(^{15,69,70}\) 8 charge-discharge cycles were performed for each MCDI experiment of which the first 3 were not considered in the analyses because the system took some initial cycling to reach dynamic equilibrium. In designing our experimental protocol, a baseline configuration of MCDI with Tokuyama IEMs was used to identify an appropriate current density value for charge-discharge cycling that would not exceed a voltage limit of 1.6 V to prevent significant water splitting. Furthermore, it was not anticipated that carbon corrosion would be so
prevalent as it occurs at extreme pHs and its kinetics are slow. The justification for the 1.6 V cell limit was: i.) it enables a large enough current density to removal salt at measurable rates, while also ensuring that parasitic side-reactions were not significant; and ii.) it is in-line with other reports in the literature.19,69,72

Figure 3.3. a.) Arrangement of material components in a single flow through MCDI cell. b.) A photograph of the home-built MCDI setup.
Table 3.1 Flow cell configuration of MCDI with the different IEM pairs.

<table>
<thead>
<tr>
<th>IEM</th>
<th>Negative electrode</th>
<th>Positive electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tokuyama IEMs 1</td>
<td>Tokuyama CEM</td>
<td>Tokuyama AEM</td>
</tr>
<tr>
<td>Perfluorinated IEMs 2</td>
<td>Nafion&lt;sup&gt;TM&lt;/sup&gt; CEM</td>
<td>Perfluorinated AEM</td>
</tr>
<tr>
<td>PAE IEMs 3</td>
<td>SPEEK CEM</td>
<td>QAPPO AEM</td>
</tr>
</tbody>
</table>

3.3.5 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy was performed using the Scienta Omicron GmbH with a mono AlKα source radiation. Hi-res XPS elemental analysis performed for carbon 1s on the pristine carbon cloth and the positively charged electrode and negatively charged electrode post running the MCDI desalination cycles in the case of each configuration (8 cycles with different current density operation and a feed flow rate of 10 mL min<sup>−1</sup>).

3.4 For RW-EDI Study

3.4.1 Preparation and characterization of ionomer binders

Poly(arylene ether) ionomer synthesis procedures

PEEK was sulfonated based on our previous work as described in section 3.2.2,<sup>14</sup> the procedure given in section 3.2.2. However, the degree of sulfonation (DS) in PEEK was monitored by assaying the reactor periodically throughout the reaction. After an aliquot was removed from the reactor, the sample was precipitated in DI H<sub>2</sub>O and rinsed excessively in DI H<sub>2</sub>O. After drying in a fume hood, the sample was dissolved in d6-DMSO and analyzed via <sup>1</sup>H NMR (see Appendix Figure A.2. for synthesis of SPEEK and <sup>1</sup>H NMR spectrum with assignments). This procedure was repeated two or three times until the desired DS value of SPEEK was obtained. After the desired DS value was achieved, the remainder of the SPEEK in sulfuric acid batch was precipitated and
rinsed as shown in section 3.2.2. In this report, a DS of 0.4 was found suitable for making conductive but mechanically robust RWs. A high DS value (i.e., > 0.5) resulted in excess swelling of the RW. The ionomer solution used to prepare the resin wafer was prepared by dissolving SPEEK in NMP to make a 14 wt% solution.

QAPSf ionomer: Udel® PSF was chloromethylated following the procedure by Arges et al. Udel® PSF was dissolved in CHCl₃ at room temperature to prepare a 2 wt% solution in a round bottom flask with equipped with a magnetic stir bar. Paraformaldehyde and chlorotrimethylsilane (5:5:1 molar ratio to PSf repeat unit) was added to the flask. The flask was sealed with a rubber septum and the silicon oil bath containing the flask was heated to 55 °C. Then, SnCl₄ (Lewis acid catalyst), a 2 wt% ratio to PSf added, was added slowly by syringe through the rubber septum. To monitor the degree of chloromethylation (DC) of PSf, samples were assayed from the flask over time. After withdrawing an aliquot from the flask, the chloromethylated polysulfone (CMPSf) solution was precipitated in methanol (5:1 volume ratio) and then vacuum filtered. The degree of chloromethylation (DC) of the batch obtained was 0.88 (see Figure 3.4 for QAPSf synthesis and Figure A.2. b-c for ¹H NMR spectra of CMPSf and QAPSf). Any CMPSf batch used above 0.9 DF yielded a QAPSf material that resulted in a swollen resin wafer with poor mechanical integrity.

To prepare the QAPSf solution used to make RWs, chloromethylated polysulfone in (NMP) was dissolved in NMP to make a 14 wt% solution. 1-methyl pyrrolidine was then added to the solution in the ratio of 2:1 to the amount of chloromethyl groups per repeat unit in CMPSf. The conversion of chloromethyl groups to quaternary benzyl N-methylpyrroloidinum chloride groups was carried out for 24 hours at 60°C. The ionomer solution was then cooled to room temperature and stored until use in the manufacture of the RW.
3.4.2 Resin wafer preparation

Conventional resin wafer (RW) synthesis: Synthesis of the conventional RW, a replica of Argonne’s benchmark material, is done by the addition of cation-exchange resins and anion-exchange resins in the ratio 1:1.3, to which polyethylene binder and sodium chloride are added to yield a mix ratio by mass of 2.0:1.0:0.5 of resins to binder to salt. The resulting mixture is packed to a resin mold. The typical dimensions of the mold for this work was 14 cm x 14 cm x 0.3 cm. The mold is hot pressed around 109 °C and with 2 metric tonnes of force for 30 minutes.

RW with cation-exchange ionomer (CEI) binder: A resin mixture is prepared by adding cation-exchange resins and anion-exchange resins in the ratio 1:1.3 and 13.8 wt% solution of SPEEK in NMP and sodium chloride in the mass ratio of 2.4:2:1 of resins to binder to salt. The resin mixture is packed into a mold and dried in the oven at 60 °C for 12 hours to remove residual solvent. It is then hot pressed at 125 °C for 1.5 hours with 2 metric tonnes of force. The same procedure was followed for the resin-wafer consisting of anion-exchange resin particles only with
the CEI binder. Here, the mixture was prepared in the ratio of 2.4:2:1 of resins particles to CEI binder to salt.

RW with anion-exchange ionomer (AEI) binder: A resin mixture is prepared by adding cation-exchange resins and anion-exchange resins in the ratio 1:1.3 and 14 wt% solution of QAPSf in NMP and sodium chloride in the mass ratio of 2.4:2:1 of resins to binder to salt. The resulting mixture is packed into a mold and dried in the oven at 60 °C for 12 hours to remove residual solvent. It is then hot pressed at 150 °C for 1.5 hours at 2 metric tonnes. The same procedure was followed for the resin-wafer only featuring cation-exchange resin particles with the AEI binder. This mixture is prepared with the ratio of 2.4:2:1 of resin particles to AEI binder to salt.

Figure 3.5. Manufacturing scheme to prepare ionomer binder RWs

3.4.3 Ionic conductivity measurements

Flow-through conductivity tests were performed using the 4-point probe method and an LCR meter (IM3533-01, Hioki USA, Cranbury, NJ). Wafers were cut into 1 in. × 1 in. squares,
inserted into gaskets, and installed in custom-built flow-through cells consisting of stainless-steel electrodes as shown in Figure 3.6a. Five cells were arranged in series to perform measurement of five wafers simultaneously. Prior to each measurement, wafers were equilibrated in NaCl solution until steady state was achieved. Conductivity was measured as impedance using a frequency of 100 kHz and a voltage of 50 mV. The NaCl solution measurement was conducted using an identical apparatus excluding the wafer material. The wafers were rinsed thoroughly with ultrapure water after measurements were made. Duplicate measurements were performed for the mixed resin with CEI binder and mixed resin with PE binder at each NaCl concentration using freshly prepared NaCl solution. The electrical resistance across the water was continuously monitored with two electrodes during continuous flow until a steady resistance value was achieved. Equation 6 was used to determine the samples’ ionic conductivity under a flow-through setting.

Figure 3.6. Flow-through and static mode conductivity. a.) Schematic of setup used to measure flow-through conductivity of RWs. b.) High-throughput, custom-built 2-pt ionic conductivity (κ) static cell for downselecting new RW materials.

Static conductivity tests were performed using a 2-point probe method (see Figure 3.5b). The cell consisted of platinum foil working electrodes adhered with silver epoxy onto stainless steel collectors in a polytetrafluoroethylene (PTFE) housing. A stainless-steel screw was used for making contact between the electrodes and the RW samples. The RWs were immersed and
equilibrated in NaCl solution for 5 minutes. Conductivity was measured using galvanostatic electrochemical impedance spectroscopy as mentioned in section 3.1.3, with 1 mA perturbation and at 0 mA background current. The high frequency resistance from the Nyquist plot was used in Equation 3.6. The NaCl solution measurement was conducted using an identical apparatus and procedure excluding the wafer material.

\[ \kappa = \frac{t}{A R} \]  

<3.6>

Where \( \kappa \) denotes the ionic conductivity of the wafer, \( t \) denotes the wafer thickness, \( A \) denotes the surface area, and \( R \) is the measured resistance value.

3.4.4 Imaging by scanning electron microscopy (SEM)

Cross-sectional and surface images of the resin wafer under were imaged under vacuum with a Quanta™ 3D Dual beam focused-ion beam scanning electron microscope instrument operated at 5 kV with field emission gun. The working distance ranged from 6-13 mm. For imaging the cross-section of resin-wafers, the samples were cut by pouring liquid nitrogen over them and cutting the sample immediately across the thickness. For the PE binder RWs only, a thin layer of 0.5 nm palladium-platinum was sputtered on the samples to enhance the contrast during imaging.

3.4.5 Porosity measurements

A blue dextran solution (Sigma Aldrich D5751) of 5 g L\(^{-1}\) concentration was prepared, and the concentration recorded as \( C_{\text{initial}} \) was made by recording the UV-Vis absorbance of the solution at 620 nm and using a calibration curve that relates absorbance at 620 nm to concentration of blue dextran. The resin-wafer sample is then immersed into DI H\(_2\)O to hydrate the ion-exchange materials. Then, the wafer was immersed in the 5 g L\(^{-1}\) blue dextran solution. After the immersion for a period of time, the excess blue dextran solution residing on the wafer surface was removed
by blot drying using a Kimwipe. The adsorbed blue dextran from the wafer was purged from the resin-wafer using DI H$_2$O, and the total volume of water used is recorded as $V_{\text{final}}$. The blue dextran concentration of the rinse solution was recorded as $C_{\text{final}}$ by measuring the UV-Vis absorbance at 620 nm and using a calibration curve that relates absorbance at 620 nm to concentration of blue dextran. The free-liquid-void-space (FLVS), or also known as pore volume and the porosity (P), are estimated using the following equations (3.7-3.8):

$$V_{\text{FLVS}} = \frac{C_{\text{final}} \times V_{\text{final}}}{C_{\text{initial}}} \quad <3.7>$$

$$P = \frac{V_{\text{FLVS}}}{w \times l \times h} \quad <3.8>$$

Where $w$ is the width, $l$ is the length, and $h$ is the height of the wafer.

### 3.4.6 Evaluation of ion-exchange capacities of resin wafers

The theoretical IECs of the resin wafers were computed by averaging the IEC values of each of the components by weight and volume (see equations 3.9 and 3.10).

$$IEC \text{ (by weight)} = \frac{\text{IEC}_{\text{CER}} \times m_{\text{CER}} + \text{IEC}_{\text{AER}} \times m_{\text{AER}} + \text{IEC}_{\text{binder}} \times m_{\text{binder}} \times \text{x}_{\text{polymer}}}{m_{\text{Total}}} \quad <3.9>$$

$$IEC \text{ (by volume)} = \frac{\text{IEC (by weight)} \times m_{\text{Total}}}{V_{\text{Total}} \times (1-\theta)} \quad <3.10>$$

Where $\text{IEC}_{\text{CER}}, \text{IEC}_{\text{AER}}, \text{IEC}_{\text{binder}}$ denote the ion-exchange capacities of the cation-exchange, anion-exchange resins and binder respectively in milliequivalents per gram. $m_{\text{CER}}, m_{\text{AER}}$ and $m_{\text{binder}}, m_{\text{Total}}$ denote the weight of the cation-exchange, anion-exchange resins, binder and total weight of the wafer respectively. $\text{x}_{\text{polymer}}$ denotes the weight ratio of polymer in the ionomer binder used and $V_{\text{Total}}$ denotes the total volume of the wafer which is measured as the product of the wafer area and
wafer thickness. \( \Phi \) denotes the wafer porosity. Salt weight is not considered in these calculations as it is leached out by immersing the wafer in DI water.

### 3.4.7 Resin-wafer electrodeionization stack setup and experiments

RW-EDI experiments were conducted using a homemade electrodialysis stack (see Figure 3.7) consisting of a stainless-steel cathode and dimensionally stable anode (DS A). Ion exchange membranes (active area = 14 mm\(^2\)) were arranged in an alternating pattern as shown in Figure 3.7 to create feed/diluate compartments (~3.0 mm thick) containing resin wafers and concentrate compartments (~1.0 mm thick) for a total of four cell pairs. Experiments were conducted in batch mode using an initial concentration of 5 g L\(^{-1}\) NaCl for both the feed and concentrate solutions, a feed flow rate of 25 mL min\(^{-1}\), a concentrate flow rate of 50 mL min\(^{-1}\), and cell voltage of ~1 V/cell pair.

![Figure 3.7. RW-EDI partial stack assembly. Each cell pair contains an anion exchange membrane (AMX), cation exchange membrane (CMX), resin wafer (IEX resin), and spacer. Bipolar membranes (BP) separate the electrode rinse compartments from the remainder of the stack.](image-url)

Chloride ion concentrations were measured with ion chromatography (882 Compact IC plus; Metrohm, Riverview, FL) equipped with chemical and CO\(_2\) suppression systems. Analyses were performed with Metrosep A Supp 5 150/4.0 analytical and guard columns, 3.2 mM
Na₂CO₃/1.0 mM NaHCO₃ as the eluent, a flow rate of 0.7 mL min⁻¹, and 20 μL sample loop and injection volumes.

The energy consumption for salt removal in kWh per kg of salt removed during the RW-EDI demonstration was calculated by equation 3.11:

\[
\text{Energy consumed (kWh kg}^{-1}) = 2.78 \times 10^{-7} \times \frac{\int I dt}{m} <3.11>
\]

Where \( V \) is the constant voltage applied per cell pair in V, \( I \) denotes the current in A which is integrated over the charging time, \( t \) is the time, \( m \) denotes the mass of salt removed in kg, and \( 2.78 \times 10^{-7} \) is the unit conversion factor from Joules to kWh.

3.4.8 Experimental setup and method for water splitting measurements

Water splitting in bipolar junction interfaces of the resin wafers and bipolar membranes was assessed using a home-built two compartment, 4-point electrochemical cell setup (see Figure 3.8). The cell consists of two Pt/Ir working electrode meshes, one in each compartment, and Ag/AgCl reference electrodes with Luggin capillaries intimately pressed against the membrane interfaces (in one instance a bipolar membrane and in another instance RW materials). The potential drop is measured across the RW bipolar membrane samples. The active area for the cell was 1.27 cm², and the concentration of supporting electrolytes in each compartment was aqueous 0.5 M Na₂SO₄ electrolyte. Linear sweep voltammetry (LSV) was used to assess the current-voltage relationships of the samples in the 4-point cell. The LSV scan was carried out from 0.0 to 2.0 V at a 5 mV s⁻¹ scan rate.
Figure 3.8. Water splitting experiments a.) Schematic of the two-compartment cell b.) Junction of the cell where wafer sample is sandwiched between IEMs in the four-point bipolar measurement cell. c.) Photograph of the home-built cell in our laboratory.
3.5. For TRBs Study

3.5.1 Preparation of electrolytes

The anolyte solution consists of 0.2 M Cu(NO$_3$)$_2$, 3 M NH$_4$OH, and 3 M NH$_4$NO$_3$ in DI H$_2$O, while the catholyte consists of 0.2 M Cu(NO$_3$)$_2$ and 3 M NH$_4$NO$_3$ in DI H$_2$O. However, it should be noted that the NH$_4$OH is not added to the anolyte until the start of the electrochemical experiments. The 0.2 M Cu(NO$_3$)$_2$ and 3 M NH$_4$NO$_3$ solutions in DI H$_2$O, as well as the 0.2 M Cu(NO$_3$)$_2$ in DI H$_2$O alone, are a pale blue. The 0.2 M Cu(NO$_3$)$_2$ and 3 M NH$_4$NO$_3$ solution turns royal blue upon the addition of NH$_4$OH. A Teflon® coated magnetic stir bar was added to both Pyrex® glass containers featuring the liquid solutions plumbed to the Scribner Redox Flow Battery System

3.5.2 Anion-exchange membrane and ionomer coated electrode preparation

Chloromethylation of SEBS was carried out using the procedure by Wang et al, similar to the Chloromethylation of PSf as described in section 3.2.2.$^7$ However, the reaction mixture for SEBS chloromethylation was heated to 80 °C. The reaction was terminated once the degree of chloromethylation (DC) of SEBS was 0.13 (Figure 6.1; note: it took 7 days to complete the reaction). At the end of the reaction, the solution was cooled and precipitated in methanol using the aforementioned ratio. The solid was vacuum filtered, dried, re-dissolved in chloroform at 5 wt% and then precipitated in methanol (5:1 ratio) to remove impurities. The solid was collected by vacuum filtration and then vacuum dried for 16 hours at room temperature. The reaction mechanism is shown in Figure 3.9.

To prepare the QASEBS membrane, CMSEB was dissolved in chlorobenzene to prepare a 5 wt% solution. 9 mL of the CMSEBS solution was drop casted on to 9 cm x 9 cm glass plates and the solvent was evaporated from the membrane at 60 °C. The membrane was peeled off the glass
plate and then immersed in a 40 wt% trimethylamine aqueous solution for 48 hours at room temperature. Afterwards, the membrane was rinsed with copious amounts of deionized water (DI \( \text{H}_2\text{O} \)) to remove residual trimethylamine and then dried in a fume hood overnight.

![Chemical structures and reaction mechanism](image)

**Figure 3.9. Reaction mechanism for preparation of QASEBS**

To prepare the SPEEK ionomer coating, SPEEK was prepared as described in section 3.1.2. To make the ionomer solution, a 2 wt% of SPEEK was dissolved in n-methyl pyrrolidone (NMP) and the resulting solution was used as the ionomer. This solution was spray painted directly onto
the Cu mesh. After several spray applications, the Cu mesh was placed on a hotplate at 100 °C to evaporate the NMP solvent. The applications and drying were continued until a loading of 0.44-0.75 mg cm$^{-2}$ SPEEK on a 5 cm$^2$ Cu mesh was achieved.

3.5.3 Non-zero gap and zero gap mode setup of Thermally regenerative ammonia battery (TRAB)

A non-zero gap mode of operation was tested using a two-compartment glass cell (i.e., H-cell) from Pine Research Instruments (Figure 3.10). The AEM divided the anolyte and catholyte compartments. Each compartment contained a copper wire electrode with a 1.628 mm diameter and that was 3.5 cm long when immersed in the electrolytes. Both the cell compartments were subjected to continuous stirring with Teflon® coated magnetic stir bars to reduce mass transfer resistances.

![Figure 3.10. Schematic of two-compartment glass cell (H-cell) used for non-zero gap mode operation and study of cathode side reaction kinetics.](image)
3.5.4 TRB experiments

Figure 3.11. a) Schematic of the zero-gap AFB used to convert low-grade waste heat to electrical energy. b) Photograph of the bench-scale AFB setup and schematic of the assembly of components in the zero-gap AFB. Each of the components are labeled and they are: a- anodized aluminum housing plates, b- gold plated current collectors, c- graphite serpentine flow field channel, d- rubber gaskets, e- copper mesh electrodes, f- AEM.

Figs. 3.11a and 3.11b show the zero gap AFB design and cell hardware for electrochemical experiments. The 5 cm² active cell was assembled with the following order of cell components: gold current collector, serpentine style graphitic carbon flow field, a Cu mesh electrode (with or
without ion selective ionomer coating), AEM, Cu mesh electrode (with or without ion selective ionomer coating), serpentine style graphitic carbon flow field, and gold current collector. The cell was sealed with Teflon® and rubber gaskets placed over the AEM-Cu mesh assembly that comes into contact with the serpentine style flow fields. The assembled cell was sealed under 40 lb-in of force. The solution flowrates for the anolyte and catholyte compartments was set to 10 mL min\(^{-1}\).

The polarization curves were attained using a programmed sequence of chronopotentiometry experiments using Gamry 3000 Reference Potentiostat. The voltage was assessed in the chronopotentiometry runs starting at open-circuit voltage with a 10 mA increment from open-circuit for each scan. The power density (P) was determined by \( P = i \times V \) where ‘i’ is the cell current density (A m\(^{-2}\) – geometric area) for a given cell voltage ‘V’. EIS was performed at open circuit voltage to identify and quantify different sources of resistances within the cell (e.g., the ohmic and charge-transfer resistances) using the same procedure as mentioned in section 3.1.3.

3.5.5 Cathode polarization studies

The cathode kinetics were evaluated by collecting polarization behavior of the cathode side as the working electrode and using a HgO/Hg/KOH (4.24 M) reference electrode (standard potential, \( E_0 = 0.098 \) V vs. SHE). The anode in the other compartment served as the counter electrode. Polarization behavior was assessed by performing linear sweep voltammetry (LSV) with a scan rate of 5 mV s\(^{-1}\) across the voltage range of 0 to 1.0 V using a Gamry 3000 Reference Potentiostat. The Tafel slope and exchange current density data were extracted from the LSV data. The tafel plot represents the log of current densities versus surface overpotential (\( \eta_s \)) obtained from the LSV data. To calculate \( \eta_s \), the cell potential values (E) versus HgO/Hg/KOH were converted into E vs SHE, by adding the conversion factor for HgO/Hg/KOH to SHE (+0.098 V). The potential vs. SHE was iR corrected for each measured value at a particular current. The ‘R’ term
in iR was determined from the HFR through impedance spectroscopy. This corrected potential value ($E'$) was subtracted from the standard half-cell potential for the $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$ reduction reaction in the cathode ($E^0_c = 0.34 \text{ V}$). This yielded the surface overpotential ($\eta_s$) at different current density values. Equations 12-14 were used for these calculations.

$$E_{\text{iR corrected},c} = E_{\text{measured},c}(\text{vs SHE}) - iR \tag{<3.12>}$$

$$\eta_{s,c} = E_{\text{iR corrected},c} - E^0_c(\text{vs SHE}) \tag{<3.13>}$$

$$\log i = \frac{\alpha_c zF}{2.303RT} \eta_{s,c} + \log i_o \tag{<3.14>}$$

$E_{\text{measured},c}(\text{vs SHE})$: Cathode potential measured in Volts vs SHE

$E_{\text{iR corrected},c}$: Cathode potential corrected for ohmic resistance from electrolyte in Volts

$i$: Current density in A cm$^{-2}$

$i_o$: Exchange- current density in A cm$^{-2}$

$R$: HFR measured using EIS in $\Omega$ cm$^2$

$E^0_c$: Cathode equilibrium potential in Volts

$\eta_{s,c}$: Cathode surface overpotential in Volts

$\frac{\alpha_c zF}{2.303RT}$: Tafel slope term

Anode kinetics could not be evaluated in this work due to the large fraction of parasitic side reactions (e.g., reaction of the copper electrode with oxygen in a basic environment) that competed with the Cu oxidation reaction with the ammonia.
3.5.6 Evaluation of Faradaic efficiencies of electrodes

The Faradaic efficiency of the individual electrode reactions in the zero gap AFB cell at room temperature were calculated for both pristine Cu and SPEEK coated Cu electrodes. This procedure was carried out by operating the AFB cell under a constant voltage (0.2 V) for 10 minutes with each type of electrode (coated and non-coated). Both experiments were conducted in the AFB cell employing a QASEBS AEM as separator and a zero gap design. The weight values of the Cu electrodes were recorded before and after the experiments. For the cathode, some Cu was deposited on the flow field and hence the change in mass for the flow field was also assessed. Equation 15 was used to calculate the anode and cathode Faradaic efficiencies in each case.

\[
\text{Faradaic efficiency (\%)} = \frac{\int I \times dt}{\Delta m \times n \times F / M} \times 100
\] <3.15>

I: current discharged during the constant voltage (A)

\(t\): time (s)

\(\Delta m\): change in mass of the electrode before and after operation (g)

n: number of electrons participating in the redox reaction

F: Faraday’s constant (C mol\(^{-1}\))

M: molecular weight of the reactant (g mol\(^{-1}\))

3.5.7 Recyclability and cell regeneration

The stability of the zero gap AFB cell was examined at room temperature by operating it under constant voltage hold of 0.3 V at intervals of 5 mins and alternating the anolyte and catholyte flow paths for 7 cycles. This experimental setup inhibited complete dissolution of the anode Cu
electrode. A low flow rate (2 mL min\(^{-1}\)) was used to reduce exhaustion of the electrolyte reactants. Additionally, fresh anolyte and catholyte was used for each cycle.

### 3.5.8 Evaluation of membrane conductivity

The Selemion\textsuperscript{TM}, QASEBS AEM were ion-exchanged into the nitrate form by immersing the AEMs in 0.1 M Cu(NO\(_3\))\(_2\) for 24 hours and then rinsed with DI water to remove any excess salts. Similarly, the SPEEK CEM was ion-exchanged into its Cu\(^{2+}\) form. These AEMs and CEM were measured for the membrane resistance using EIS, using the same procedure as described in section 3.2.3.
Chapter 4. Low-Resistant Ion-Exchange Membranes for Energy Efficient Membrane Capacitive Deionization (MCDI)

4.1 Introduction

Membrane capacitive deionization (MCDI) is promising, energy efficient desalination technique\textsuperscript{75,76} that has gained recognition commercially for desalination of brackish waters, selective removal and concentration of ions.\textsuperscript{77,19} It is known that freshwater is a limited resource (0.7\% of Earth’s water supply) and due to an incremental population and economic activity, there is an increasing drive towards water reuse rather than freshwater withdrawals. Capacitive deionization (CDI), and MCDI, are attractive technologies for water desalination due to their low energy consumption of operation and the ability to recover a substantial fraction of the energy for separations. Because of the energy recovery, the overall energy consumption for desalination of brackish water streams was shown to be as low as 0.26 kWh m\textsuperscript{-3} (or 18.91 kT ion\textsuperscript{-1}, constrained to a 50\% water recovery with 83\% energy recovery upon discharge) making it more efficient than reverse osmosis (note: this result was for a 10 mM reduction in salt concentration).\textsuperscript{19} However, upon exploring the focus of materials research for MCDI, most studies investigate new carbon electrode designs with greater salt storage capacity and high conductivity\textsuperscript{78,79}. Research on membrane materials for improving MCDI performance and energy efficiency has been negligible. Primarily, previous MCDI reports have incorporated commercially available electrodialysis membranes that are thick and mechanically robust\textsuperscript{80,81}. Unlike the membranes for ED, IEMs for MCDI, do not function as separators for liquid compartments and are just a conformal layer for ion-selectivity.\textsuperscript{82,83,84} Hence the incorporation of a thinner IEM seems justified.

This chapter was previously published as, Varada Menon Palakkal, Juan E. Rubio, Yupo J. Lin and Christopher G. Arges, “Low-Resistant Ion-Exchange Membranes for Energy Efficient Membrane Capacitive Deionization (MCDI)” ACS Sustainable Chem. Eng. 2018, 6, 11, 13778-13786\textsuperscript{82}
However, there is a lack of clarity on how IEM properties would impact MCDI performance and energy consumption. Therefore, the motivation for a systematic investigation on IEMs for MCDI was aimed at comprehending how IEM properties influence the performance parameters for MCDI – i.e., salt removal efficiency, energy expended for salt removal and coulombic efficiency. This chapter reports the results and discussions on this study.

4.2 Results and Discussion

4.2.1 Evaluation of membrane properties

Table 4.1 Thickness, ionic conductivity, and permselectivity values of IEMs used in MCDI experiments

<table>
<thead>
<tr>
<th>MCDI dataset</th>
<th>Membrane type</th>
<th>Thickness (µm)</th>
<th>Ionic Conductivity (mS cm⁻¹)</th>
<th>Area specific resistance (ohm-cm²)</th>
<th>Perm-selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Tokuyama CEM</td>
<td>141</td>
<td>5.9</td>
<td>2.39</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>Tokuyama AEM</td>
<td>141</td>
<td>5.4</td>
<td>2.61</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>Nafion™</td>
<td>25</td>
<td>7.7</td>
<td>0.32</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Perfluorinated AEM</td>
<td>25</td>
<td>15.2</td>
<td>0.16</td>
<td>0.92</td>
</tr>
<tr>
<td>2</td>
<td>SPEEK CEM</td>
<td>24</td>
<td>13.2</td>
<td>0.18</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>QAPPO AEM</td>
<td>55</td>
<td>10.7</td>
<td>0.51</td>
<td>0.97</td>
</tr>
</tbody>
</table>

Table 4.1 reports the characteristics of IEMs used in this study. The various properties measured and reported were membrane thickness, ionic conductivity, and permselectivity. The perfluorinated based IEMs and the PAE based IEMs were both thinner in comparison to the commercially available Tokuyama membranes. Also, the PF and PAE based IEMs displayed
higher ionic conductivity when measured in DI water, 250 ppm NaCl as well as 540 ppm NaCl. The area specific resistance (ASR) values were calculated by dividing the thickness of the IEM over its conductivity value as shown in equation 2.3. Here, the IEMs were assumed to conduct ions in an isotropic manner and thus the in-plane conductivity values were sufficient for calculating the ASR values. The ASR captures the areal resistance of the IEM in MCDI by combining both ionic conductivity and IEM thickness. The combined effect of higher ionic conductivity and low membrane thickness translated to a 5 to 10 fold reduction in ASR for the perfluorinated and PAE IEMs over the Tokuyama IEMs for a given electrolyte solution composition. This drastic reduction in ASR predicted better MCDI performance with the perfluorinated and PAE IEMs which would translate to greater energy of efficiency of MCDI. Finally, all IEM types demonstrated high selectivity values, as shown in the table- 0.92 or greater, implying minimal co-ion adsorption.

4.2.2. Figures of merit for MCDI

After IEM characterization, the different sets of IEMs were tested in the home-built single-cell MCDI setup. Figure 4.1a depicts the cell voltage response under constant current charge-discharge cycles with the different types of IEM chemistries evaluated with a 250 ppm sodium chloride solution feed. Figure 4.1b shows the corresponding response of the effluent stream’s total dissolved salt content (mg L\(^{-1}\)) from the MCDI cell. Figure 4.1a shows that the perfluorinated IEMs displayed a considerably lower maximum voltage apex (by about 450 mV) in comparison to Tokuyama IEMs and PAE IEMs. Whereas, a slightly lower voltage apex was observed for the PAE IEMs when compared to the Tokuyama IEM as baseline data. The lower voltage values with the alternative IEMs indicated less energy consumption per ion removed.

Upon looking at the effluent concentration profile for the MCDI operation with the different IEMs, the lowest effluent salt concentration attained varied. The PAE IEMs gave the
greatest salt removal when compared to the other IEMs. Whereas, the salt removal with perfluorinated IEMs was marginally better than the Tokuyama IEMs. If the MCDI configuration had achieved 100% coulombic efficiency, then the salt removal rate would be the same for a constant current operation regardless of the IEM type. Hence, the exit concentration would not vary during charging and only the cell voltage response would change based upon the specific ASR values of the IEMs. However, due to parasitic reactions, the different IEM sets displayed different salt removal rates. The calculated MCDI performance parameters: salt removal efficiencies, coulombic efficiencies, energy efficiencies (during the charge cycle, discharge cycle, and overall), and energy recovery rates for the MCDI cell with different IEM configurations are reported in Table 4.2 for 250 ppm NaCl feed. The data displays gains in coulombic efficiency and salt removal rates for the perfluorinated IEMs and PAE IEMs over the conventional Tokuyama IEMs. A noteworthy result is the near 50% reduction in the energy expended to remove ions from water during the charge cycle with both sets of alternative IEM materials (note: when the MCDI was operated at 0.5 mA cm\(^{-2}\)). Similar observations were made with the higher feed salt concentration (540 ppm) as well, but with a smaller reduction in energy expended per ion removed, as shown in Figures 4.2a-b and Table 4.2. The in-line pH probe monitored the exit stream pH throughout each cycle and it varied between 6-8, not differing substantially with the different IEMs. The energy recovery values were calculated from the discharge data and were used to determine the net MCDI energy expended for a complete charge-discharge cycle. The energy recovery values, for all of the IEM sets, were quite low. Based on work by Długołęcki and van der Wal\(^{19}\), energy recovery is improved in MCDI when charging and discharging the MCDI stack at low current values. The consequence of low current density operation is lower removal rates of
salt and this translates into a larger stack and higher capital costs. For this study, we focused more on the effect of energy expended per ion removed during the charging cycle.

Figure 4.1. a) MCDI cell voltage response under constant current operation during the charge-discharge cycles for 250 ppm NaCl feed with Tokuyama IEMs (red), perfluorinated IEMs (green), and PAE IEMs (blue); b) The corresponding effluent salt concentration over time with the different IEMs used in MCDI charge-discharge cycling.

Table 4.2. Figures of merit for MCDI with the different IEM configurations at 250 ppm feed inlet concentrations

<table>
<thead>
<tr>
<th>Performance parameters</th>
<th>Tokuyama IEMs</th>
<th>Perfluorinated IEMs</th>
<th>PAE IEMs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salt removal rate</td>
<td>43.2%</td>
<td>51.4%</td>
<td>57.8%</td>
</tr>
<tr>
<td>Coulombic efficiency</td>
<td>56.2%</td>
<td>85.1%</td>
<td>95.5%</td>
</tr>
<tr>
<td>Energy expender per ion removed (kT ion⁻¹) *note charging only</td>
<td>56.2</td>
<td>21.0</td>
<td>22.3</td>
</tr>
<tr>
<td>Energy recovery (%)</td>
<td>16.4%</td>
<td>10.5%</td>
<td>7.4%</td>
</tr>
</tbody>
</table>
Figure 4.2. a) MCDI cell voltage response under constant current operation during the charge-discharge cycles for 540 ppm NaCl feed with Tokuyama IEMs (dark red), perfluorinated IEMs (green), and PAE IEMs (blue); b) The corresponding effluent salt concentration over time with the different IEMs used in MCDI charge-discharge cycling.

Table 4.3. Figures of merit for MCDI with the different IEM configurations at 540 ppm feed inlet concentrations

<table>
<thead>
<tr>
<th>Performance parameters</th>
<th>Tokuyama IEMs</th>
<th>PF IEMs</th>
<th>PAE IEMs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salt removal rate</td>
<td>48.1%</td>
<td>48.3%</td>
<td>53.7%</td>
</tr>
<tr>
<td>Coulombic efficiency</td>
<td>48%</td>
<td>86.0%</td>
<td>81.3%</td>
</tr>
<tr>
<td>Energy expended in charging cycle (kT ion$^{-1}$)</td>
<td>57.6</td>
<td>25.8</td>
<td>31.2</td>
</tr>
</tbody>
</table>

The results shown in Figures 4.1a-b and Table 4.2, highlight that a reduction in energy expended per ion removed from the MCDI cell was achieved by lowering the cell voltage rise, which was made possible by minimizing the ASR, and removing more salt from water for the given amount of electrical charge applied (i.e., greater coulombic efficiency). Using the calculated ASR values reported in Table 4.1, a general heuristic emerges where a 5 to 10 fold reduction in
ASR yields about a two-fold reduction in energy expended per ion removed from 250 ppm sodium chloride solutions. Hence, further reduction in the ASR by making IEMs thinner and more conductive will inevitably lower the energy consumption of MCDI. It is important to point out that these results are less pronounced when using a more concentrated salt solution as observed in Figures 4.2 a-b and Table 4.3. The greater concentration of salt in the spacer channel supplements the ionic conductivity in the IEM making their role less prominent in determining the energy efficiency of MCDI. Finally, the coulombic efficiency values for MCDI at 540 ppm feed concentrations was lower than anticipated: 48%. The alternative IEMs provided higher coulombic efficiency values (81.3 to 86%).

The characterization of MCDI performance is also found to be reported in literature in terms of the average salt adsorption rate (ASAR), which is the amount of salt adsorbed during the charging cycle normalized to the area of the porous electrode and energy normalized to adsorbed salt (ENAS), which denotes the amount of salt adsorbed corresponding to the energy expended in charging the electrodes. The ASAR and ENAS values for each MCDI configuration were calculated using equations 4.1 and 4.2 respectively and reported in Table 4.4.

Average salt adsorption rate (ASAR):

\[
ASAR = \frac{\Gamma_{ads}}{N_A A_t \text{cycle}} = \frac{\varnothing}{N_A A_t \text{cycle}} \int_0^{t_{charge}} (C_o - C_{eff})dt
\]  \hspace{1cm} <4.1>

Energy normalized adsorbed salt (ENAS):

\[
ENAS = \frac{\varnothing \int_0^{t_{charge}} (C_o - C_{eff})dt}{E_{charge} - E_{discharge}}
\]  \hspace{1cm} <4.2>

\(\Gamma_{ads}\) = Amount of salt adsorbed during charging (in units of moles)

A = Area of the porous carbon electrodes; 100 cm\(^2\) is the single electrode area

\(t_{cycle}, t_{charge}\) = Cycle time and charging time
∅ = Flow rate of the feed stream

C_{eff}, C_0 = Effluent and feed stream salt concentrations

Table 4.4 Calculated values of average salt adsorption rate (ASAR) and energy normalized adsorbed salt (ENAS) with different IEM configurations at 250 ppm and 540 ppm feed inlet concentrations

<table>
<thead>
<tr>
<th>Performance Parameters</th>
<th>Tokuyama IEMs</th>
<th>PF IEMs</th>
<th>PAE IEMs</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASAR (mmol m^{-2}s^{-1})</td>
<td>3.5</td>
<td>7.5</td>
<td>5.3</td>
</tr>
<tr>
<td>ENAS (mmol J^{-1})</td>
<td>0.008</td>
<td>0.007</td>
<td>0.019</td>
</tr>
</tbody>
</table>

4.2.3 MCDI performance as a function of cell current density

Figure 4.3a presents the energy expended per ion removed for the MCDI cell at different constant current density values with the different IEM chemistries. The alternative perfluorinated and PAE configurations showed a 33% to 50% reduction in energy expended per ion removed over the baseline Tokuyama IEMs when the current density values exceeded 0.3 mA cm^{-2}. Additionally, the alternative IEMs showed a relatively constant energy expended per ion removed when increasing MCDI cell current density. The Tokuyama IEMs displayed a dramatic rise in energy expended per ion removed when increasing current density. Figure 4.3b reports the coulombic efficiency values for the different IEMs tested in the MCDI under different current density operation. The alternative IEMs had greater coulombic efficiency values and they tended to increase towards 50% when the cell current density got larger – up to 0.5 mA cm^{-2}. Similar results for energy expended per ion removed and coulombic efficiency were observed with the higher feed salt concentration of 540 ppm NaCl as shown in Figures 4.4a and 4.4b.
The smaller energy consumed per ion removed with the alternative IEMs at high current density values (≥ 0.3 mA cm\(^{-2}\)) seen in Figure 4.3a was attributed to the lower ASR values of the perfluorinated and PAE membrane sets. The coulombic efficiency gains with the alternative IEMs are ascribed to the smaller cell voltage rise that derived from the smaller ASR of the membranes. Large cell current densities spur higher cell voltages that trigger unwanted, parasitic side reactions. The implication of these results indicates that the MCDI cell with alternative IEMs can operate at higher current density to remove more salt from water without detriment to the MCDI energy efficiency while simultaneously aiding better current utilization – another important goal in achieving better energy efficiency in MCDI.

![Figure 4.3](image)

Figure 4.3. a) Energy expended per ion removed in the charge cycle at different MCDI constant current density values for a 250 ppm NaCl feed stream with the different IEMs (Tokuyama (red), perfluorinated (green), and PAE (blue)), and b) the corresponding Coulombic efficiencies for those data sets.
Figure 4.4. a.) Energy expended per ion removed in the charge cycle at different MCDI constant current density values for a 540 ppm NaCl feed stream with the different IEMs (Tokuyama (red), perfluorinated (green), and PAE (blue)), and b.) the corresponding Coulombic efficiencies for those data sets.

Figure 4.5. An MCDI Ragone plot depicting the deionization rate (mg m\(^{-2}\)s\(^{-1}\)) versus the deionization capacity (mg m\(^{-2}\)) with the different IEMs at a feed salt concentration of 250 ppm.

Figure 4.5 depicts the MCDI Ragone plot which relates MCDI deionization rate to deionization capacity. This plot demonstrates that the new IEMs enhanced the deionization rate in
MCDI for a given deionization capacity. The results illustrate that the thinner and low resistant IEMs improve the performance of MCDI because the deionization rate is faster, while also yielding a larger deionization capacity.

4.2.4 Development of an electric circuit equivalent circuit model for MCDI

![Electric circuit equivalent model](image)

Figure 4.6. a) The electric circuit equivalent model, Bisquert open model with transmission lines, for the MCDI system for fitting Nyquist plot data form EIS; b) Nyquist plots and the corresponding data fit depicted as dashed lines for 0 mA of applied current in the background.

In-situ EIS was leveraged to understand the current distribution within MCDI. This technique allowed quantitative analysis of the individual resistance contributions in the cell and
helped us correlate \textit{ex-situ} properties of the IEMs to MCDI performance. EIS was performed under different current loads to examine how the resistance contributions evolved as function of applied current to the cell. A transmission line model approach (Bisquert open model) was adopted to fit Nyquist data attained from \textit{in-situ} EIS experiments (see Figure 4.6a for ECE model and Figure 4.6b for the model fits), because it has been used for modeling impedance behavior in CDI cells (a similar device). This model accounts for the distributed nature of interfacial impedance throughout the pores in the electrode layers. The first element is the resistor in series, $R_S$, and it corresponds to the membranes’ and spacer channel’s ohmic resistance. The electronic contact resistance between current collector and porous electrodes are assumed negligible in $R_S$. $R_M$ corresponds to the impedance of the electrolyte resistance in the electrode pore. The resistance $R_k$ within the loop accounts for all the resistances related to Faradaic reactions that may occur within the electrode. The constant phase element $Y_M$ constitutes the impedance due to non-faradaic charge storage. Finally, $L$ corresponds to the length of the porous electrode, which is fixed to a dimensionless value of 1, and is not varied during data fitting as the same type of electrodes were used for all MCDI experiments. Although the Nyquist plots did not reveal a second time constant, a capacitance effect could arise from ion charge accumulation at the spacer-IEM interface.

The fitted resistance components from EIS modeling results are listed in Table 4.5. The estimated $R_s$ values indicated that adopting alternative IEMs with lower ASR values yielded a 25% reduction in the HFR regardless of the applied current density. Hence, the key takeaway here is that substantially reducing the membranes’ ASR can only reduce the energy expended per ion removed so much because the resistance in the spacer channel can be fairly large. Nevertheless, a 50% reduction in energy expender per ion removed is still laudable. Additionally, the EIS revealed that the reduction in HFR, which was 25%, does not fully account for the 50% reduction in energy.
expended per ion removed. The other resistance that contributed to improved MCDI energy efficiency is the increase in the charge-transfer resistance of faradaic reactions (R_k). The alternative membranes displayed larger R_k values meaning they partially mitigated unwanted, parasitic side-reactions (e.g., carbon corrosion, water splitting). Because the alternative IEMs display a smaller cell voltage rise, they reduce the thermodynamic driving force for the parasitic side reactions. The R_k values explain why greater coulombic efficiency values in the MCDI were seen with the alternative IEMs. Greater coulombic efficiency assists in attaining better energy efficiency of MCDI, because a larger fraction of the current is used to remove salt from water.

Table 4.5 List of fitted parameters of the equivalent circuit model at different charging currents

<table>
<thead>
<tr>
<th>Circuit Elements</th>
<th>Tokuyama IEMs</th>
<th>PF IEMs</th>
<th>PAE IEMs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 mA</td>
<td>20 mA</td>
<td>40 mA</td>
</tr>
<tr>
<td>R_s (Ω)</td>
<td>3.2</td>
<td>2.8</td>
<td>4.0</td>
</tr>
<tr>
<td>L</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>R_M (Ω)</td>
<td>1.1</td>
<td>1</td>
<td>1.8</td>
</tr>
<tr>
<td>R_k (Ω)</td>
<td>3.6</td>
<td>4.3E-3</td>
<td>0.1</td>
</tr>
<tr>
<td>Y_M (S.s^a)</td>
<td>1.4</td>
<td>1.3</td>
<td>0.6</td>
</tr>
<tr>
<td>A</td>
<td>0.6</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Finally, the EIS experiments showed that the alternative IEMs produce higher electrolyte resistance values within the porous electrode layers in comparison to the conventional Tokuyama IEMs. The R_M values, which denotes the pore electrolyte resistance, differs from the bulk electrolyte resistance (R_S – the IEM and spacer channel). The higher R_M values for PF and PAE could be attributed to their superior water transport properties, which dilute the dissolved ionic
species within the porous electrode compromising ionic conductivity. However, the $R_m$ contribution may not be so significant, because better MCDI performance was attained with the alternative IEMs.

4.2.5 Evaluation of carbon corrosion in MCDI electrodes using XPS

XPS of the pristine and porous carbon electrodes post-mortem MCDI operation showed reduction of carbonyl and ether/alcohol moieties that were present in the pristine samples prior to MCDI runs. Figure 4.7a depicts the C 1s hi-res scan for pristine carbon electrodes and carbon electrodes interfaced with a Tokuyama AEM. The reduction of these moieties account for the low current utilization and it was seen in both the positive and negative electrodes for MCDI and for electrodes interfaced with the different IEMs as shown in Figures 4.7b and 4.7c. XPS is a surface technique that probes 5 nm into the sample. Hence, XPS was only qualitatively interpreted here and was not quantified to explain the coulombic efficiency value trends. The alternative IEMs, however, did display greater coulombic efficiency values and as a result a lower cell voltage rise during MCDI charging. Reduction of the cell voltage can mitigate the parasitic side reactions – e.g., a cell voltage of 1.23 V is needed for water splitting and carbon corrosion can occur at either electrode at 0.21 V (vs. SHE). Note that the porous electrodes were chemically modified using nitric acid, as recommended by the literature.
Figure 4.7. a) XPS C 1s spectrum of pristine and post-mortem MCDI operation (positive and negative) carbon cloth electrodes. The signals at 292 eV and 287 eV correspond to the carbonyl and ether/alcohol moieties in the pristine carbon cloth and they are absent in the post-mortem samples because of parasitic electrochemical reduction reactions in MCDI. b) High resolution XPS scans of carbon for the cathodes post desalination runs and c) anodes post desalination.
4.3 Conclusions

In summary of this chapter, the IEM ionic conductivity and thickness, united into an ASR term, were correlated to MCDI Figures of merit that include salt removal efficiency, energy expended per ion removed, and coulombic efficiency for three different sets of IEM chemistries. Reducing the ASR by a factor of 5 to 10 times with unconventional IEMs, PAE and perfluorinated chemistries, translated to a 50% reduction in energy expended per ion removed in the MCDI cell. However, in-situ EIS revealed only a 25% reduction in the high frequency resistance with the unconventional IEMs. The other contributing factor that reduced the energy consumption of MCDI was the unconventional IEMs creating a larger resistance barrier (Rk component from the modeled EIS data) for the unwanted, Faradaic charge-transfer reactions that compromise MCDI current utilization (i.e., coulombic efficiency). XPS showed that reduction of carbonyl and ether/alcohol moieties in the porous electrodes accounted for the loss in current utilization. Overall, MCDI efficiency stands to benefit immensely by adopting rationally designed IEMs. Future research will investigate reduction of ASR of the membranes without jeopardizing ion-selectivity, while simultaneously exploring alternative spacer channel material for addressing the spacer channel resistance (Chapter 7 of this Dissertation).
Chapter 5. Advancing Electrodeionization with Conductive Ionomer Binders that Immobilize Ion-Exchange Resin Particles into Porous Wafer Substrates

5.1 Introduction

EDI is a commercial separation technology primarily deployed for ultrapure water production and remediation of industrial process waste streams. Its modular design and flexible operating parameters (e.g., adjustment of the cell’s operating voltage or current) make it uniquely versatile to carry-out a wide-range of ionic separations for various applications. EDI is similar to ED because both devices utilize the same basic structure consisting of two electrodes that are separated by a stack of alternating liquid compartments, which are partitioned by alternating cation and anion exchange membranes. Application of an electric field drives the transport of ions towards their respective, oppositely charged electrode. As a result, charged species are continuously removed from the diluate chambers and transferred into the adjacent concentrate chambers. The loosely packed cation and anion exchange resin (CER and AER) particles in the diluate chamber in EDI, augment the ionic conductivity of dilute aqueous solutions. By lowering the ohmic resistances in the diluate compartment, the EDI stack is more efficient for removing ions in the more challenging dilute concentration regime.

A disadvantage of incorporating loose resin beads is the inconsistency in process performance, stack leakage, disruption of bulk liquid flow and routine maintenance requirements. Over the past two decades, Argonne National Laboratory has addressed some of the challenges associated with EDI by substituting the packed compartment consisting of loose ion-exchange resin particles with a rigid, yet porous, ion-exchange resin wafer (RW) in which the ion-
exchange resin particles are immobilized. The RW constitutes a mixture of CER and AER bound by polyethylene (PE) – a thermoplastic polymer. The ion-exchange resin beads supplement ionic conductivity and ion-exchange across the RW, while the PE binder keeps the resin beads stationary. Conventional RWs are about 20 to 35% porous and contain macropores that facilitate bulk liquid flow. Previous work has shown that RW-EDI provides significant advantages over conventional EDI in terms of the rate of removal of ions from liquids, energy efficiency, and process stability and consistency.

The first generation of RW materials incorporated a latex based binder, but this was later replaced by PE, a thermoplastic, that exhibited better ionic separation and efficiencies and required shorter processing time for wafer manufacture. The ion-exchange resin bead chemistry has remained the same in RWs for desalination applications, and most activities related to manufacturing RW materials has focused on the composition of the RW (i.e., the binder content, porosigen amount, and the ion-exchange resin particles’ content), and variation of the type of resin particles, which affects ion binding affinities and the ion-exchange capacity (IEC). The porosigen added to the RW during manufacturing serves as a sacrificial component that is leached in the final processing step to yield a porous material.

Although the RW has a successful track record for augmenting the ionic conductivity of the diluate liquid streams and assisting in ion removal by ion-exchange, at the start of this work, it was posited that the presence of the non-conductive binder in the RW limits energy efficiency gains in EDI. The non-conductive binder obfuscates pathways for ion-exchange and ion transport between the solution and resin particles leading to larger ohmic drops that compromise EDI energy efficiency. Additionally, it was hypothesized that the non-conductive nature of the PE compromises the population of bipolar junction sites in the RW. These bipolar junctions are
formed at the interface where CERs come into contact with AERs. The oppositely charged tethered ionic moieties at this interface lead to an abrupt p-n type junction that dissociates water under an applied electric field $^{54-58}$. Under dilute conditions, the electric field drives water-splitting forming hydronium ($H^+$) and hydroxide ($OH^-$) ion carriers that enable electrical current flow in the unit, and these ions may undergo four fates: i.) they participate in ion-exchange with the resin-particles to regenerate the bed; ii.) they migrate to their respective ion-exchange membrane and are transferred into the concentrate stream; iii.) they recombine to form water; and iv.) the ions leave in the effluent stream, in different ratios, leading to a change in pH $^{45, 64, 65}$. Observations for water-splitting in the ion-exchange resin bed in EDI derive from measuring pH changes in the effluent stream and analyzing the device’s current efficiency$^{64}$. Water-splitting can also occur at the solution-ion-exchange membrane interface under the application of large voltages in ED resulting in pH changes of the effluent $^{91}$ and with unequal ratios of fixed cations to fixed anions in the ion-exchange resin bed. From a theoretical perspective, ineffective water-splitting in the ion-exchange resins may hinder deionization and current efficiency of EDI. To summarize, it is likely that a PE binder would not only derail the ionic conductivity of the RW but would also jeopardize the population of bipolar junction regions needed for water-splitting.

This chapter reports the manufacture and performance of ionomer binder RWs with different configurations: i.) mixed resin with a cation exchange ionomer (CEI) binder, ii.) anion exchange resin (AER) only with CEI binder, iii.) mixed resin with an anion exchange ionomer (AEI) binder, and iv.) cation exchange resin (CER) only with AEI binder. The new ionomer binder RWs showed an impressive 3- to 5-fold improvement in ionic conductivity in the presence of dilute sodium chloride (NaCl) solution concentrations ($\leq 500$ mg L$^{-1}$). The ionomer binder RWs provided a 25% faster separation in bench scale EDI, and they also displayed a modest improvement in the
energy efficiency ($\approx 5\%$) when removing 99% NaCl from a 5,000 mg L$^{-1}$ NaCl aqueous solution. Finally, water-splitting in RWs was assessed in an external experimental setup. When compared to commercially available bipolar membranes, water-splitting in RWs was substantially less effective because of the absence of a water dissociation catalyst. Overall, the implications of this chapter highlights two salient points: i.) ionomer based RWs offer the potential to reduce both the required capital equipment (e.g., size of EDI stack) and energy consumption for a particular electrochemical separation; and ii.) designing new RWs with effective bipolar junctions via the inclusion of a water dissociation catalyst will facilitate water-splitting and provide more thermodynamically efficient ionic separations in EDI desalination, especially for the dilute regime.$^{54}$

5.2 Results and Discussion

5.2.1 Determination of ion-exchange capacities of resin wafers

Table 5.1 IEC and porosity values of the resin wafers

<table>
<thead>
<tr>
<th>Resin wafer type</th>
<th>IEC (meq g$^{-1}$)</th>
<th>IEC (meq mL$^{-1}$)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixed resin with PE binder</td>
<td>0.69</td>
<td>0.93</td>
<td>26.5 ± 3.8</td>
</tr>
<tr>
<td>Mixed resin with CEI binder</td>
<td>0.77</td>
<td>1.11</td>
<td>23.8 ± 1.2</td>
</tr>
<tr>
<td>Mixed resin with AEI binder</td>
<td>0.79</td>
<td>1.08</td>
<td>18.6 ± 3.4</td>
</tr>
<tr>
<td>CER with AEI binder</td>
<td>0.57</td>
<td>0.80</td>
<td>24.3 ± 0.5</td>
</tr>
<tr>
<td>AER with CEI binder</td>
<td>1.05</td>
<td>1.34</td>
<td>13.0 ± 1.9</td>
</tr>
</tbody>
</table>

Table 5.1 provides the IEC values of the RWs, and the different RWs’ porosity values (i.e., free liquid void space divided by wafer volume). Two of the ionomer binder RWs, the mixed resin with CEI binder and CER with AEI binder, provided comparable porosity values to the benchmark PE binder RW (e.g., 23.8% and 24.3% versus 26.5%). The RWs consisting of mixed resin with
AEI binder and the AER with CEI binder yielded lower porosity values – 18.6% and 13.0%, respectively.

5.2.2 Ionic conductivity of resin wafers

Figure 5.1. a) Ionic conductivity (κ) of resin wafers at different NaCl concentrations. Error bars (n=2; absolute difference from the average for the same sample – the error bars are very small) for mixed resin with CEI binder and mixed resin with PE binder. b) Ionic conductivity normalized to ion-exchange capacity by weight (κ_{wt} ) at different salt concentrations. c) κ values of different RW materials from static mode measurements (error bars represent standard error for n=3 for independent RW samples acquired from the same manufactured batch). d) Comparison of static mode and flow-through mode conductivity measurement values.
Figure 5.1a reports the ionic conductivity values of the RWs measured at different salt concentrations. Repeat measurements were performed for the mixed resin with PE binder and the mixed resin with CEI binder. The error bars are the absolute difference from the average. The ionic conductivity was measured in a flow-through mode device that encloses the RW in a cell and allows the salt solution to pass through continuously (see Figure 3.5b). Figure 5.1a and Figure 5.1c demonstrate that the ionic conductivity for each ionomer binder RW was higher across all salt concentrations when compared to the PE binder RW. Notably, the ionomer binder RWs composed of mixed resin with CEI and AEI binders showed the highest ionic conductivities across the NaCl concentrations. The ionomer binder RW demonstrated that it can augment the spacer channel’s ionic conductivity up to 8 g L\(^{-1}\) NaCl solutions, while the PE binder RW only improves the ionic conductivity of NaCl solutions up to 3.5 g L\(^{-1}\). In other words, at 4 g L\(^{-1}\) NaCl solution concentration or greater in the spacer channel, the PE binder RW can no longer boost the ionic conductivity. These results emphasize the ionomer binder RWs’ versatility because they can supplement the ionic conductivity in RW-EDI’s diluate or concentrate compartments when the solution concentration is high as 8 g L\(^{-1}\) NaCl.

Figure 5.1b replots the ionic conductivity data normalized by the IEC of the RW on the basis of RW weight (meq g\(^{-1}\)). Table 5.1 reports the RWs’ IEC values per mass and per volume on a dry basis. These values account for fixed charge carrier contributions from both the binder (if applicable) and the ion-exchange resin particles. The normalized conductivity to IEC shown in Figure 5.1b yielded similar trends to those shown in Figure 5.1a indicating that the ionomer binder RWs’ ionic conductivities were higher than the benchmark PE binder RW. Notably, a four-fold increase in normalized ionic conductivity was observed in the dilute salt concentration regime of < 0.3 g L\(^{-1}\) when compared to PE binder RWs.
Because the flow-through mode conductivity measurement is time consuming, high-throughput conductivity measurements were made with a 2-point static conductivity cell (see Figure 3.5a for the setup). Figure 5.1c provides the conductivity values for all RW variants (n=3; standard error reported) and it is clear that the ionomer binders provide higher RW ionic conductivity over the non-conductive PE binder RW. Figure 5.1d compares the flow-through mode conductivity versus the static mode conductivity. Despite slight difference in absolute values, the trends for conductivity at different solution concentrations of NaCl are in agreement with those observed in the flow-through mode.

The presence of ionic groups in the binder provides more fixed charge carriers to supplement the ionic conductivity of the RW. The Nernst-Planck relationship shown in equation 2.11 indicates that ionic conductivity in electrolytes is a linear function of the fixed concentration of charge carriers. Based on the theoretical relationship, it is plausible that the improvement in ionic conductivity might be solely attributed to the addition of fixed charge groups in the ionomer binder. However, the newly formulated RWs require less binder than the benchmark RW with PE binder, and normalizing the ionic conductivity of each RW to the RW’s IEC shows the concentration of fixed charge carriers alone cannot account for the increased ionic conductivity of the ionomer based RWs. To better understand the ionic conductivity performance differences of the ionomer binder RWs versus PE binder RWs, electron microscopy was leveraged to inspect the RWs’ porous structure and binder distribution. It is important to mention that RW-EDI demonstrations were carried out with RWs composed of AER with CEI binder and mixed resin with CEI binder (these results are presented in the section 5.2.5). The RW with AER and CEI binder had the smallest porosity value but still operated effectively in a RW-EDI bench scale unit and with better performance than the benchmark PE binder RW. The RW-EDI with RWs
consisting of mixed resin with a CEI binder exhibited similar performance to the separation run with RWs of AER with CEI binder. These results suggest that the RWs operate effectively in RW-EDI units with porosity values in the range 13 to 24%.

5.2.3. SEM image analysis of resin wafers

Figure 5.2. SEM images of RWs (left: cross-section and right: surface): a) mixed resin with PE binder, b) mixed resin with CEI binder, c) mixed resin with AEI binder, d) AER with CEI binder, and e) CER with AEI binder
Figure 5.2a-e gives cross-sectional (left) and surface (right) SEM images of PE binder RW and ionomer binder RWs. The resin beads observed in each micrograph vary from 300 to 500 μm in size. Figure 5.2a corresponds to the PE binder RW, and the images show PE enveloping the surface of the ion-exchange resin particles with a relatively thick layer of PE and poor ion-exchange resin particle to ion-exchange resin particle contact. The large surface coverage with a thick PE binder hinders liquid solution contact with the ion-exchange resins, resulting in less ion-exchange and fewer pathways for ion transport from particle to particle. Figure 5.2b-e shows distinctly different distributions of binder and particle confinement within the ionomer binder RWs when compared to the PE binder RW. From these images, the ionomer binder in each RW sample is thinner and more evenly distributed to provide better adhesion between the ion-exchange resin particles. Furthermore, the ionomer binder seems to cover particles’ surfaces less when compared to the PE binder RW. The ionomer binder RW structures also feature notably large, porous gaps that facilitate bulk liquid flow. This is important because the ionomer binder and exposed resin particles are capable of ion-exchange with the liquid solution.

**5.2.4 Analysis of desalination runs in RW-EDI setup**

The superior ionic conductivity of the ionomer binder RWs, in addition to their adequate porosity, motivated bench-scale RW-EDI studies to remove 99% NaCl (fed at 3,000 mg L\(^{-1}\)) from solution. This feed concentration was selected because it represents the upper end of the brackish water concentration regime with a model solution. The bench-scale unit featured 4 pairs of anion and cation exchange membranes, and 4 diluate and concentrate compartments. Thus, the bench-scale EDI unit utilized 4 RWs for each EDI run with the different RW materials. The bench-scale RW-EDI was operated under constant voltage and with recirculation of the diluate and concentrate streams. Figure 5.3a reports the concentration of Cl\(^-\) in the concentrate solution and the diluate solution versus time. The bench-scale RW-EDI unit was run continuously under
recirculation until 99% removal of NaCl (measured as Cl\(^-\)) occurred from the diluate solution. Both ionomer binder RWs, mixed resin with CEI binder and AER with CEI binder, resulted in a 25% faster removal of NaCl from the diluate solution when compared against the RW-EDI run with the benchmark wafer.

Figure 5.3. EDI performance results with NaCl solutions and different RW materials. The EDI demonstrations were carried out in batch mode under recirculation until 99% of NaCl was removed from the diluate compartment. a) Concentration of concentrate and diluate streams versus time. b) Removal productivity of NaCl (i.e., ion removal flux) vs removal ratio. c) Energy consumption for Cl\(^-\) removal. Two EDI runs were performed with each RW material. The average result is given in each plot for each RW material, and the error bars represent the difference between the average and one of the collected data points for the same RW sample.
The faster removal of ions from the diluate stream with the ionomer binder RW was ascribed to the materials’ ability to promote a higher rate of ion removal flux over the range of NaCl concentrations in the diluate chamber. Figure 5.3b plots the removal productivity (the ion removal flux) from the diluate compartment versus the removal ratio (see equation 5.1). As the removal ratio increases, the amount of dissolved salt in the RW decreases resulting in greater ohmic resistance for the dilute chamber. The larger resistance hinders the ion removal flux from the diluate chamber, and thus, at constant applied voltage, the amount of electrical current that can be passed through the RW-EDI stack is lowered. Under the same operation conditions of applied voltages and feed flow rates, the removal productivity for the ionomer binder RWs as shown in Figure 5.3b is 25% or more higher than the PE binder RW regardless of the removal ratio. The higher removal productivities are attributed to the ionomer binder RWs’ higher ionic conductivity values.

\[ \text{Removal ratio (\%)} = (1 - \frac{c_{\text{dilute}}}{c_{\text{feed}}}) \times 100\% \quad \text{<5.1> } \]

Figure 5.3c presents the energy use (kWh) per kg of Cl⁻ removed for the RW-EDI runs performed with different RWs along with their respective removal productivities attained at 99% removal. The ionomer RWs provided up to 4.3% reduction in energy consumption during the RW-EDI run in comparison to the benchmark RW. Although the ionomer binder RWs exhibited substantially better ionic conductivity and ion removal rates in RW-EDI, their improvement to energy consumption was marginal but still laudable. The energy consumption could be reduced to a greater extent by operating the RW-EDI unit in optimal condition of modulated applied electric field (i.e., constant current), cation/anion-exchange capacity ratio in RW and the feed flow rate. However, a constant current process would yield roughly the same time for clearing 99% of the NaCl from diluate stream (assuming similar charge efficiency values for each EDI run with the
different materials). Each RW would likely require different optimal operating conditions for EDI, and in order to provide comparative data, the operation was not optimized in favor of any RW sample. Under optimal operating conditions (i.e., applied electric field, flow rate, etc.), RW-EDI has been reported to achieve <0.66 kWh/m$^3$ for 90% removal of 5,000 mg L$^{-1}$ NaCl$^{93}$ whereas the desalination with a conventional resin wafer in this study corresponded to an average energy consumption of approximately three times greater.

From a process economics viewpoint, energy consumption for RW-EDI is directly related to the operating cost, whereas a RW-EDI unit capable of faster removal of ions from the dilute solution translates to lower capital costs (due to a smaller unit for deionization) and operational costs (primarily caused by using less ion-exchange membranes and RWs)$^{39}$. The results in Figure 5.3a-c demonstrate that ionomer binder RWs display faster ionic separations, while co-currently using less energy, making them extremely advantageous for RW-EDI processes.

5.2.5 pH analysis of RW-EDI runs

![Chart showing pH changes](image)

Figure 5.4. pH changes in dilute solution over time during RW-EDI runs under recirculation with different RW samples.
Figure 5.4 depicts the change in diluate solution pH during the RW-EDI runs. This is similar to other literature reports showing pH shifts in the effluent of EDI. It appears that the AER-CEI wafer shows the biggest change in pH for the diluate stream during EDI and this was ascribed to greater water-splitting by this material. Since the CEI makes contact with the AER across the whole RW and thus increases the number of bipolar junction sites for splitting water.

5.2.6 Demonstration of water splitting in ionomer binder resin wafers

Figure 5.5. Current-voltage (I-V) curves of bipolar membranes and RWs tested in a 4-point cell used to assess water-splitting. The bipolar membranes tested include Fumatech® (commercially available) and SPEEK-QAPPO with and without water dissociation catalysts. RWs evaluated include mixed ion-exchange resins with PE binder (benchmark material), CEI binder with AER, and an AEI binder with CER.

Figure 5.5 shows the current-voltage (I-V) response (i.e., polarization curves) of RWs and bipolar membranes in a homemade 4-point cell used to assess water-splitting kinetics in bipolar membranes. The inset in Figure 5.5 illustrates the low current response of RW materials and a bipolar membrane without a water dissociation catalyst. The bipolar membranes were assessed as a control against the RWs, and they include a commercial variant (Fumatech®) and homemade variants with and without water dissociation catalysts. The homemade bipolar membranes
consisted of a SPEEK cation-exchange membrane (CEM) adjoined to a QAPPO anion exchange membrane (AEM). One homemade bipolar membrane contained a water dissociation catalyst (aluminum hydroxide (Al(OH)$_3$) nanoparticles) and another did not contain a water dissociation catalyst. The RW materials assessed include the benchmark material (mixed resin with PE binder), CER with AEI binder, and the AER with CEI binder. Figure 3.7a-c shows the experimental setup and configuration of RWs, which was sandwiched between a CEM and an AEM, for testing. For the Fumatech® and SPEEK-QAPPO bipolar membrane with a water dissociation catalyst, the onset potential drop for current flow was observed at 0.8 V indicating relatively facile water dissociation into H$^+$ and OH$^-$ ion carriers in the bipolar junction of the membranes (note: the thermodynamic potential to split water in a bipolar junctions is 0.83 V$^{56}$). However, the SPEEK-QAPPO bipolar membrane without a water dissociation catalyst, and all RWs, displayed onset potentials greater than 1 V and substantially lower current responses. These values indicate that the bipolar junctions within these materials have large overpotentials for water dissociation and a smaller population of bipolar junction regions (i.e., fewer sites to dissociate water which is needed for amplifying the current response).

EDI processes can run continuously and without the need for chemicals for ion-exchange bed regeneration because oppositely charged ion-exchange resin particles adjacent to each other and distributed throughout the bed can dissociate water into H$^+$ and OH$^-$ charge carriers$^{45,64}$. While processing the diluate stream in EDI, very dilute conditions near the exit of the unit favor water dissociation to provide the ionic charge carriers and maintain EDI current flow. Once the H$^+$ and OH$^-$ counterions are formed, a subset of them can exchange onto their oppositely charged resins. The regenerated bed can then remove remaining salt ions from the interstitial solution through ion-exchange$^{64}$ or by facilitating ion migration through the ion-exchange membranes. The reports for
detecting water-splitting in mixed ion-exchange beds for EDI typically rely on monitoring the pH of the effluent stream and current efficiency of EDI under very dilute conditions. Herein, an external methodology was adopted in this report to assess water-splitting in RW materials. Because the ion-exchange particles are immobilized in RWs, these materials were conducive for assessment in a 4-point cell that is traditionally used for assessing water-splitting in bipolar membranes\textsuperscript{54}.

Figure 5.5 shows water-splitting of AER with CEI binder RW that is 20-fold lower in current response at 2 V than bipolar membranes with a water dissociation catalyst (Fumatech\textsuperscript{®}) and 4-fold lower current response than a bipolar membrane without a water dissociation catalyst (SPEEK-QAPPO bipolar membrane without catalyst) at that same voltage. The previously described RWs fabricated with ionomer binder were hypothesized to facilitate better water-splitting over benchmark RWs by increasing the population of bipolar junction sites throughout the RW bed. In order to test this hypothesis, RWs composed of a CEI binder with only AER and an AEI binder with CER were formulated. The current response for the RW with a CEI binder and AER was marginally better than the mixed RW with PE binder but it was significantly lower than the response observed with bipolar membranes featuring a water dissociation catalyst. In fact, it was more similar to a bipolar membrane without a water dissociation catalyst.\textsuperscript{55} The improved current response for the CEI binder AER RW over the benchmark mixed RW with PE binder was attributed to larger population of bipolar junctions throughout the RW sample. The higher ionic conductivity and better water-splitting kinetics of the CEI binder AER RW over the benchmark material explained why this material has an almost 25\% faster separation with a 4.3\% reduction in energy usage for 99\% removal. We justify this increase in water-splitting through a continuum, theoretical model (presented on the next page/paragraph) that relates the current response to the concentration of effective bipolar junctions in the RW material.
Mallouk and co-workers\textsuperscript{55} modelled the steady-state polarization behavior that conveys water-splitting in bipolar membranes by equating the divergence of the molar flux equal to the production rate term:

\[ \nabla \cdot \mathbf{N}_i = R_i \quad <5.2> \]

Where \( \mathbf{N}_i \) is the molar flux of a particular ion (e.g., the hydroxide ion or hydronium ion) and \( R_i \) is the production rate term of that ion.

We can assume that the reaction follows the following form and we assume it is not reversible in the bipolar junction under reverse bias

\[ \text{H}_2\text{O} \xrightarrow{\text{BPJ}} \text{H}^+ + \text{OH}^- \]

\( \text{E} \): is the applied electric field

\( \text{BPJ} \): bipolar junction

Here, the following rate-law is proposed

\[ R_i = v_i r_i = k'_d C_{\text{H}_2\text{O}} C_{\text{BPJ}} \quad <5.3> \]

\( C_{\text{BPJ}} \): concentration of bipolar junctions in the RW

\( k'_d \): water-splitting reaction-rate coefficient

Because \( C_{\text{H}_2\text{O}} \) is in excess we can state that

\[ k'_d = k_d C_{\text{H}_2\text{O}} \quad <5.4> \]
And we assume that $k_d$ is a constant at a constant temperature and with no water dissociation catalyst. $v_i$, the stoichiometric coefficient is one.

Now, equation 5.1 can be integrated across the whole control volume in the wafer to get the total molar flux of ions from water-splitting and plug in equation 5.2.

\[ N_i = \int_V R_i \, dV = \int_V k'_d \, C_{BPJ} \, dV \quad <5.5> \]

Recall the assumption that $k'_d$ is a constant

\[ N_i = k'_d \int_V C_{BPJ} \, dV \quad <5.6> \]

The total molar flux can be related to the current density using Faraday’s Law of Electrolysis

\[ i = nF N_i = nF k'_d \int_V C_{BPJ} \, dV \quad <5.7> \]

It is clear from the above derivation that the current response from water-splitting in the 4-pt cell is dependent upon the reaction rate coefficient for water-splitting and the amount of effective bipolar junctions in the RW control volume. The AER with CEI binder RW has a larger $C_{BPJ}$ value resulting in a greater current response observed in Figure 5.5. Future research will look to incorporate a water dissociation catalyst that can boost the reaction rate coefficient for water-splitting.

The insights attained from the results presented in Figure 5.5 motivate future studies to incorporate water dissociation catalysts in RWs and to maximize populations of bipolar junctions. Some examples include poly(acrylic acid), graphene oxide, or poly(vinyl pyridine) or metal oxides/hydroxide$^{95,96}$.
Finally, it should be noted that pH changes were detected in the diluate stream under recirculation during RW-EDI runs (Figure 5.4) and the greatest pH change was observed for the RW composed of AER with CEI binder. The larger pH change observed during the run suggested that this RW material was most effective for water-splitting in EDI. This observation is in agreement with the water-splitting measurement using the external 4-pt measurement which indicated greater water splitting for the AER with CEI binder RW in comparison to the mixed resin with PE binder. However, it should be mentioned that unequal ratios of fixed anion exchange and cation exchange sites in the RW (see Table 5.1 for the amount of fixed anion exchange and cation exchange sites in RW samples) may also cause pH changes in the diluate chamber.97

5.3 Conclusions

Ionomer binder RWs were developed for EDI as a replacement for benchmark RWs, which are fabricated with a non-conductive PE binder. The ionomer binder RWs displayed superior ionic conductivity (3-5x improvement), while maintaining adequate porosity, resulting in faster removal of ions from aqueous streams with greater energy efficiency in RW-EDI demonstrations. Electron micrographs revealed that the ionomer binders were a thinner and better distributed adhesive throughout the RW bed to immobilize ion-exchange resin particles. The better binder distribution facilitated greater ion exchange between the liquid and resin particles and delivery of ions to the membranes. The water-splitting characteristics of these RWs were assessed in an external setup, and it was determined that all RW materials split water 20x less effectively in comparison to bipolar membranes that contain water dissociation catalysts. Notably, the ionomer binder RWs’ ability to split water was on the same order of magnitude to bipolar membranes not featuring a
water dissociation catalyst. These observations motivate future efforts to develop RW materials with water dissociation catalysts strategically placed in bipolar junction regions of RWs.

6.1 Introduction

Harvesting low-grade waste heat as electrical power has been gaining popularity due to its vast potential and abundant availability. Solid-state thermoelectric generators (TEGs) that use p- and n-type semiconductor materials are currently the most mature direct thermal-electrical energy conversion devices. However, this technology is economically unfavorable for large scale conversions due to its high costs, poor modularity, and lack of energy storage capability.22,23

Liquid-based thermo-electrochemical cells (TECs) have advantages over TEGs being cheaper and scalable with opportunities for energy storage.26,27 Thermally regenerative ammonia-batteries (TRABs), a type of TEC, emerged as a relatively new approach for waste heat energy recovery.26,28,29,47,48,59,60 The distillation unit integrated with the battery, converts waste heat to chemical energy and stores it where it can later be discharged as electrical energy upon demand.

The copper (Cu) meshes, which are used as electrodes, are immersed in aqueous copper salt solutions and separated by an anion exchange membrane (AEM). The ammonia (NH₃) added into the anolyte, but not the catholyte, results in different potentials between the Cu electrodes. The Cu anode gets oxidized and dissolves into the NH₃ solution, forming a Cu²⁺ amine complex as per the reaction, Cu + 4NH₃ → Cu(NH₃)₄²⁺ + 2e⁻, Eₒ = −0.04 V vs. SHE, while aqueous Cu²⁺ is reduced and deposited on the cathode as per the reaction- Cu²⁺ + 2e⁻ → Cu, Eₒ = +0.34 V vs. SHE, during battery discharge. After discharging, NH₃ is separated from the anolyte by distillation using waste

This chapter was previously published as, Varada Menon Palakkal, Thu Nguyen, Phuc Nguyen, Mariia Chernova, Juan E. Rubio, Gokul Venugopalan, Marta Hatzell, Xiuping Zhu, Christopher G. Arges “A high power thermally regenerative copper-ammonia redox flow battery enabled by a zero gap cell design, low-resistant membranes and protective electrode coatings” ACS Applied Energy Materials, 2020, DOI 10.1021/acsaem.0c00400.
heat and the designation of the chambers as anode and cathode are switched. The alternating cycle of electrode dissolution/deposition allows the Cu electrodes to be maintained in closed-loop cycles, and waste heat energy is stored in concentrated NH₃ solutions that can later be recovered as electricity on demand.

Previous reports have only considered two cell designs for the assessing the performance of a TRAB: i.) a closed batch system (see Figure 6.1a) that embodies a traditional electrochemical H-cell configuration and ii.) an electrodialysis type setup that has a spacer gasket between the electrodes and membranes for the liquid solutions to flow through (see Figure 6.1b). Until now, a zero gap design for the TRAB with flow of the anolyte and catholyte has not been considered despite its ubiquitous use in redox flow batteries (RFB). There is significant merit for the zero gap flow design for a TRAB (which is termed here as the ammonia flow battery (AFB)) because this battery has a 0.4 V open-circuit voltage (OCV) and thus any sources of resistance can quickly diminish the power output from the battery when extracting electrical current. A zero gap design entails direct contact of the Cu mesh electrodes with an AEM separator. The ohmic losses between the membrane and the electrode across the liquid electrolyte, which are found in a traditional configuration, are eliminated with a zero gap design (see Figure 6.1d).

This chapter demonstrates substantial gains in the power density and ηth values of TRABs by adopting a zero gap design, deploying a low-resistant and low cost AEM (quaternary benzyl trimethylammonium poly(styrene-block-(ethylene-random-butylene)-block-styrene) (QASEBS)), and by using highly conductive and selective ionomer coatings on the Cu mesh electrodes. The use of more functional materials and re-engineering the cell resulted in an AFB peak power density
of 280 W m⁻² at 55 °C – which is the highest peak power density for AFB in the peer-reviewed literature.

Figure 6.1. a) Schematic figure of a closed-batch system of TRAB; b) Schematic figure of a electrodialysis type flow design with non-zero gap. c) Sources of resistances with a non-zero gap (i.e., electrodialysis or batch) setup; d) Sources of resistances in a zero-gap flow mode operation.

With a much higher power density AFB, a $\eta_{\text{th}}$ value of 2.99 % was attained (37.9 % relative to the Carnot efficiency $\eta_{\text{th/C}}$) and this is the highest value reported to date for an TRAB. Also, the work here represents the highest $\eta_{\text{th/C}}$ value for any type of electrochemical platform (e.g., TRBs or thermally regenerative electrochemical cells (TRECs)) aimed at recovering low-grade waste heat while also generating power density values over 100 W m⁻². For example,
TRBs have never achieved $\eta_{\text{th/C}}$ values over 15%. However, a TREC platform report by Lee et al. has displayed a $\eta_{\text{th/C}}$ value of about 39.3%, which is close to what is reported here (37.6%), but this report demonstrated a substantially lower power density (10 W m$^{-2}$). High power density, which is shown in this report, helps minimize the size of the system and alleviates capital costs that can stymie commercialization of the technology. In summary, cell engineering and judicious selection of functional materials were paramount for making a transformative change in AFB performance.

6.2 Results and Discussion

Table 6.1 compares the performance of TRAB in this study to previous literature reports in terms of maximum power densities attained.

Table 6.1 TRAB specifications and performance metrics from the literature and this work

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Membrane type</th>
<th>Cell type</th>
<th>Anolyte</th>
<th>Catholyte</th>
<th>Temperature ($^\circ$C)</th>
<th>$P_{\text{max}}$ (W m$^{-2}$)</th>
<th>$\eta_{\text{th}}$ (%)</th>
<th>$\eta_{\text{th/C}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>Selemion$^{\text{TM}}$ AMV</td>
<td>Batch</td>
<td>0.1 M Cu(NO$_3$)$_2$, 5 M NH$_4$NO$_3$ and 2 M NH$_3$OH</td>
<td>0.1 M Cu(NO$_3$)$_2$ and 5 M NH$_3$NO$_3$</td>
<td>23</td>
<td>95</td>
<td>0.53</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>46</td>
<td>170</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>56</td>
<td>200</td>
<td>-</td>
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<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>72</td>
<td>236</td>
<td>0.29</td>
</tr>
<tr>
<td>9</td>
<td>Selemion$^{\text{TM}}$ AMV</td>
<td>Batch</td>
<td>0.1 M Cu(NO$_3$)$_2$, 3 M NH$_3$ and 5 M NH$_3$NO$_3$</td>
<td>0.1 M Cu(NO$_3$)$_2$ and 5 M NH$_3$NO$_3$</td>
<td>20-30</td>
<td>136</td>
<td>0.86</td>
<td>10.9</td>
</tr>
<tr>
<td>14</td>
<td>Selemion$^{\text{TM}}$ AMV</td>
<td>Flow</td>
<td>0.2 M Cu(NO$_3$)$_2$, 3 M NH$_3$NO$_3$, and 3 M NH$_3$OH</td>
<td>0.2 M Cu(NO$_3$)$_2$ and 3 M NH$_3$NO$_3$</td>
<td>23</td>
<td>45</td>
<td>0.70</td>
<td>5</td>
</tr>
<tr>
<td>11</td>
<td>Quaternary benzyl trimethylammonium poly(phenylene oxide)</td>
<td>Batch</td>
<td>0.1 M Cu(NO$_3$)$_2$, 5 M NH$_3$NO$_3$, and 2 M NH$_3$OH</td>
<td>0.1 M Cu(NO$_3$)$_2$ and 5 M NH$_3$NO$_3$</td>
<td>20-25</td>
<td>106</td>
<td>0.76-0.97</td>
<td>7</td>
</tr>
<tr>
<td>13</td>
<td>Selemion$^{\text{TM}}$ AMV</td>
<td>Flow</td>
<td>0.1 M AgNO$_3$, 5 M NH$_3$NO$_3$, and 2 M NH$_3$OH</td>
<td>0.1 M AgNO$_3$ and 5 M NH$_3$NO$_3$</td>
<td>23</td>
<td>31</td>
<td>0.41</td>
<td>3.8</td>
</tr>
</tbody>
</table>

*(table cont’d.)*
Table 6.2 Properties of Selemion™ and QASEBS AEMs and SPEEK materials

<table>
<thead>
<tr>
<th>AEM</th>
<th>Thickness (μm)</th>
<th>IEC (mmol g⁻¹)</th>
<th>Conductivity (mS cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>25 °C</td>
</tr>
<tr>
<td>Selemion™</td>
<td>85</td>
<td>1.85 ± 0.04</td>
<td>18.7 ± 2.5</td>
</tr>
<tr>
<td>QASEBS</td>
<td>89</td>
<td>0.34 ± 0.03</td>
<td>55.7 ± 8.9</td>
</tr>
<tr>
<td>SPEEK</td>
<td>64</td>
<td>1.61 ± 0.01</td>
<td>15.7 ± 0.5</td>
</tr>
</tbody>
</table>

AEMs’ ionic conductivity values are reported for the NO₃⁻ counterion form. SPEEK’s ionic conductivity was assessed in the Cu²⁺ counterion form. The error bars represent the absolute difference from the average for n=2 samples tested.

6.2.1 TRAB performance with zero gap and non-zero gap design

Figure 6.2a presents the cell voltage (V) versus current density (i.e., polarization curve) and power density versus current density (i) for zero gap and non-zero gap TRAB configurations with a commercially Selemion™ AEM separator. The V-i curve for the non-zero gap design displayed a steep, linear curve indicating that there were large ohmic resistances within the cell.
that limited the power density. Conversely, the slope of the zero gap AFB’s polarization curve with Selemion™ AEM was less steep and showed a pseudo-exponential drop in cell voltage at low current density – which was indicative that the activation overpotential was more prominent at the lower current density for the zero gap configuration. With the adoption of a zero gap configuration, the peak power density of the AFB increased by 1.6× (55 W m⁻² versus 35 W m⁻²).

Figure 6.2. a) Voltage (left y-axis) and power density (right y-axis) versus current density for the different TRAB cell configurations: non-zero gap with commercially sourced Selemion™ AEM and zero gap mode with Selemion™ AEM at 25 °C. b) Nyquist plots from EIS experiments during TRAB operation at 25 °C in a zero gap and non-zero gap design with Selemion™ AEM.

To substantiate the role of the reduction in ohmic resistances for improving TRAB power density, electrochemical impedance spectroscopy (EIS) was collected for the different configurations of the TRABs. Figure 6.2b presents the Nyquist plots attained from EIS. The high frequency resistance (HFR) was reduced by 4.2× (7.5 Ω-cm² to attained 1.8 Ω-cm²) for the zero gap configuration over the non-zero gap when using the Selemion™ AEM. The reduction in ohmic resistances accounted for the higher power density of the zero gap configuration over the non-zero
gap configuration observed in Figure 6.1a. The reduction in ohmic resistances for the zero gap design was achieved by eliminating the ohmic contributions from the liquid electrolyte that normally separate the AEM and Cu mesh electrodes in non-zero gap design (Figures 6.1c and 6.1d).

### 6.2.2 AFB performance with different AEM separators

![Figure 6.3](image.png)

**Figure 6.3.** a) Voltage and power density versus current density at 25 °C for the zero gap AFB with different AEMs: Selemion™ and QASEBS; b) Nyquist plots of the AFB at 25 °C and open circuit voltage with Selemion™ AEM and QASEBS AEM.

Figure 6.3a depicts the V-i curves for the zero gap design for two types of AEMs at room temperature. Compared to the commercially Selemion™ AEM, the QASEBS AEM in the AFB generated a smaller ohmic drop as the slope of the line in the middle part of the polarization curve was less steep. The reduction in ohmic resistances in the zero gap AFB with a more conductive AEM (Table 6.2) boosted the peak power density from 55 W m⁻² to 183 W m⁻². Interestingly, a limiting current density (i.e., the asymptotic drop in the V-I curve) was observed in Figure 6.3a with the AFB featuring a zero gap configuration and QASEBS AEM. To the best of our knowledge, this is the first time a limiting current, which corresponds to mass transfer resistances
in the electrodes, has been observed in an AFB. The observation of limiting current highlights that the ohmic resistances have been minimized in the AFB cell and running the cell at high current density becomes limited by delivery of reactants to the electrode surface.

Coupling the zero gap design with the low resistant QASEBS AEM substantially improved the peak power density of the AFB (from 35 W m$^{-2}$ for non-zero gap with Selemion™ AEM at 25 °C to 183 W m$^{-2}$ with a zero gap and QASEBS AEM – a 5.2× improvement). There has only been one other literature report\textsuperscript{47} assessing AFB performance with an alternative AEM to commercially available Selemion™. This previous report investigated quaternary benzyl trimethylammonium functionalized poly(phenylene oxide) AEM and it showed a 25% improvement in AFB power density due to its 30% lower ohmic resistance. However, this report only studied a non-zero gap AFB design and showed a maximum peak power density of 110 W m$^{-2}$ at room temperature. In comparison, the combined effect of a zero gap AFB and a low resistant QASEBS AEM yielded a much better peak power density of 183 W m$^{-2}$ at room temperature. Hence, more conductive AEMs only have a limited effect on improving the power density of AFBs. Further, it was also observed that a zero gap AFB with the commercially available Selemion™ AEM had marginal gains in peak power density. The substantial improvements in AFB peak power density hailed from combining a low-resistant AEM and zero gap AFB design that worked additively for reducing ohmic resistances.

To substantiate that the QASEBS AEM fostered smaller ohmic resistances in the zero gap AFB, EIS experiments were performed with the zero gap AFBs with the different AEMs. The QASEBS AEM reduced the HFR seen in the Nyquist plot (Figure 6.3b) for the AFB from 1.5 Ω-cm$^2$ to 0.2 Ω-cm$^2$. This represents a 7× reduction by just switching the AEM material. The higher ionic conductivity of the QASEBS AEM over the Selemion™ AEM (Table 6.2) was responsible
for the further reduction in HFR. Comparing the HFR of the non-zero gap configuration with a Selemin™ AEM to the zero gap design with a QASEBS AEM, there is a 32× difference in the HFR values. The EIS experiments presented in Figs. 6.2b and 6.3b convey that it takes a drastic reduction in ohmic resistances to extract more power from the AFB. Hence, other resistances, like reaction kinetics and mass transfer, contribute more to the AFB’s polarization as ohmic resistances have been significantly reduced.

The peak power density of 183 W m⁻² for the zero-gap AFB was obtained with a QASEBS AEM separator at room temperature (20~25 °C) and this marks a 32% improvement over the state-of-the-art peak power density reported at room temperature: 136 W m⁻². The peak power density values for room temperature AFBs in the literature using a non-zero gap design ranged from 20 W m⁻² to 136 W m⁻² (Table 6.1). The previous state-of-the-art value was attained for a case that used a higher NH₃/NH₄ concentration (3 M NH₃ in the anolyte and 5 M NH₄NO₃ in the catholyte). Overall, a low resistant AEM separator and a zero gap design provided a 32% enhancement in peak power density compared to the state-of-the-art peak power density value for an AFB at room temperature.

6.2.3. Zero gap AFB performance with SPEEK coated Cu electrodes

Prior to studying how temperature affects TRAB polarization and power density, we attempted to improve the TRAB power density by addressing the kinetics and Faradaic efficiency of the Cu electrodes. Notably, TRABs are known to suffer from poor Faradaic efficiency due to parasitic site reactions that involve Cu oxidation with hydroxide ions and oxygen species. As a result, the reported anodic Faradaic efficiencies for the cell are typically less than 40%. Herein, it was initially hypothesized that cation selective ionomer coating on the Cu mesh electrodes may mitigate interaction of hydroxide anions and dissolved oxygen during Cu oxidation. To keep the
TRAB costs down, a low-cost hydrocarbon cation exchange ionomer solution was synthesized via sulfonation of commercially available PEEK. This ionomer was dissolved in NMP solvent and spray deposited on to both Cu mesh electrodes and tested in the zero gap AFB setup with a QASEBS AEM.

Figure 6.4a shows the V-i curves and power density curves for the zero gap AFB with QASEBS AEM with SPEEK coated Cu mesh electrodes and non-coated Cu mesh electrodes. The SPEEK coated Cu electrodes provided an extension of the current density in V-i curves leading to an increase in the limiting current from 1150 A cm$^{-2}$ to about 1450 A cm$^{-2}$. Extracting more current at a higher cell voltage generated a maximum power density of 204 W m$^{-2}$ at 25 °C – which is about a 15% improvement in the peak power density at 25 °C over the zero gap configuration with QASEBS AEM but featured no coating on the Cu mesh electrodes. EIS data provided in Figure 6.4b shows that the SPEEK coated Cu electrodes reduced the charge-transfer resistance (R$_{ct}$, the diameter of the semi-circle in the Nyquist plots) from 2.0 Ω-cm$^{-2}$ to 0.7 Ω-cm$^{-2}$ without changing the HFR values of the AFB. Table 6.3 provides the HFR and R$_{ct}$ values from fitting the Nyquist plot data to an electric circuit equivalent model presented in Figure 6.4c. It is worth noting that the R$_{ct}$ values are higher than the 0.24 Ω-cm$^{2}$ HFR for the zero gap AFB with the QASEBS AEM. However, the R$_{ct}$ values when using SPEEK coated Cu mesh electrodes are lower than the HFR values observed for the non-zero gap AFB (7.8 Ω-cm$^{2}$) and smaller than the zero gap AFB with the Selemion™ AEM (1.8 Ω-cm$^{2}$).
Figure 6.4. a) V-i and power density curves for the zero gap AFB with QASEBS AEM featuring non-coated Cu mesh electrodes and SPEEEK coated Cu mesh electrodes. b) Nyquist plots for the zero gap AFB with QASEBS AEM with non-coated Cu mesh electrodes and SPEEK coated Cu mesh electrodes at 25 °C with fitted data using c) electric circuit equivalent model. d) V-i curves and power density curves of SPEEEK coated Cu mesh electrodes with QASEBS AEM in zero gap AFB operated at the different temperatures of 25 °C, 40 °C, and 55 °C.

Table 6.3 Ohmic and charge-transfer resistances from EIS experiments

<table>
<thead>
<tr>
<th>Electrode type and AEM type</th>
<th>( R_s (\Omega \text{-cm}^2) )</th>
<th>( R_{ct} (\Omega \text{-cm}^2) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-coated Cu meshes + QASEBS</td>
<td>0.24</td>
<td>2.00</td>
</tr>
<tr>
<td>SPEEEK coated Cu meshes + QASEBS</td>
<td>0.19</td>
<td>0.69</td>
</tr>
</tbody>
</table>
In a separate experiment, the Faradaic efficiency of Cu mesh electrodes with and without SPEEK coatings were assessed. The cathode Faradaic efficiencies for both electrode variants were near 100% (a non-coated Cu cathode exhibited 103% efficiency and SPEEK coated Cu cathode displayed 104%) and this was in agreement with other literature reports.\textsuperscript{48,50} The addition of SPEEK to the Cu mesh electrode boosted the anode Faradaic efficiency from 37% (non-coated Cu) to 46%. Overall, a reduction in $R_{ct}$ with SPEEK coated Cu electrodes and increase in the anode’s Faradaic efficiency, plus the zero gap AFB with a low-resistant AEM, gave rise to an AFB capable of generating 204 W m\textsuperscript{-2} at 25 °C. Note that the Nyquist plot in Figure 6.2b for the non-zero gap TRAB and zero gap AFB with Selemon™ AEM did not display tails in the low-frequency regime signaling that these cells were dominated by ohmic and charge-transfer kinetic resistances. Conversely, Figure 6.4b shows tails in the low-frequency regime of the Nyquist plot and this signifies that the ohmic resistances have been reduced so much that the cell performance is under mixed kinetic-diffusion control. Hence, diffusion-control aspects observed in the Nyquist plots in Figure 6.4b accounts for the limiting currents seen in polarization curves (Figures 6.3a and 6.4a) for the zero gap AFB with QASEBS AEM.

Now that the SPEEK coated Cu meshes have moderately reduced the kinetic losses in the AFB, the polarization and power density of the zero gap AFB with the QASEBS AEM was evaluated at elevated temperatures of 40 °C and 55 °C (Figure 6.4c). Elevated temperatures enhance the ionic conductivity of the QASEBS AEM (Table 6.2) and electrode kinetics (e.g., the exchange current density is linearly proportional to the reaction rate coefficient which can be described by the Arrhenius equation). As a result of the elevated temperatures, the peak power density of the AFB increased to 280 W m\textsuperscript{-2} at 55 °C. Additionally, the increase in operating temperature of the AFB extends the limiting current: 1500 A m\textsuperscript{-2} versus 1450 A m\textsuperscript{-2}. 
Unexpectedly, the open circuit voltage (OCV) for the AFB increases with the SPEEK coated Cu electrodes to 0.5 V and slightly rises with increasing temperature (0.52 V at 40 °C and 55 °C). The OCV for all zero-gap AFB configurations was about 50 to 100 mV higher than what was expected based upon the half-cell potentials (Figure 6.2a). The origin(s) for the slightly higher OCV values is currently unknown, but it is not due to the Donnan potential across the AEM as the concentration differences only manifests about a 10 mV rise. It is suspected that the deviations in OCV may be attributed to parasitic reactions in the anode (e.g., copper with hydroxide ions). As seen on the copper Pourbaix diagram\textsuperscript{102}, it is possible that up to 95 to 100 mV could be added to the cell voltage for the Cu electrode being converted to Cu$_2$O at about pH 10.

In summary, deploying a cation selective ionomer on Cu mesh electrodes in the AFB with a low-resistant AEM and a zero gap design yielded a peak power density of 280 W m$^{-2}$ at 55 °C. This is the highest power density value for an AFB in the peer-reviewed literature. Table 6.1 compares the peak power density values in this report against other data available in the literature for different AFB configurations. Results here demonstrate that cell engineering and new membrane and electrode coating materials have made an indelible impact on the power density of the AFB.

**6.2.4 Evaluation of cathode kinetics and current distribution analysis of the AFB with different configurations.**

This section examines how the reduction in ohmic overpotential, in relation to cathode kinetics, impacted AFB performance. First, the intrinsic kinetic parameters (Tafel slope and exchange current density ($i_{o,c}$)) for the Cu$^{2+}$ reduction reaction were measured in H-cell setup with a reference electrode by performing linear sweep voltammetry (Figure 6.5a). The polarization behavior of the cathode was processed and analyzed using the Butler-Volmer equation to attain
the Tafel slope and $i_{o.c.}$. These values were used to inform the cathode overpotential for the various AFB configurations as a function battery current density.

![Tafel plot of the cathode for both non-coated and SPEEK coated Cu electrodes; Polarization curve and contributions of ohmic and cathodic overpotentials at different discharge current densities for b) Non-zero gap mode with non-coated Cu; c) Zero gap mode non-coated Cu with QASEBS AEM in AFB; d) SPEEK coated Cu with QASEBS AEM in AFB operated at 25 °C.](image)

Figure 6.5. a) Tafel plot of the cathode for both non-coated and SPEEK coated Cu electrodes; Polarization curve and contributions of ohmic and cathodic overpotentials at different discharge current densities for b) Non-zero gap mode with non-coated Cu; c) Zero gap mode non-coated Cu with QASEBS AEM in AFB; d) SPEEK coated Cu with QASEBS AEM in AFB operated at 25 °C.

Figures 6.5b – 6.5d compare the cathode overpotential contribution against the ohmic overpotential term for the different AFB configurations at room temperature. The ohmic
overpotential was determined by using the measured HFR of the AFB and Ohm’s Law. The anode overpotential could not be considered because of the poor Faradaic efficiency of the anode due to parasitic reactions. In other words, the competing reactions prevent the experiment from extracting reliable kinetic parameters for the desired reaction. The overpotential losses for the non-zero gap AFB presented in Figure 6.5b shows that the ohmic overpotential was similar in magnitude to the cathode activation overpotential. Conversely, Figs. 6.5c and 6.5d depict that the ohmic overpotential is significantly smaller than the cathode activation overpotential for the zero gap AFB with and without SPEEK coated Cu mesh electrodes. For instance, operating the AFB at 1000 A m$^{-2}$ results in an ohmic overpotential of about 30 mV whereas the cathode activation overpotential for the zero gap AFB with a QASEBS AEM without and with SPEEK coated Cu mesh electrodes was about 200 mV and 110 mV, respectively.

As seen in Figure 6.5a, the cathode kinetic parameters are more favorable when the Cu electrode contains a SPEEK coating as the Tafel slope is reduced from 345 mV per decade of current to 200 mV per decade of current and the exchange current density is higher (3.2 A cm$^{-2}$ versus 2.5 A cm$^{-2}$). Hence, the SPEEK coating on the electrodes not only boosts the Faradaic efficiency for the anode, but the coating also enhances the cathode reaction that reduces Cu$^{2+}$ to metallic Cu. Recall, that a reduction in charge-transfer resistance was observed for the AFB that featured SPEEK coated Cu electrodes (Figure 6.4b) and this signified improved reaction kinetics in the AFB. The improved Cu$^{2+}$ reduction kinetics with the SPEEK coating are attributed to the selectivity of cation exchange ionomer coating that favors Cu$^{2+}$ uptake and transport to the electrode surface and that prevents unwanted anion (e.g., nitrate) interference with the electrode surface.
Overall, the current distribution analysis herein shows: i.) the ohmic overpotential has been
minimized in the AFB through a zero gap design and the implementation of a low-resistant
QASEBS AEM, ii.) the addition of a SPEEK, a cation selective coating, improves the anode
Faradaic efficiency and the reaction kinetic parameters for the cathode, and iii.) the anodic Faradaic
efficiency and cathode activation overpotential both need to be improved further for extracting
great power density from the AFB. Any further reduction in AFB ohmic resistances would result
in diminished returns for improving the AFB power density as activation overpotentials, and even
mass transfer overpotentials (observed by the limiting current density and the tails in the Nyquist
plots), are now hampering battery performance.

6.2.5 Evaluation of thermal energy efficiency

Figure 6.6. a) Thermal energy efficiency ($\eta_{th}$) values plotted against AFB maximum power
density for different battery configurations. The ‘X’ symbols correspond to the thermal energy
efficiency values relative to the Carnot efficiency ($\eta_{th/C}$). b) The $\eta_{th}$ and $\eta_{th/C}$ values of the
regenerative electrochemical platforms for recovering low-grade waste heat. The TREC values
(red)\(^{16}\), the TRB in this work (SPEEK coated Cu with QASEBS AEM in zero gap mode) at
various temperatures, TRB values from previous reports- (black)\(^{59}\) and (green).\(^{48}\)
Figure 6.6a plots the $\eta_{th}$ and $\eta_{th/C}$ values versus peak power density values for the different AFB demonstrations. These calculated efficiency values were based upon previous literature reports\textsuperscript{48,59} that used 30% ammonia utilization in the anolyte. From this plot, it is clear that a linear, commensurate scaling relationship exists between power density and $\eta_{th}$ and $\eta_{th/C}$ values indicating that cell engineering and new materials for increasing AFB power density can manifest significant improvements in waste heat recovery. A maximum $\eta_{th}$ value of 2.99 % ($\eta_{th/C} = 37.9$ %) was achieved at 55 °C when using the optimal AFB configuration and these efficiency values are the highest in the peer-reviewed literature for TRBs (Table 6.1). They are also competitive with the largest $\eta_{th/C}$ values seen in TRECs\textsuperscript{99} but the optimized AFB reported herein have over a 20× greater power density (Figure 6.6b). The advantage of a system with greater power density translates to a smaller system size and reduced capital costs.

Although substantial gains were made in $\eta_{th}$ and $\eta_{th/C}$, it is important to mention that TEG devices show $\eta_{th}$ values around 5 to 8% and that the drastic improvements in AFB performance have yet to achieve parity with TEGs. However, it may be possible to put the AFB on the same performance plane as TEGs through optimizing electrolyte composition and electrode structure – both integrated with the optimal AFB design reported here. Furthermore, if the AFB could operate with a lower NH$_3$ content in the anolyte, it is possible to reduce the heating energy needed for NH$_3$ distillation ($Q_{in}$). Another strategy for improving the $\eta_{th}$ values for the AFB is to leverage NH$_3$ membrane distillation. Outfitting traditional distillation units\textsuperscript{103} with membranes can reduce the energy duty for distillation. In summary, improving AFB power density can increase $\eta_{th}$ and $\eta_{th/C}$ values, but efforts should also be made to increase $\eta_{th}$ values through re-engineering the solution composition and considering alternative distillation techniques.
6.2.6 Cycling stability analysis

Figure 6.7. a) Discharge current and b) power produced for the AFB run under constant voltage hold of 0.3 V for 8 cycles with the anolyte and catholyte exchanged every 10 minutes, at a flow rate of 2 mL min\(^{-1}\)

Another important consideration for the AFB beyond its power density and its relation to thermal efficiency is its cycling stability. The cyclability limitations of the zero gap AFB with a QASEBS AEM and SPEEK coated Cu mesh electrodes (i.e., the best variant to date of the technology) was evaluated by switching the electrolyte solutions to the respective compartments every 5 minutes and measuring the battery’s current response when discharging it at a constant voltage of 0.3 V. Because of the nascent stage of the AFB technology, a distillation system for transferring NH\(_3\) between compartments was not pursued in this work but will be evaluated in future studies. Figs. 6.7a and 6.7b report the AFB’s current and power as a function of time at 25 °C when reversing the electrolyte solution paths. These plots show an increase in current as time passes because the electrolyte solutions finally reach the electrode layers and remove the residual deionized water from cleaning the battery between cycles (note: the AFB is flushed with DI water between cycles). The best variant of the zero gap AFB operates at a fairly large current and thus excess discharge time could lead to dissolution of the electrode. Figs. 6.7a and 6.7b demonstrate that the AFB can continue to operate over 7 five-minute cycles. After the seventh cycle, the side
of the battery that contained that anode initially was completely dissolved. The fading of the zero gap AFB performance after 7 cycles reflected observations made in other AFB studies and thus illustrates that the zero gap AFB has the same stability limitations of non-zero gap AFB literature results.

The inability to maintain battery stability past 7 cycles with the zero gap AFB was attributed to the poor anodic Faradaic efficiency – which causes Cu leaching from the anode side that does not match the electrical current passed. Additionally, non-uniform Cu plating on the cathode when reversing the battery can also exacerbate battery instability when the cathode chamber becomes the anode chamber in the next cycle. In other words, the Cu mesh electrodes eventually become thin in some places and thick in other places. The thin areas eventually become severed and when enough of these connections have been eliminated the battery fails. The problems of poor anodic Faradaic efficiency and uniform Cu plating needs to be addressed in future studies for the AFB to be a viable option for low-grade waste heat recovery.

Today’s commercialized TEGs typically cost $0.50 to $20 per Watt of energy delivered. To exceed the proposition of TEGs as a means for converting low-grade waste heat to electrical energy, it is important to realize an AFB constructed with low-cost materials that manifest a cost of <$0.50 per Watt of energy delivered. The AFB already uses Cu, NH$_3$ and nitrate type salts – all of which are very low cost. The most expensive component relates to the AEM and all literature reports, except one, typically use thick and high-cost electrodialysis membranes that run about > $500 m$^{-2}$. The QASEBS AEM reported herein utilizes a base polymer (SEBS) that costs of about $1.70 per kg. Because the reaction steps for the conversion of SEBS to QASEBS is simple and deploy cheap reactants, it is possible to realize an AEM at < $70 m$^{-2}$. Bae and co-workers have recently shown a more facile scheme to produce AEMs from commercially available SEBS at
large scales. The SPEEK coating applied to the Cu mesh electrodes is less than 1 mg cm\(^{-2}\) and its small loading is considered negligible when factoring the total material costs of the AFB. Plus, SPEEK is synthesized from commercially available PEEK using a simple and straightforward direct sulfonation reaction. With the peak power density of 280 W m\(^{-2}\) and a low-cost AEM, it is possible to deliver an AFB at a cost near $0.50 Watt\(^{-1}\) putting it on a par with TEG costs.

6.3 Conclusions

The highest power density to date for an AFB, 204 W m\(^{-2}\) at 25 °C and 280 W m\(^{-2}\) at 55 °C, was demonstrated in this work. As a result of improving AFB power density, the \(\eta_{th}\) increased to 2.99 % (37.9 % to the Carnot efficiency) and this represents the highest efficiency relative to Carnot for any type of TRB. The significant gains in AFB performance were achieved by i.) reducing the ohmic overpotentials through the use of zero gap design and incorporating a highly conductive QASEBs AEM, and ii.) application of a SPEEK ionomer coating on the Cu mesh electrodes that reduced reaction kinetic losses at the cathode and parasitic reactions at the anode. The new materials employed in the AFB derive from low-cost, commercially available polymers (e.g., SEBS and PEEK) and the newly redesigned AFB configuration has a cost that is on par with today’s TEG devices (~ $0.50 Watt\(^{-1}\)). Future work will look to examine the stability of these materials under relevant TRAB conditions. A current distribution analysis of the zero gap AFB design showed that the cell is now primarily limited by reaction kinetics and mass transfer as the ohmic losses in the cell have been minimized. Finally, a critical factor to the maturation of AFB technology is addressing the Faradaic efficiency problem of the anode and improving the cycling stability of the battery. Further, efforts are also needed to reduce the energy needed for NH\(_3\) distillation by optimizing the electrolyte composition of the newly
redesigned AFB configuration and considering non-traditional NH$_3$ separation methods for extracting greater $\eta_{th}$ values.
Chapter 7. Addressing Spacer Channel Resistances in MCDI Using Porous Ionic Conductors

7.1 Introduction

The spacer channel is the component that facilitates the flow of the feed saline solution through the MCDI unit. The traditionally used spacer material constitutes a nylon or any electrically insulating woven mesh material\textsuperscript{105,106}. Literature reports on spacer channel studies in MCDI show that the geometry and construction materials of the spacer strongly affects the MCDI's overall cell resistance and the flow patterns of the feed.\textsuperscript{107} Additionally, the ion transport is hampered in the spacer compartment at low concentrations as there are no fixed charge carriers to augment the ionic conductivity. As a result of the low ion transport, the device is regulated by the sluggish ion transport when compared to electrode charging.\textsuperscript{108} Alternatively, improving ion-transport rate can be achieved by a turbulent flow type within the spacer channel compartment. The turbulent flow can be achieved by packing the compartment with MCDI's spacer compartment with granular fiber or spongy separators.\textsuperscript{107}

Previous literature reports show enhanced deionization rate by incorporating activated carbon fibers, loose ion-exchange resin beads etc. From the results of experiments and EIS characterization, in Chapter 4, it was revealed that the spacer channel is a source of high resistance in the MCDI unit. A 5-10-fold reduction in membrane ASR reveled only a 2-fold reduction in energy consumption. Any further reductions in the ohmic resistance of the MCDI unit would require addressing the spacer channel resistance. Deriving inspiration from the cell design of electrodeionization (EDI), the incorporation of a resin wafer – which serves the purpose of an electrical insulator as well as a porous ion-conductive material, was hypothesized as a potential spacer material for MCDI. However, incorporation of the resin wafer into the MCDI unit has been challenging due to stack leakage and large pressure build ups. Hence, resin wafers were
unsuccessful for addressing spacer channel resistances in MCDI. Since ionomer binders enhance ionic conductivity in resin wafers, they were postulated to enhance ionic transport when used as coatings in spacer channel. Thereby, it was decided to coat the traditional nylon spacer with solution processable ionomers. This section details preliminary studies done on developing and testing ionomer coated nylon spacers for addressing spacer channel resistances in MCDI.

7.2 Results and Discussion

7.2.1 Imaging by scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDX)

![Sem images](image)

Figure 7.1. SEM images of ionomer coated nylon meshes: a) SPEEK coated at 200 micron scale bar; b) QAPSf coated at 50 micron scale bar.

Figure 7.1 shows the SEM images of the ionomer coated spacer channel: both SPEEK and QAPSf coated. The spray coated ionomer forms a layer on the mesh without blocking the pores. These SPEEK coated nylon and QAPSf coated nylon meshes were introduced into the MCDI setup and desalination runs were performed at constant current densities for 2 different concentrations of NaCl feed solutions – 500 ppm and 1000 ppm TDS.
Figure 7.2. Images from EDX mapping performed on the ionomer coated nylon spacers- a) SPEEK coating- Carbon (grey), Sulfur (yellow); b) QAPSf coating on nylon – Carbon (red), Chlorine (red).

Figure 7.2 shows the energy-dispersive x-ray spectroscopy (EDX) mapping performed to ascertain the elemental composition for characterizing the deposited ionomer material on the nylon spacer. Figure 7.2a shows a 35% relative composition of S, compared to C content denoting sulfonic acid groups in the SPEEK, whereas in Figure 7.2b, shows 17% relative percentage of Cl, denoting the presence of counterion of QAPSf.

7.2.2 MCDI runs

Figure 7.3a depicts the charge-discharge cycles for MCDI in both configurations: employing the traditional nylon spacers and SPEEK and QAPSf ionomer coated spacers. These desalination runs were performed with 500 ppm NaCl as feed solution. It is evident from Figure 7.3a that the voltage rise during the charging cycles are higher with the pristine nylon compared to the coated nylon spacer for constant current application. This implies that the energy expended in the charging process would be lower with the ionomer coated spacer. This is substantiated by the results in Table 7.1 which shows a 39.5% reduction in energy expended per ion removed from the MCDI cell. This was achieved by lowering the cell voltage rise, which was made possible by employing
ion-conductive spacer materials that improve ionic conductivity and transport for the given amount of electrical charge applied.

Figure 7.3. Charge discharge cycles for inlet of 500 ppm NaCl solution comparing MCDI desalination runs with regular nylon spacer (black) and ionomer coated nylon spacer (red) b) corresponding effluent concentration over time

Table 7.1. Figures of merit for MCDI with the different spacer configurations at 500 ppm (operated at 0.08A/-0.08A constant current for charge and discharge) and 1000 ppm (operated at 0.12A/-0.12A constant current for charge and discharge) feed inlet concentrations

<table>
<thead>
<tr>
<th>Spacer type</th>
<th>Salt removal rate (500 ppm) (%)</th>
<th>Coulombic efficiency (500 ppm) (%)</th>
<th>Energy consumed (1000 ppm) (kT ion⁻¹)</th>
<th>Energy recovery (1000 ppm) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>500 ppm</td>
<td>1000 ppm</td>
<td>500 ppm</td>
<td>1000 ppm</td>
</tr>
<tr>
<td>Regular nylon</td>
<td>28</td>
<td>24.9</td>
<td>69.9±2.3</td>
<td>60.8±1.3</td>
</tr>
<tr>
<td>Ionomer coated nylon</td>
<td>28.8</td>
<td>24.8</td>
<td>83.9±8.8</td>
<td>76.2±6.6</td>
</tr>
</tbody>
</table>

Similarly, for a feed NaCl solution of 1000 ppm, the energy expended for salt removal when MCDI was operated under a constant current density showed a 37.25% reduction with the ionomer coated spacer. The salt removal efficiencies attained were the same since the current applied was constant. The coulombic efficiency values of the process were enhanced with the ionomer coated spacer in
the MCDI. Another parameter that displayed significant improvement was the energy recovery. The discharge step in each desalination run was executed by the application of a reverse constant current until the voltage reached 0. As observed from Figure 7.3, the time taken for desorption/discharge was shorter with the ionomer coated spacers than with the pristine nylon.

7.3 Conclusions

The investigation of the ohmic overpotentials in an MCDI setup revealed that the spacer channel is a major source of resistance, contributing to the highest source of ohmic loss in the cell. Further improvements in the energy efficiency of MCDI process would require addressing ion-transport in the spacer channel resistance. A modified spacer channel based on a cation-exchange ionomer coated nylon and anion-exchange ionomer coated nylon were explored as potential ion-conductive spacer channel materials to improve the ion-transport rate and reduce the energy consumption for desalination. These improved spacers rendered up to 40% reduction in energy consumption for charging and enhanced the rate of discharge in addition to improving the percentage energy recovery during the discharge cycle. This study highlights the importance of separator materials for an energy efficient operation of MCDI and desalination performance. Further, it motivates future studies on alternate spacer materials based on ion-conductive polymer coating or grafted ionic polymers on the traditional nylon mesh to aid faster ion-transport that accelerates deionization and desorption rates. Another concept to explore is to examine how grafted-type ion-exchange polymers onto the nylon supports affect ionic conductivity and deionization. This architecture could promote ionic conductivity in spacer channels without impeding bulk fluid flow.
Chapter 8. Conclusions and Future Work

8.1 Conclusions

This Dissertation demonstrates improvements in thermodynamic efficiency and performance of MCDI, RW-EDI, and TRABs through addressing ohmic resistances. The reduction of ohmic resistances were realized through thinner, and more conductive ion-exchange membranes, in addition to new porous ion-conducting materials being developed to address spacer channel resistances – which is a significant challenge for the electrochemical separations community. In addition to device level demonstrations, the material and structural properties of various ion-exchange chemistries, as membranes and porous conductors, were investigated. The Dissertation unequivocally shows that ohmic resistances with the new materials are primarily addressed by the addition of fixed charge carriers that are distributed uniformly over the control volume for promoting ionic conduction.

In MCDI, the implementation of thinner and highly ion-conductive ion-exchange membranes resulted in reduction of area specific resistance (ASR) of the IEMs, which in turn reduced the ohmic losses that stem from IEMs in the MCDI cell. Consequently, reducing the ASR by a factor of 5 to 10 times with unconventional IEMs, poly(arylene ether) and perfluorinated chemistries, translated to a 50% reduction in energy expended per ion removed in the MCDI cell. However, further gains in energy efficiency demanded addressing ohmic resistance of the spacer channel in MCDI. For this purpose, resin wafer materials that are porous substrates in which ion-exchange resins are immobilized using a polymeric binder. The traditional non-conductive polymer binder in these RWs were replaced by ionomer binders that improved material performance. These new ionomer binder RWs displayed superior ionic conductivity (3-5x improvement), while maintaining adequate porosity, resulting in faster removal of ions from
aqueous streams with greater energy efficiency when used in RW-EDI demonstrations. The distribution of binder facilitated greater ion exchange between the liquid and resin particles and delivery of ions to the membranes. These improved performance in desalination using ion-conductive porous substrates motivated implementing them as spacer materials in MCDI as well. However, ionomer binder RWs were not successful for use in MCDI because of obfuscation of bulk fluid flow in thin channels. To overcome this problem, thin ionomer coatings were deposited on to porous nylon fabrics leading to thin, porous ionic conductors. Initial experiments demonstrate the effectiveness of this strategy for improving MCDI energy efficiency and performance, and surprisingly energy recovery.

With respect to energy conversion, ammonia-copper redox flow batteries, a type of thermally regenerative battery was upgraded in performance by deploying high performance ion-exchange materials. The remarkable gains in power production and thermal to electrical conversion efficiencies which are desirable parameters in TRABs, were achieved by reducing the ohmic overpotentials through the use of zero gap design and incorporating a highly conductive QASEBs AEM, and also the application of a SPEEK ionomer coating on the Cu mesh electrodes. This assisted further reduction in reaction kinetic losses at the cathode and parasitic reactions at the anode.

8.2 Future Work

8.2.1 Ion-conductive porous substrates for addressing spacer channel resistances in MCDI

Transmission line models for fitting EIS data signaled that further reduction in IEM’s ASR values would lead to diminished improvements in MCDI energy efficiency and further gains in energy efficiency necessitates addressing spacer channel resistances. RWs deployed as porous ion-
conductive substrates in RW-EDI highlighted that porous ionic conductors can address spacer channel resistances in electrochemical separations. However, the RWs could not be adopted for MCDI. Chapter 8 presented preliminary results of addressing spacer channel resistances in MCDI by developing ionomer coated nylon spacer materials. The aerosolized deposition of ionomers on Nylon resulted in stable, but still porous, woven fabric for MCDI. The ionomer coated nylon displayed improved the deionization rate and lowered the energy consumption. The ionomer coatings and properties have yet to be optimized but warrants further investigation for improving MCDI performance. Further, alternative architectures, such as ion-conducting polymers grafted to nylon should be considered. The ion-conducting brushes would be less than 5 nm thick and prevent obfuscation of bulk fluid flow while still augmenting ionic conductivity.

8.2.2 Water-dissociation catalysts in resin wafer fabrication

Upon inspecting the water splitting characteristics of the ionomer binder based RWs, it was found that increasing the concentration of bipolar junction sites in RWs through CER RW with AEI marginally improved water-splitting kinetics. However, as shown in Chapter 5, when the water splitting kinetics were compared to that of bipolar membranes, the RWs were found to display large overpotentials due to the absence of water-dissociation catalyst. Further improvements in water splitting characteristics were made by a modification of RW design – Janus type resin wafer that features cation-exchange resin on one side and anion-exchange resins on the other, implementing Al(OH)$_3$ nanoparticles as catalyst at the junction between the AER and CER. These Janus type resin wafers with a water-dissociation catalyst were tested and found to show enhanced water splitting in comparison to mixed type RWs due to its pre-polarizing effect.$^{109}$ These newly designed wafers with improved water splitting can be extended for niche applications in deionization such as organic acid capture and recovery and removal of silica from water. In both
of the latter applications, the formation of hydroxide ions from water-splitting creates an alkaline environment that ionizes organic acids through deprotonation and then the organic acid can be removed through ion-exchange, and the hydroxide ions can ionize silica to silicate that can remove the silicate anions through ion-exchange.

8.2.3 Addressing cell cyclability in thermally regenerative batteries

As observed from the results in Chapter 6, the next steps in improving TRBs using ammonia-copper redox couples necessitates addressing the poor Faradaic efficiency of the anode and the charge-transfer resistances for both electrodes. The drastic improvement in AFB performance has made this TRB platform competitive for waste-heat recovery. But, demonstration with a combined distillation unit and cycling stability is required to make this technology a serious alternative to TEGs.
Appendix. $^1$H-NMR Spectra for Polymer Characterization

Figure A.1. Characterization of synthesized membranes $^1$H NMR spectra of a) BrPPO, b) QAPPO, and c) SPEEK.
$^1$H-NMR was performed to determine the degree of functionalization (DF) of bromine at the aryl and benzyl positions for BrPPO polymer. The DF was calculated using equations A1 and A2. The conversion of bromine at the benzyl position to quaternary benzyl trimethylammonium was determined using equations A3 to A5. Additionally, the IEC of QAPPO (in the chloride form) was determined using equation A6. Calculated values of DF of bromine to the benzyl position was 0.33 to 0.35 and the DF value to the aryl position was 0.06 to 0.10. The conversion of bromomethyl benzyl groups to quaternary benzyl trimethylammonium was 100% and the IEC calculated was 2.1 mmol g$^{-1}$.

$$DF_{Br \text{ to benzyl}} = \frac{\text{Area (δ=4.3)CH}_2\text{Br substituent}}{\text{Area (δ≈6.4−7.0)PPO substituent} + 2 \times \text{Area (δ≈6.0−6.4) Aryl substituent}}$$  \hspace{1cm} \text{<A1>}

$$DF_{Br \text{ to aryl}} = \frac{2 \times \text{Area (δ≈6.0−6.4) Aryl substituent}}{\text{Area (δ≈6.4−7.0)PPO substituent} + 2 \times \text{Area (δ≈6.0−6.4) Aryl substituent}}$$  \hspace{1cm} \text{<A2>}

$$\text{Conversion} = \frac{\text{Area}_{\text{cation substituent}}(δ=3.7 \text{ to } 3.8)}{\text{Ratio} \cdot DF_{\text{benzyl}} \cdot \text{Area}_{\text{PPO substituent}}(δ)}$$  \hspace{1cm} \text{<A3>}

$$\text{Area}_{\text{PPO substituent}}(δ) = \text{Area}(δ=6.6 - 7.3) + 2 \times \text{Area} (δ=6.0 - 6.4)$$  \hspace{1cm} \text{<A4>}

$$\text{Ratio} = \frac{\# \text{ of Protons for cation substituent}}{\# \text{ of protons for PPO substituent}}$$  \hspace{1cm} \text{<A5>}

Determining IEC of QAPPO AEM in the chloride form

$$\text{IEC [mmol g}^{-1}] = \frac{DF_{\text{benzyl}} \times 1000 \cdot \text{Conversion}}{(\text{MW}_{\text{PPO, monomer}} + DF_{\text{benzyl}} \cdot (\text{MW}_{\text{cation}} + \text{MW}_{\text{CH}_2} + \text{MW}_{\text{chloride}} - 1) + DF_{\text{aryl}} \cdot (\text{MW}_{\text{bromide}} - 1)}$$  \hspace{1cm} \text{<A6>}

Theor. IEC = theoretical ion-exchange capacity of PPO AEMs in the chloride form (mmol g$^{-1}$)

$DF_{\text{benzyl}}$ = Degree of functionalization of bromine to the benzyl position of PPO

$DF_{\text{aryl}}$ = Degree of functionalization of bromine to the aryl position of PPO
The degree of sulfonation (DS) was determined using equation A7. Equation A8 calculated the IEC from the degree of sulfonation. The DS was 0.60 and the calculated IEC in the sodium form for SPEEK CEM was 1.8 mmol g\textsuperscript{-1}.

\[
DS = \frac{4 \cdot \text{Area}(\delta = 7.5)}{\text{Area}(\delta = 7.65 \text{ to } 8.1)} < A7
\]

\[
\text{IEC [mmol g}^{-1}]= \frac{DS \cdot 1000}{(\text{MW}_{\text{PEEK,monomer}} + DS \cdot (\text{MW}_{\text{SO}_3} + \text{MW}_{\text{sodium}} - 1))} < A8
\]

DS  = Degree of sulfonation to PEEK

\(\text{MW}_{\text{PEEK,monomer}} = \text{Molecular weight of PEEK repeat unit (g mol}^{-1}\)

\(\text{MW}_{\text{sodium}} = \text{Molecular weight of the sodium ion (g mol}^{-1}\)
Figure A.2. Characterization of synthesized ionomers a) $^1$H NMR spectra of CMPSf. b) $^1$H NMR spectra of QAPsf.
References


Vita

Varada Menon Palakkal was born in Calicut, India. She graduated with a Bachelors’ in Chemical Engineering from National Institute of Technology, Calicut. Her research work on nanocomposite thin film reverse osmosis membranes for desalination, as a summer research fellow at Ben Gurion University, Israel motivated her to pursue a PhD degree at Louisiana State university. During her PhD, she worked on projects on polymer functionalization and membrane development, finding applications in electrochemical technologies such as electrodeionization, redox-flow batteries and membrane capacitive deionization at the Arges Laboratory in collaboration with Argonne National Laboratory, Illinois. Besides research, she enjoys traveling, singing, and reading.