5-2015

Novel Separation Methods using Electrodialysis/Electrodeionization for Product Recovery and Power Generation

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Recommended Citation

Lopez-Rosa, Alexander Miguel, "Novel Separation Methods using Electrodialysis/Electrodeionization for Product Recovery and Power Generation" (2015). *Theses and Dissertations*. 1027.
http://scholarworks.uark.edu/etd/1027

Novel Separation Methods using Electrodialysis/Electrodeionization for Product Recovery and Power Generation

Novel Separation Methods using Electrodialysis/Electrodeionization for Product Recovery and Power Generation

A dissertation submitted in partial fulfillment
of the requirements of the degree of
Doctor of Philosophy in Chemical Engineering

by

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University of Arkansas
Bachelor of Science in Chemical Engineering, 2011

May 2015
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Abstract

The use of electrodialytic separations for the purification of products has been a vital technique for the past 50 years in the chemical industry. Originally used for demineralization and desalination, electrodialysis and its counterparts have expanded to assist in product purification, waste and hazard removal, and power generation. This research focused on the development of high purity organic acids purification with low power requirements. Work resulted in the development of a new type of electrodialysis process, specifically the use of ionic liquids as a secondary solvent for the development of dual solvent electrodialysis. Through dual solvent electrodialysis, ions were recovered and concentrated from products streams while enacting a solvent change. This allowed the requirements and scope of secondary purification steps to be greatly reduced and, in some cases, no longer necessary. Application of ion exchange wafers further improved separation performance of dual solvent electrodialysis. This electrodeionization technique resulted in separation efficiencies and power consumption levels similar to those of commercially implemented organic acid recovery methods with reduced complexity. Additional efforts in power generation through a technique known as reverse electrodialysis were also pursued and a discussion on the implication technology on meeting future energy demands will presented. Through this research, new avenues and applications for electrodialytic separation are now possible.

Acknowledgments

I would like to acknowledge my committee members Dr. Christa Hestekin, Dr. Shannon Servoss, Dr. Ranil Wickramasinghe, and Dr. Julie Carrier for their support and feedback throughout my graduate career. Special thanks to my primary research advisor Dr. Jamie Hestekin for the many years of support and mentorship during my graduate career.

I would like to acknowledge my fellow graduate students Tom Potts, Alice Jernigan, Lauren Woods/Merriman, James Phillip (Phil) Turner, German Perez, and Dhaval Shah for the many years of friendship and support in my studies.

I would like to acknowledge the many undergraduate students who assisted me on projects and who I had the pleasure to mentor during their studies. They include Alfonso Puente, Alex Moix, Hailey Dunsworth, Kaley Quintin, Royal McClendon, Fatima Khalid, Kassidy Boyle, and Candace Park.

Special thanks would like to be awarded to the University of Arkansas Graduate School and National Science Foundation for their support and funding for this degree. Additional thanks to the Ralph E. Martin Department of Chemical Engineering for their guidance and support throughout the degree process.

Dedication

To my loving wife, Brittany Lopez, for providing unending support through my graduate career and beyond.

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1. Chapter 3: Separation of Organic Acids from Water using Ionic Liquid Assisted Electrodialysis

Citation: A.M. Lopez, J. a. Hestekin, Separation of organic acids from water using ionic liquid assisted electrodialysis, Sep. Purif. Technol. 116 (2013) 162–169. doi:10.1016/j.seppur.2013.05.028.

I. Introduction

Electrodialysis (ED) is a charged based membrane separation technique that has a multitude of applications across the chemical industry. Its use has mainly been in ion product recovery and water desalination [1–3]. Throughout its 50 years of industry implementation, novel ion exchange membranes have been synthesized and processes have been adapted to incorporate ED in order to maximize production while minimizing costs [4–7]. Knowing this, research efforts have been underway looking for new challenges facing the chemical industry and the development of novel solutions that utilize ED with little or no modification of existing commercial modules.

A slight modification of ED is electrodeionization (EDI). EDI is the use of ion exchange resin in the solution compartments to drastically improve the solution conductivity during operation [8]. EDI is especially useful when high purity water or high ion removal is desired, such as deionized water for microelectronics processing or the recovery of low concentration ionic products [9–11]. EDI requires more power than ED due to the regeneration of the ion exchange resins through water splitting; however, energy savings result due to the enhanced solution conductivity provided by the resins [12]. Development and modeling of electrodeionization wafer has resulted in highly recyclable EDI operating at low power levels at high ion removal rates [13,14].

ED and EDI hold great potential in a multitude of industries; however, several process limitations hinder implementation. Specifically, renewable organic acid recovery has been stymied by high energy requirements for product recovery, process waste, and complex separation techniques required to achieve desired product purity [15,16]. Many separation techniques have been considered, yet few have been successfully implemented due to energy and cost constraints [17,18]. These issues include dewatering solutions and maintaining product integrity. ED can address these issues, yet a simple, cost-effective solution has not been produced [16,18]. Organic acid production requires the use of large amounts of acid and base for pH control and acid formation, resulting in the production of large amounts of waste [19,20]. The waste produced from these processes must be removed, requiring time, energy, and money. Another issue with organic acid production is dewatering. Organic acid production, especially through fermentation processes, results in low titer solutions of acid (≤ 20 wt %) with the remaining solution being water and other impurities [21–23]. Water is generally removed via LLE and salting out the organics, yet these can result in low yields which may have significant impact on overall production costs, especially when dealing with high value products [24,25].

Ionic liquids contain tremendous potential for use in electrodialytic separations. Ionic liquids are molten salts at room temperature due to bulky cation and anion structures [26,27]. They are non-flammable, highly recyclable, and possess little to no vapor pressure [28]. Manipulation of the structure of an ionic liquid also has a direct impact upon the physical and chemical characteristics of the liquid, making the design of these solvents tunable for use in a wide variety of applications [29–31]. In electrodialysis, ionic liquids have mainly been used for synthesis, recovery of solutions contaminated with other solvents, and the development of liquid membranes [27,32,33]. There has been little use for ionic liquids as solvents in ED; however, their potential for organic product recovery is high due to low vapor pressure as well as the tunable nature of these solvents.

When considering power generation, electrodialysis holds great promise through a technique known as reverse electrodialysis (RED). RED is the use of natural salinity gradients to create an electric current as opposed to using a current to create a salinity gradient [34,35].

Salient gradient energy produces power from natural estuaries where Gibbs free energy of mixing is released [36,37]. Controlled mixing of these solutions allows the generation of power with little impact to the environment. It is believed that 2.4 TW of energy is available globally through natural salinity gradients [38]. The two prevailing methods for extracting this type of power are pressure retarded osmosis (PRO) and RED. PRO uses draw solutions to generate osmotic pressure which is then removed via a turbine which generates electricity. PRO has shown promise; however, concentration polarization, membrane fouling, and regeneration of the draw solution have greatly limited the potential of this process [36,39,40]. Research into optimizing and commercializing both methods of salinity gradient energy have made great strides, yet the commercial benchmark of 5 W/m^2 membrane area has not been achieved to date. Several papers have been published above this benchmark, but most testing done was on small scales in idealized situations in which correction for real-world testing drastically reduces the expected power potential [36,39]. This emphasizes the need for directly applicable studies in which direct conversion from lab to pilot-scale experiments can occur with minimal losses.

Purpose and Significance

The purpose of this work was to develop new techniques for ED in organic acid product recovery and power generation. Using ionic liquids as a solvent, ED allowed the recovery of organic acid products from aqueous solutions with minimal operating cost and high recovery rates. In ED, the ions migrate from the aqueous solvent to the ionic liquid solvent via the ion exchange membrane and applied electrical current. Through ionic liquid assisted electrodialysis, a novel separation technique for organic acid product recovery was developed. Incorporation of EDI techniques focused on the improvement of the ED process through enhanced ion diffusion. Power production through RED incorporating ion exchange wafers resulted in reduced stack resistance and increased power output at some voltage potentials. In general, ion exchange wafers enhanced ion mobility in low conductivity solutions by shortening the diffusive pathways between solutions. This resulted in higher ion transfer rates, higher effective solution conductivities, and lower system resistances. With a reduction in solution resistance, power generated through natural salinity mixing was increased. However, correcting for wafer regeneration and pumping requirements resulted in lower than expected power densities. Results indicated that the use of wafers in this technology may not be as beneficial as expected. Additionally, a brief discussion on additional sources of salient gradient energy, including hydraulic fracturing sites, was investigated and will be discussed in subsequent chapters.

Through this research, several questions were explored and answered. When studying organic acid purification, we investigated how the incorporation of ionic liquid in membrane separations can influence ion mobility, water co-transport, and system performance. *Through ionic liquid assisted electrodialysis, organic salts were transferred from an aqueous phase into and ionic liquid phase, resulting in simplified purification at lower costs. Furthermore, through bipolar electrodialysis, organic salts were hydrated into an acidified form, resulting in the development of a simple and cost-effective method for organic acid purification via flash separation.* In our study in reverse electrodialysis, we investigated how ion exchange wafers can reduce ion diffusive pathways lowering system resistances and increasing net power densities. Additionally, we investigated the major factors in the development of commercialized RED technology focusing on the use of RED at hydraulic fracturing sites. *We proposed and investigated the potential of RED with ion exchange wafers to minimize system resistances, resulting in lower system conductivities and higher power densities over traditional systems.* Unfortunately, due to the capacitive nature of electrodeionization as well as the power requirements for system operation, the high power densities obtained cannot be extracted as usable power [39]. Further, exploration of novel processes can result in more applications for salient gradient energy.

Research Design and Methodology

Research Overview

The bulk of this research focused on the optimization of ED with ionic liquids though proper system design for this separation. For proper ionic liquid selection, the solvent would possess high solubility for organic acids with little to no solubility for water. Low water solubility allows ionic liquids to enhance the ED separation without having to consider water contamination, thus reducing the amount of acid that must be vaporized from the ionic liquid during product recovery. Further, water insolubility reduces the environmental impact of ionic liquids when applied in industrial settings due to simple clean up in cases of contamination. For modeling the ion transport, several theories on ionic transport in aqueous and non-aqueous phases were considered. Calculations focused on optimizing system performance through current efficiency and ion and water flux calculations. Through this project a method for separating organic acids from model solutions, mixed solutions, and fermentation broth using ionic liquids was developed.

After the ED proof-of-concept experiments were completed, EDI techniques were employed to determine the influence that ion exchange wafers had on the recovery of organic acid products. Ion exchange wafers were placed in the concentrate compartment in order to improve ion mobility within the ionic liquid solution. Additionally, a second ionic liquid was tested to determine the effect of ionic liquid structure on separation performance. A second model organic salt was also used in order to investigate the influence of ionic species on separation efficiency and ionic liquid affinity. Effects of current density and water and ion transfer rates were also investigated. Energy requirements for separation were calculated in order to compare the developed electrodeionization technique to existing technology. Results indicated that incorporation of ion exchange wafer substantially reduces energy requirements for organic acid product recovery, resulting from enhanced ion mobility within the ionic liquid phase.

Reverse electrodialysis was studied through a few methods. Preliminary experiments consisted of constructing single and multi-cell stacks with and without a salinity gradient present in order to measure the base power output measured using a digital multimeter. Power output was determined using voltage, current, and resistance measurements obtained from the multimeter while solutions were recirculated through the system. Single pass studies were eventually tested in order to determine if power readings were higher and more stable than the initial trials. Completion of proof-of-concept experiments resulted in low power densities and high system resistances; therefore, a new RED system was designed with thinner solution compartments. Reduction of solution compartments resulted in lower system resistances and higher power densities. However, use of a passive current to measure power potential resulted in inflated gross power densities. Elimination of this artificial power resulted in power output incapable of sustaining wafer regeneration. Subsequent chapters will discuss the overall efficacy of this technology and how RED can progress towards commercialization with and without the use of wafer technology.

Design of Experiments and Materials Overview

Preliminary studies focused on the use of a single commercially available ionic liquid for proof-of-concept experiments. Once completed, additional organic salts and ionic liquids were investigated for their impact on membrane selectivity, ion transfer, water and organic ion solubility, and overall product affinity. Experiments were conducted using a PC-Cell 64-4 for ED experiments and a Micro Flow Cell supplied by Ameridia. Concentrations of ionic species were determined though Waters HPLC system. The system consisted of a Waters 717 plus autosample injector, a Waters 1525 binary HPLC pump, an IC-Pak™ ion-exclusion column (7.8mm x 150mm), and a Waters 2414 refractive index detector set at 440 nm. Water leakage into the ionic liquid phase was determined using a Mettler-Toledo L31 Karl-Fischer titrator. Presence of organic acid in solution was confirmed by gas chromatography using a Shimadzu GC-2014 equipped with a Zebron ZB-FFAP column.

Ionic liquids in electrodialysis required certain characteristics in order to make the separation effective and economical. The solvent must have a high affinity for the product to be separated, be immiscible with contaminants, in this case water, and should be able to be synthesized in large volumes at low cost. Unfortunately, most ionic liquids available in today's market are still sold at high cost and in low quantities in order to maximize commercial revenue. Currently, imidazolium based ionic liquids have been tested in our lab due to their availability at reasonable prices and non-hazardous nature. The effect of ionic liquid structure on ED performance was investigated with specific emphasis on the influence of hydrophobicity, molecular weight, and electrical conductivity.

Reverse electrodialysis experiments were conducted using a Micro Flow Cell ED system supplied by Ameridia. Power measurements were obtained through use of a Klein Tools digital multimeter and through passive power measurements obtained using an AMEL 2053 potentiostat. Open circuit voltage was measured directly through the multimeter and stack resistance was obtained through application of voltage potential across the stack and measuring the current through the stack.

Summary and Overview of Dissertation

In summary the use of electrodialysis technology improved membrane separations where selective ion recovery was limited due to side-products or low yields. Ionic liquids in electrodialysis resulted in the development of a novel process where ion migration occurred from an aqueous phase into an ionic liquid phase. The addition of ion exchange resin wafers improved separation performance by lowering the diffusion pathway required for ion migration, resulting in higher solution conductivities and process current efficiencies. Recovery of the organic acid can then be achieved using flash separations allowing the ionic liquid to be recycled back into the ED or EDI process with no degradation of ionic liquid solvent. Main limitations of this technique were that co-water transport reduced final product concentrations. Water leakage into the ionic liquid phase resulted in higher energy requirements for product removal and solvent regeneration. Further research into the reduction of water transport during ED/EDI operation can mitigate the contamination of the product stream, substantially improving the quality of finished product; however, that study is outside the scope of this work. Reverse electrodialysis benefited marginally from electrodeionization techniques, specifically ion exchange wafers. Incorporation of wafers resulted in lower stack resistance, higher power densities, and higher gross power generation from salient gradient energy; however, consideration of current passivation and power requirements for wafer regeneration resulted in net power generation that was less than anticipated. Investigations of RED at hydraulic fracturing sites demonstrated that this technology can hold tremendous potential at unnatural salinity gradients, provided that a sufficient driving force is available for power generation. Through the following chapters, outlined in Table 1, the scope of this research will be detailed and the impact that this technology holds in product recovery and power generation applications will be discussed.

Table 1. Outline of Dissertation

CHAPTER	MAIN RESEARCH QUESTION	TOPIC OF INVESTIGATION
2	What is the current state-of-the-art for organic acid production and reverse electrodialysis?	Background and literature survey on organic acid production, electrodialytic techniques, and power generation through salinity gradients.
3	Can ionic liquids be incorporated into electrodialysis in order to improve separation performance and overall product quality?	Organic acid purification through ionic liquid assisted electrodialysis.
4	Can ion exchange wafers improve ion mobility and separation efficiencies within ionic liquids during electrodialytic separations?	Improvements of separation performance using wafer enhanced electrodeionization using ionic liquid solvents.
5	What influence can ion exchange resin technology have on reverse electrodialysis?	Incorporation of ion exchange wafers in reverse electrodialysis for improved power generation
6	How can this research further progress the fields of electrodialysis and improve upon state-of-the-art technologies used in industry?	Summary of presented research, future direction and implications of subject matter, and overall impact to the field.

References

[1] R.K. McGovern, A.M. Weiner, L. Sun, C.G. Chambers, S.M. Zubair, J.H. Lienhard V, On the cost of electrodialysis for the desalination of high salinity feeds, Appl. Energy. 136 (2014) 649–661. doi:10.1016/j.apenergy.2014.09.050.

[2] A. H. Galama, M. Saakes, H. Bruning, H.H.M. Rijnaarts, J.W. Post, Seawater predesalination with electrodialysis, Desalination. 342 (2014) 61–69. doi:10.1016/j.desal.2013.07.012.

[3] F. Valero, A. Barceló, R. Arbós, Electrodialysis Technology. Theory and Applications ., (2010) 3–20.

[4] V.D. Grebenyuk, O. V Grebenyuk, Electrodialysis : From an Idea to Realization, 38 (2002) 806–809.

[5] S. Sridhar, C. Feldmann, Electrodialysis in a non-aqueous medium: A clean process for the production of acetoacetic ester, J. Memb. Sci. 124 (1997) 175–179. doi:10.1016/S0376-7388(96)00221-9.

[6] E. Korngold, L. Aronov, N. Daltrophe, Electrodialysis of brine solutions discharged from an RO plant, Desalination. 242 (2009) 215–227. doi:10.1016/j.desal.2008.04.008.

[7] L. Yu, A. Lin, L. Zhang, C. Chen, W. Jiang, Application of electrodialysis to the production of Vitamin C, Chem. Eng. J. 78 (2000) 153–157.

[8] L.L. Alvarado, A. Chen, Electrodeionization: Principles, Strategies, and Applications, Electrochim. Acta. 132 (2014) 583–597. doi:10.1016/j.electacta.2014.03.165.

[9] Ö. Arar, Ü. Yüksel, N. Kabay, M. Yüksel, Various applications of electrodeionization (EDI) method for water treatment—A short review, Desalination. 342 (2014) 16–22. doi:10.1016/j.desal.2014.01.028.

[10] Simplified electrodeionization technology reduces operating costs, Chem. Eng. 117 (2010) 9. http://0-search.ebscohost.com.library.uark.edu/login.aspx?direct=true&db=a9h&AN=53013195&site=ehost-live.

[11] W. Su, R. Pan, Y. Xiao, X. Chen, Membrane-free electrodeionization for high purity water production, Desalination. 329 (2013) 86–92. doi:10.1016/j.desal.2013.09.013.

[12] Y. Tanaka, Ion Exchange Membranes, Elsevier, 2015. doi:10.1016/B978-0-444-63319-4.00018-3.

[13] T. Ho, A. Kurup, T. Davis, J. Hestekin, Wafer Chemistry and Properties for Ion Removal by Wafer Enhanced Electrodeionization, Sep. Sci. Technol. 45 (2010) 433–446. doi:10.1080/01496390903526709.

[14] A.S. Kurup, T. Ho, J. a. Hestekin, Simulation and Optimal Design of Electrodeionization Process: Separation of Multicomponent Electrolyte Solution, Ind. Eng. Chem. Res. 48 (2009) 9268–9277. doi:10.1021/ie801906d.

[15] C. Huang, T. Xu, Y. Zhang, Y. Xue, G. Chen, Application of electrodialysis to the production of organic acids: State-of-the-art and recent developments, J. Memb. Sci. 288 (2007) 1–12. doi:10.1016/j.memsci.2006.11.026.

[16] A. Vertova, G. Aricci, S. Rondinini, R. Miglio, L. Carnelli, P. D'Olimpio, Electrodialytic recovery of light carboxylic acids from industrial aqueous wastes, J. Appl. Electrochem. 39 (2009) 2051–2059. doi:10.1007/s10800-009-9871-9.

[17] F.S. Oliveira, J.M.M. Araújo, R. Ferreira, L.P.N. Rebelo, I.M. Marrucho, Extraction of l-lactic, l-malic, and succinic acids using phosphonium-based ionic liquids, Sep. Purif. Technol. 85 (2012) 137–146. doi:10.1016/j.seppur.2011.10.002.

[18] J.A.L. Blinco, W.O.S. Doherty, Review of extraction technologies for organic acid production, Proc. Conf. Aust. Soc. Sugar Cane Technol. 27th (2005) 480–488.

[19] G. Liu, H. Luo, H. Wang, B. Wang, R. Zhang, S. Chen, Malic acid production using a biological electrodialysis with bipolar membrane, J. Memb. Sci. 471 (2014) 179–184. doi:10.1016/j.memsci.2014.08.014.

[20] C.S. López-Garzón, A.J.J. Straathof, Recovery of carboxylic acids produced by fermentation., Biotechnol. Adv. 32 (2014) 873–904. doi:10.1016/j.biotechadv.2014.04.002.

[21] S. Liang, C. Wan, Carboxylic acid production from brewer's spent grain via mixed culture fermentation, Bioresour. Technol. 182 (2015) 179–183. doi:10.1016/j.biortech.2015.01.082.

[22] Z.Y. Zhang, B. Jin, J.M. Kelly, Production of lactic acid from renewable materials by Rhizopus fungi, Biochem. Eng. J. 35 (2007) 251–263. doi:10.1016/j.bej.2007.01.028.

[23] C. Park, H.-G. Nam, K.B. Lee, S. Mun, Optimal design and experimental validation of a simulated moving bed chromatography for continuous recovery of formic acid in a model mixture of three organic acids from *Actinobacillus* bacteria fermentation., J. Chromatogr. A. 1365 (2014) 106–14. doi:10.1016/j.chroma.2014.09.005.

[24] M. Blahušiak, Š. Schlosser, J. Marták, Extraction of butyric acid by a solvent impregnated resin containing ionic liquid, React. Funct. Polym. 71 (2011) 736–744. doi:DOI: 10.1016/j.reactfunctpolym.2011.04.002.

[25] D.G. Cherkasov, K.K. Il'in, Salting out of butyric acid from aqueous solutions with potassium chloride, Russ. J. Appl. Chem. 82 (2009) 920–924. doi:10.1134/S1070427209050346.

[26] A. Mell, U. Kragl, 2.73 - Ionic Liquids, in: E.-C.M.M.-Y.B.T.-C.B. (Second Edition) (Ed.), Academic Press, Burlington, 2011: pp. 999–1006. doi:http://dx.doi.org/10.1016/B978-0-08-088504-9.00151-3.

[27] K. Haerens, P. De Vreese, E. Matthijs, L. Pinoy, K. Binnemans, B. Van der Bruggen, Production of ionic liquids by electrodialysis, Sep. Purif. Technol. (n.d.). doi:10.1016/j.seppur.2012.02.017.

[28] M.J. Earle, K.R. Seddon, Ionic liquids. Green solvents for the future, Pure Appl. Chem. 72 (2000) 1391–1398. doi:10.1351/pac200072071391.

[29] Z. Qiu, J. Texter, Ionic liquids in microemulsions, Curr. Opin. Colloid Interface Sci. 13 (2008) 252–262.

[30] H. Luo, C. Xu, D. Zou, L. Wang, T. Ying, Hydrothermal synthesis of hollow MoS2 microspheres in ionic liquids/water binary emulsions, Mater. Lett. 62 (2008) 3558–3560. doi:10.1016/j.matlet.2008.03.050.

[31] C. Yue, D. Fang, L. Liu, T.-F. Yi, Synthesis and application of task-specific ionic liquids used as catalysts and/or solvents in organic unit reactions, J. Mol. Liq. 163 (2011) 99–121. doi:http://dx.doi.org/10.1016/j.molliq.2011.09.001.

[32] X. Wang, Y. Nie, X. Zhang, S. Zhang, J. Li, Recovery of ionic liquids from dilute aqueous solutions by electrodialysis, Desalination. 285 (2012) 205–212. doi:10.1016/j.desal.2011.10.003.

[33] T. Hoshino, Preliminary studies of lithium recovery technology from seawater by electrodialysis using ionic liquid membrane, Desalination. 317 (2013) 11–16. doi:10.1016/j.desal.2013.02.014.

[34] J. Veerman, M. Saakes, S.J. Metz, G.J. Harmsen, Reverse electrodialysis: A validated process model for design and optimization, Chem. Eng. J. 166 (2011) 256–268. doi:10.1016/j.cej.2010.10.071.

[35] J.W. Post, Blue Energy : electricity production from salinity gradients by reverse electrodialysis, Wageningen University, 2009.

[36] N.Y. Yip, M. Elimelech, Thermodynamic and energy efficiency analysis of power generation from natural salinity gradients by pressure retarded osmosis., Environ. Sci. Technol. 46 (2012) 5230–9. doi:10.1021/es300060m.

[37] K. Nijmeijer, S. Metz, Sustainable Water for the Future: Water Recycling versus Desalination, Elsevier, 2010. doi:10.1016/S1871-2711(09)00205-0.

[38] D. A. Vermaas, M. Saakes, K. Nijmeijer, Doubled power density from salinity gradients at reduced intermembrane distance., Environ. Sci. Technol. 45 (2011) 7089–95. doi:10.1021/es2012758.

[39] B.E. Logan, M. Elimelech, Membrane-based processes for sustainable power generation using water., Nature. 488 (2012) 313–9. doi:10.1038/nature11477.

[40] S.C. Chen, C.F. Wan, T.S. Chung, Enhanced fouling by inorganic and organic foulants on pressure retarded osmosis (PRO) hollow fiber membranes under high pressures, J. Memb. Sci. 479 (2015) 190–203. doi:10.1016/j.memsci.2015.01.037.

II. Background

Electrodialysis: State-of-the-art Charged Based Separation

Electrodialysis (ED) is a charged based separation that selectively transports ions in solution from one compartment within the cell to another. Electric current is applied to the system and ions migrate towards the electrodes through semi-permeable membranes. Alternation of these membranes allows the removal of ions from one solution into another. ED is advantageous when separating ionic products and molecules in solution. Disadvantages include selectivity issues with membranes and limitations on final product concentrations and solvents, often resulting in secondary purification steps required [1,2]. Electrodialysis has been used in the food and beverage industry for the deacidification of fruit juices [3], demineralization of whey protein [4,5], and the removal of sodium from products [6].

Historically, electrodialysis was first proposed in 1890 by Maigrot, Sabates, and Ostwald for the demineralization of sugar syrup [7,8]. Over the early 20th century, many improvements were made to the initial system, and in the 1930's Teorell began developing charged membrane theory to mathematically describe the phenomenon found in these systems. In the 1950's the first ion exchanged membranes were produced by W. Juda, W.A. McRay, and Ionics (USA) with focus on desalination plants in South Africa and Saudi Arabia [9]. By the late 20th century, electrodialysis had emerged as a vital separation technique across the chemical industry.

A schematic of a typical electrodialysis cell is presented in Figure 1. The electrodes serve as a means for redox reactions that allow the continuous flow of electrons while the rinse solutions act as ion sinks which protect the electrode metals from dissolution. Cations pass through cation exchange membranes (CEM's) and are blocked by anion exchange membranes (AEM's) while anions pass through AEM's and blocked by CEM's. This allow the removal of ions from one solution and the accumulation of ions in another. Membranes are synthesized from a base polymer treated with charged molecules. AEM's typically contain nitrogen groups while CEM's contain sulfonated polymers. Table 1 presents common ion exchange membranes and their properties [10]. Important factors on the selection of a membrane are the ion exchange capacity, permselectivity, member thickness, and robustness in the selected solvent.

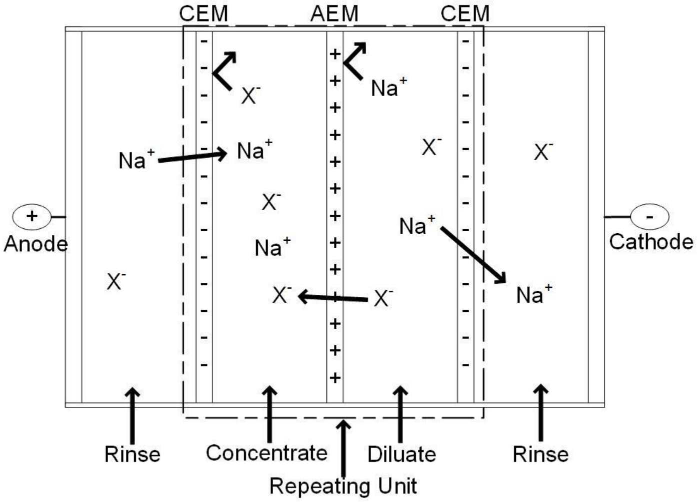

Figure 1. ED Stack Setup. Repeating unit refers to number of cells in the system.

Table 1. Ion Exchange Membrane Properties

Membrane	Permselectivity	Resistance	Membrane thickness	Burst Strength
NEOSEPTA AMX	0.98	2.4 Ω-cm^2	0.14 mm	0.25 MPa
Fumasep FAS	0.95	3.1 Ω-cm^2	0.13 mm	-
Fumasep FKS	0.96	8 Ω-cm^2	0.12 mm	-
NEOSEPTA CMB	-	4.5 Ω-cm^2	0.21 mm	0.40 MPa
NEOSEPTA BP1E	0.98	-	0.22 mm	0.40 MPa
Fumasep BPM	0.98	3 Ω-cm^2	0.25 mm	-
Nafion® N-117	0.95	1.5 Ω-cm^2	0.18 mm	-

Typical state-of-the-art ED consists of product recovery at power consumption rates of 1 kWh/kg ionic product or lower and 1 kWh/m^3 water purified [11–13]. Additionally, production rates must be scalable and minimize product loss. For example, citric acid production using ED techniques can recover product from fermentation and waste streams at high current efficiencies [14,15]. Wang *et al*. demonstrated lactic acid recovery from a continuous fermentation system by electrodialysis [16]. de Groot *et al*. also developed a method for the recovery of monoethanolamine with power requirements as low as 0.35 kWh/kg product [17]. Other research conducted has demonstrated recovery and removal of ions from wastewater [18,19] and brine solutions [20–22].

Mathematical Theory

Electrodialysis performance is quantified by a few key variables. The most important factors to consider are the ion flux through the membranes, water co-flux, and the process current efficiency. Current efficiency is calculated using equation 1.

$$\boldsymbol{\eta = \frac{VF(C_f - C_i)}{zIt}} \tag{1}$$

where V is the system volume, F is Faraday’s constant, C_f is the final ion concentration, C_i is the initial ion concentration, z is the ion valence, I is the system current, and t is the operation time. Ion and solvent flux are calculated using equations 2 and 3.

$$\boldsymbol{J_i = \lambda i_d - \mu \Delta C} \tag{2}$$

$$\boldsymbol{J_s = \phi i + \rho \Delta C} \tag{3}$$

where λ is the transport number, i_d is the current density, ϕ is the overall electro-osmotic permeability, and ΔC is the concentration gradient at the membrane surface. From these equations, the important characteristics of the ED system become evident, e.g. current density, membrane area. Another important equation used during scale-up is the determination of membrane area required to perform an ion depletion from a given set of initial conditions. This is used especially during the removal of contaminants in industry in order to reuse process water or discharge within environmental regulations. Equation 4 demonstrates how this can be determined.

$$\boldsymbol{A} = \frac{\boldsymbol{QF(C_f - C_i)}}{\boldsymbol{i\eta}} \qquad (4)$$

In this equation, Q denotes the volumetric flow rate through the electrodialysis stack due to many of these process occurring in a continuous fashion.

Electrodialysis is often modeled either by the use of the Nernst-Plank equation or through a steady-state convective diffusion equation assuming laminar flow through the cell channels [23–25]. Results of ED modeling and simulation can be summarized in the parametric plots presented in figures 2 and 3 [15,26]. In general, current efficiency is highest at low current densities, yet this results in low productivity of desired ionic products. High productivity is often desired, so current densities are raised and loss of ideal current efficiency is acceptable as long as power consumption can be justified by process economics. Additionally, continued increase in current density will lead to greater productivity until the limiting current density is reached. At this point, electrical potential supplied to the system will no longer drive ionic movement and will begin the transition to the generation of hydrogen and oxygen molecules due to water splitting. Water splitting is undesired in ED operation, thus most ED operation occurs within the ohmic region. However, during EDI operation water splitting allows the regeneration of the ion exchange resin used within the flow compartments. Successful EDI operation requires a higher voltage drop across the membrane stack to ensure sufficient water splitting for wafer regeneration.

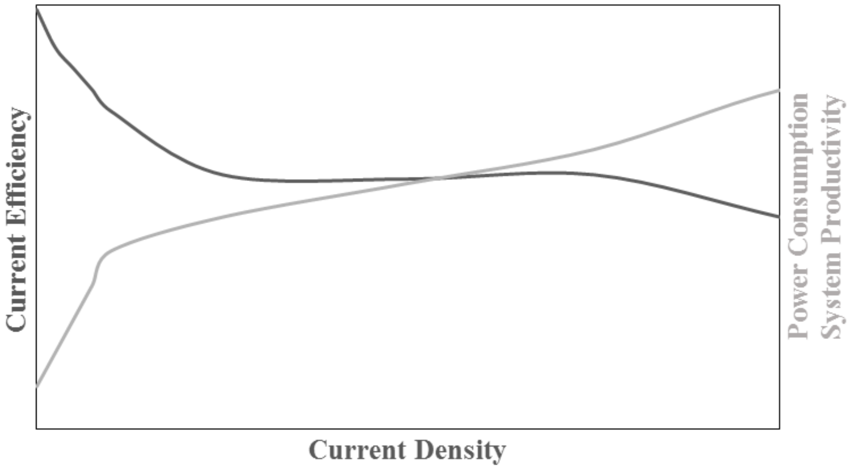

Figure 2. Parametric plot describing the effect that current density plays on current efficiency and power consumption during normal ED operation.

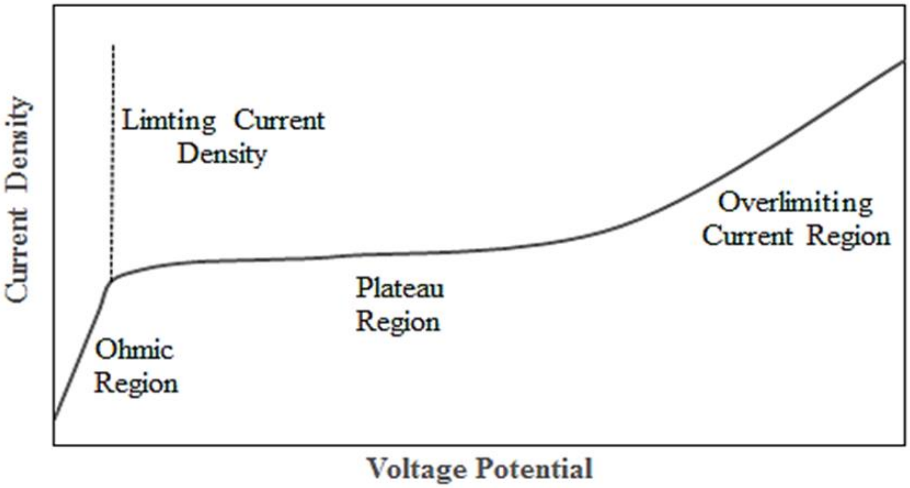

Figure 3. Parametric plot describing the influence of increased voltage supplied on electrodialytic systems.

Organic Acid Production

Organic acids have been used to produce a multitude of products ranging from pharmaceuticals and specialty chemicals to foods and biofuels [27–31]. Synthesis of these compounds can occur from chemical synthesis or through fermentation. The largest organic acid produced globally through fermentation is citric acid, with over 1.7 million tons produced per year [32,33]. Citric acid is used primarily as a food additive with some additions in cosmetics, detergents, and chemical cleaners [32]. Another organic acid with wide scale global production is acetic acid. Although produced mainly through chemical synthesis from methanol, fermentation for the production of acetic acid is crucial for the production of vinegar [34–36]. Acetic acid is produced for use in the food industry and as a natural herbicide and fungicide [37]. Butyric acid is also found in the food industry as a preservative, been incorporated into biocompatible plastics, and has recently been investigated for production of the biofuel butanol [38,39]. Trifluoroacetic acid is produced to act as a solvent, reagent, and oxidizer in a multitude of chemical reactions [40]. Sorbic acid and its derivatives are used as preservatives in foods [41,42]. Organic salts also have their uses. Sodium gluconate is used in the food and pharmaceutical industry to assist in the dissolution of metals [43,44]. Sodium salicylate is a potent drug that is used in the treatment of neurological disorders, and trolamine salicylate is an organic salt often found in cosmetics and pharmaceutical topical agents [45–47]. Table 2 summarizes the largest organic acid markets along with their methods of synthesis.

Table 2. Global production of organic acids

Organic Acid	Global Output (metric tons)	Production Methods
Citric Acid	1,700,000	Fermentation [32]
Acetic Acid	7,000,000	Fermentation/Chemical Synthesis [49]
Lactic Acid	150,000	Fermentation [48]
Propionic	130,000	Chemical Synthesis [49]
Formic acid	770,000	Chemical Synthesis [49]
Gluconic Acid	60,000	Fermentation [50]

Recently, biological pathways have gained great attention from the scientific community due to the ability to produce organic acids from renewable feedstocks instead of traditional chemical synthesis methods [51–53]. For example, citric acid is one of the most well developed fermentation pathways for industrial production with global market value over 2 billion dollars [15,30]. Production of organic products via feedstocks require many steps each with their own limitations. Typically feedstocks are broken down into simple carbohydrates and consumed by a micro-organism such as yeast or bacteria that produces desired products. Once fermentation is complete, they can be removed via filtration and purified to the desired quality. Organic acids produced are often neutralized during fermentation and require acidification. Sulfuric acid is commonly used to lower solution pH and produce the desire organic products. Excess acid is then removed and discarded [54]. Figure 4 presents a process flow diagram of citric acid production from fermentation summarizing the steps involved in synthesis. A large number of articles have been produced documenting the breakdown, conversion, and purification of organic acids from sources such as yeast [55,56], Aspergillus niger [57,58], and Rhizopus orizae [59,60]. From these articles, it becomes evident that the most energy and cost intensive steps of bioconversion are in product recovery from media and the final stages of purification.

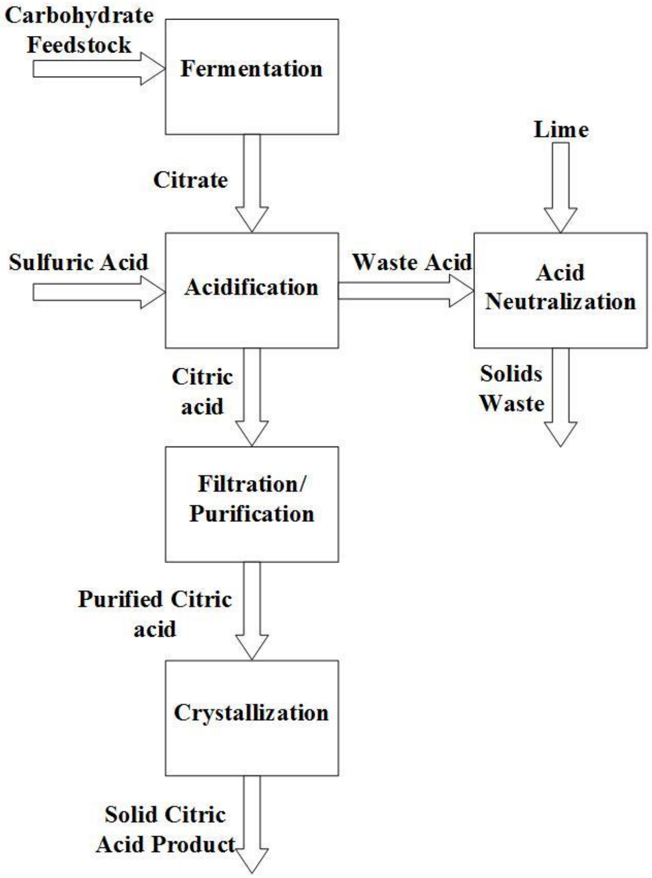

Figure 4. Citric Acid Production from Fermentation.

Separation of organic products from fermentation broth in a batch or continuous process occurs through either a multi-filtration or chromatography process [61]. The initial steps separate cells and particulates from the broth while subsequent steps remove the desired products out of the broth. Often a continuous fermentation process is preferred over batch operations due to the ability to produce and remove organic acid products simultaneously and in larger quantities as compared to batch processes [62]. Continuous removal of products serves two purposes. First, many desired products can be toxic to the species producing at high concentrations, therefore high titers are not possible. In order to maximize product formation, products are removed to reduce product toxicity, ensuring cell longevity. Second, removal of desired products can allow side products to be consumed by bacteria and converted to desired products once high concentrations of waste products have been achieved in the broth. If products are intracellular, continuous product recovery isn't possible and batch operations are conducted. Recovery of products from batch operations generally occurs by cell lysing followed by filtration or extraction of products.

Once products are recovered from fermentation, purification is often needed. This step can take many forms and can be simple or complex depending on the nature of the organic product to be recovered. For most organic acids, products are typically recovered via electrodialysis, liquid extraction, or crystallization. Liquid extraction is the most common due to its simplistic approach and high recoveries and short retention times [14,63,64]. The main drawback is that harsh chemicals are often required which produces large amounts of hazardous waste. Electrodialysis allows selective recovery of ionic products with low energy requirements. Disadvantages include selectivity issues with membranes and limitations on final product concentrations due to water and co-ion transport, often resulting in secondary purification steps required. Salting out is typically done by the addition of a stripping salt which generates an organic acid rich phase above the aqueous phase. This is effective for quick recovery of organics but requires large quantities of salt and extraction efficiency is limited to 85-90% [65,66]. Crystallization is very common and beneficial because crystals can easily be recovered via filtration and dried to high purity. Limitations result when large amounts of waste salt are produced when crystals require dissolution to an acid state.

Reduction in power consumption coupled with techniques for increased productivity are necessary for many biological pathways for organic acid production to achieve full-scale implementation. The most intensive step of product recovery is dewatering. Dewatering a solution can occur through crystallization, electrodialysis, or liquid-liquid extraction. Typical electrodialytic separations require 0.2-22.84 kWh/kg product and cost about \$0.105-0.427/kg acid recovered [67,68]. For example, succinic acid production through biological pathways has been produced at \$0.55-2.20/kg using electrodialysis and liquid-liquid extraction while the cost of lactic acid manufacturing is approximately \$0.55/kg [52,69–71]. The main targets for cost reduction in electrodialysis are decreasing membrane costs, improving anti-fouling capabilities of membranes, and improving membrane selectivity over co-ions [1,72].

Power Generation through Reverse Electrodialysis

With the growing demand for energy coupled with concerns over greenhouse gas emissions and petroleum supplies, salient gradient energy has become a topic of interest in the development of sustainable, renewable energy sources. Salient gradient energy is the extraction of mixing energy between two solutions through the application of membranes [73]. Originally proposed by Pattle in the 1950's and later by Norman and Loeb in the 1970's, salient gradient energy has emerged as a method of sustainable power generation with as much as 1.4-2.6 TW of global production possible [74–76]. This process occurs through two technologies; PRO and RED [77–79]. PRO is the use of an osmotic pressure gradient to build pressure to move and generate electricity through a turbine. RED relies on the Gibbs free energy of mixing associated with solutions of differing salinities to generate electricity [80,81]. Several papers have been published on both topics with little agreement over which technology is more economical. PRO studies have reported power outputs has high as 5 W/m^2 [76]. However, the only pilot/industrial plans for this technology underway are in the Netherlands using RED [82].

RED is the generation of electrical power through separation of solutions at different salinities by semi-permeable membranes [83]. Since the solutions are at differing salinities, ions will move from one compartment to another through controlled mixing. Careful arrangement of membranes result in negative ions flowing in one direction and positive ions flowing in the opposite direction. This directionality of ion mixing results in electric current which can be recovered as usable power. Figure 5 shows the energy production process through RED.

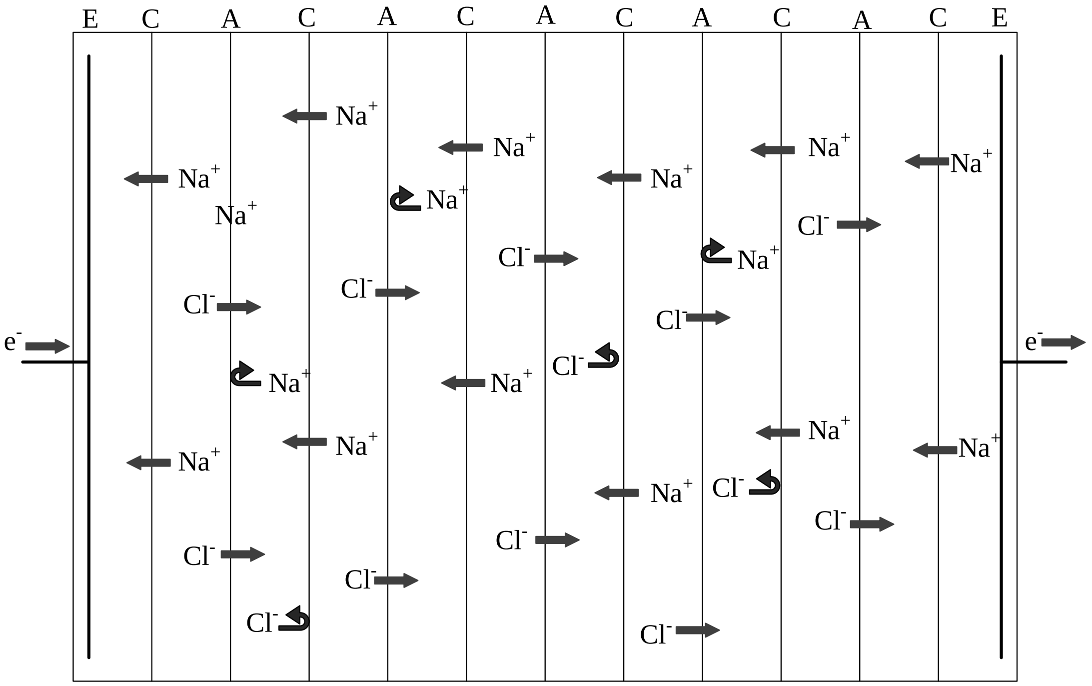

Figure 5. Power Generation through RED. E – Electrodes A – Anion Exchange Membranes C – Cation Exchange Membranes

A major issue concerning RED is that of energy recovery. Veerman *et al.* reported that 1.7 MJ is generated when 1 m^3 of seawater is mixed with 1 m^3 of riverwater [84]. The issue is the extraction of this energy at high efficiencies. Typical energy extraction efficiencies for RED are low (7-22%) [84–86]. However, Post *et al.* reported an extraction of approximately 80% of the theoretical maximum through low current densities which resulted in low power densities [87]. The main tradeoff becomes the optimization of power density and extraction efficiency. Currently, no research has been able to solve this issue.

RED has made great strides in the past decade with much of the work going to the Nijmeijer group and Harmsen group in the Netherlands as well as Bruce Logan's lab at Penn State [73,81,88–90]. Veermas *et al.* has found that minimization of the intermembrane distance significantly reduces cell resistance, maximizing power potential [88]. Further refinements have come from the use of conductive spacers [91], profiled membranes [92,93], and the design of ultra-thin ion exchange membranes [94]. Studies have also been conducted on the effects of fouling and channeling in RED systems [80,95]. At current state of the art, RED has produced power at 2.2 W/m^2 [88]. The benchmark for industrial application is currently set at 5 W/m^2 signifying that there exists a need for further research in order to commercialize this technology.

Mathematical Theory of Reverse Electrodialysis

In RED, the main objective is to maximize the power output from two mixing bodies of water. The maximum voltage obtainable from any two solutions is quantified by the Nernst equation presented in Equation 5 [81].

$$\boldsymbol{\Delta V = N_c \alpha \frac{RT}{zF} \ln \frac{C_c}{C_d}} \tag{5}$$

In this equations, N_c is the number of cell pairs, α is the membrane permselectivity, R is the ideal gas constant, T is the absolute temperature, z is the ionic valence, F is Faraday's constant, C_c is the ion concentration in the concentrate (seawater) compartment, and C_d is the ion concentration in the dilute (freshwater) compartment. For seawater and freshwater solutions, the voltage potential generated per cell is approximately 0.4 V. From this potential, the limiting factor of resistance comes into play. System resistance has been the largest limitation for high power capabilities in RED with many efforts focused on the reduction of cell and membrane resistance [94,96,97]. Stack resistance can be determined from Equation 6 [76].

$$\boldsymbol{R_{stack} = R_{electrode} + R_{CEM} + \frac{h_c}{k_c} + \frac{h_d}{k_d} + R_{AEM}} \qquad (6)$$

In this equation, $R_{electrode}$ is the electrode resistance, R_{CEM} is the cation exchange membrane resistance, R_{AEM} is the anion exchange membrane resistance, k_c is the concentrate ion conductivity, k_d is the diluate ion conductivity, h_c is the concentrate solution height, and h_d is the diluate solution height. In most cases the electrode resistance is considered negligible with the majority of system resistance occurring through the ionic solutions and system membrane. Once resistance has been determined, the maximum theoretical power obtainable from RED can be calculated. The power obtained from RED can be determined from Equation 7.

$$\boldsymbol{P = I^2 R_{load} = \frac{\Delta V^2 R_{load}}{(R_{stack} + R_{load})^2}} \qquad (7)$$

In this equation, P is power, I is the system current, and R_{load} is the load resistance placed upon the stack. Knowing that the maximum obtainable power from RED occurs when R_{load} is equivalent to R_{stack}, the maximum gross power obtainable can be calculated from Equation 8.

$$\boldsymbol{P_{gross} = \frac{\Delta V^2}{8 R_{stack}}} \qquad (8)$$

From the gross power potential, the net power can be determined by subtracting out energy required to pump solutions through the system as written in Equation 9.

$$\boldsymbol{P_{net} = P_{gross} - P_{pump}} \qquad (9)$$

With net power calculated, RED techniques can then be compared for efficacy while variables such as intermembrane distance, solution conductivity, and membrane characteristics investigated for optimum power output.

References

[1] S. H., Electrodialysis, a mature technology with a multitude of new applications, Spec. Issue to Honour Previous Ed. Miriam Balaban. 264 (2010) 268–288. doi:10.1016/j.desal.2010.04.069.

[2] S. Sridhar, Electrodialysis in a non-aqueous medium: production of sodium methoxide, J. Memb. Sci. 113 (1996) 73–79. doi:10.1016/0376-7388(95)00217-0.

[3] M. Fidaleo, M. Moresi, Electrodialysis applications in the food industry., Adv. Food Nutr. Res. 51 (2006) 265–360. doi:10.1016/S1043-4526(06)51005-8.

[4] M. Greiter, S. Novalin, M. Wendland, K.-D. Kulbe, J. Fischer, Desalination of whey by electrodialysis and ion exchange resins: analysis of both processes with regard to sustainability by calculating their cumulative energy demand, J. Memb. Sci. 210 (2002) 91–102. doi:10.1016/S0376-7388(02)00378-2.

[5] J. Balster, I. Pünt, D.F. Stamatialis, H. Lammers, a. B. Verver, M. Wessling, Electrochemical acidification of milk by whey desalination, J. Memb. Sci. 303 (2007) 213–220. doi:10.1016/j.memsci.2007.07.015.

[6] M. Fidaleo, M. Moresi, A. Cammaroto, N. Ladrange, R. Nardi, Soy sauce desalting by electrodialysis, J. Food Eng. 110 (2012) 175–181. doi:10.1016/j.jfoodeng.2011.06.002.

[7] V.A. Shaposhnik, K. Kesore, An early history of electrodialysis with permselective membranes, J. Memb. Sci. 136 (1997) 35–39.

[8] R.W. Baker, Ion Exchange Membrane Processes - Electrodialysis, in: Membr. Technol. Appl., 2004: pp. 393–423.

[9] V.D. Grebenyuk, O. V Grebenyuk, Electrodialysis : From an Idea to Realization, Russ. J. Electrochem. 38 (2002) 806–809.

[10] T. Xu, Ion exchange membranes: State of their development and perspective, J. Memb. Sci. 263 (2005) 1–29. doi:10.1016/j.memsci.2005.05.002.

[11] G. Liu, H. Luo, H. Wang, B. Wang, R. Zhang, S. Chen, Malic acid production using a biological electrodialysis with bipolar membrane, J. Memb. Sci. 471 (2014) 179–184. doi:10.1016/j.memsci.2014.08.014.

[12] A.M. Lopez, J.A. Hestekin, Separation of organic acids from water using ionic liquid assisted electrodialysis, Sep. Purif. Technol. 116 (2013) 162–169. doi:10.1016/j.seppur.2013.05.028.

[13] R.K. McGovern, A.M. Weiner, L. Sun, C.G. Chambers, S.M. Zubair, J.H. Lienhard V, On the cost of electrodialysis for the desalination of high salinity feeds, Appl. Energy. 136 (2014) 649–661. doi:10.1016/j.apenergy.2014.09.050.

[14] T. Ali, D. Bylund, S.A. Essén, U.S. Lundström, Liquid extraction of low molecular mass organic acids and hydroxamate siderophores from boreal forest soil, Soil Biol. Biochem. 43 (2011) 2417–2422. doi:10.1016/j.soilbio.2011.08.015.

[15] L.-P. Ling, H.-F. Leow, M.R. Sarmidi, Citric acid concentration by electrodialysis ion and water transport modeling.pdf, J. Memb. Sci. 199 (2002) 59–67. doi:10.1016/S0376-7388(01)00678-0.

[16] X. Wang, Y. Wang, X. Zhang, H. Feng, T. Xu, In-situ combination of fermentation and electrodialysis with bipolar membranes for the production of lactic acid: continuous operation., Bioresour. Technol. 147 (2013) 442–8. doi:10.1016/j.biortech.2013.08.045.

[17] M.T. de Groot, A.A.C.M. Bos, A.P. Lázaro, R.M. de Rooij, G. Bargeman, Electrodialysis for the concentration of ethanolamine salts, J. Memb. Sci. 371 (2011) 75–83. doi:10.1016/j.memsci.2011.01.023.

[18] Y.-N. Su, W.-S. Lin, C.-H. Hou, W. Den, Performance of integrated membrane filtration and electrodialysis processes for copper recovery from wafer polishing wastewater, J. Water Process Eng. 4 (2014) 149–158. doi:10.1016/j.jwpe.2014.09.012.

[19] T. Benvenuti, R.S. Krapf, M.A.S. Rodrigues, A.M. Bernardes, J. Zoppas-Ferreira, Recovery of nickel and water from nickel electroplating wastewater by electrodialysis, Sep. Purif. Technol. 129 (2014) 106–112. doi:10.1016/j.seppur.2014.04.002.

[20] M. Wang, K. Wang, Y. Jia, Q. Ren, The reclamation of brine generated from desalination process by bipolar membrane electrodialysis, J. Memb. Sci. 452 (2014) 54–61. doi:10.1016/j.memsci.2013.10.029.

[21] E. Korngold, L. Aronov, N. Daltrophe, Electrodialysis of brine solutions discharged from an RO plant, Desalination. 242 (2009) 215–227. doi:10.1016/j.desal.2008.04.008.

[22] C. Jiang, Y. Wang, Z. Zhang, T. Xu, Electrodialysis of concentrated brine from RO plant to produce coarse salt and freshwater, J. Memb. Sci. 450 (2014) 323–330. doi:10.1016/j.memsci.2013.09.020.

[23] M. Sadrzadeh, A. Kaviani, T. Mohammadi, Mathematical modeling of desalination by electrodialysis, Desalination. 206 (2007) 538–546. doi:10.1016/j.desal.2006.04.062.

[24] Z. Zourmand, F. Faridirad, N. Kasiri, T. Mohammadi, Mass transfer modeling of desalination through an electrodialysis cell, Desalination. 359 (2015) 41–51. doi:10.1016/j.desal.2014.12.008.

[25] V.A. Shaposhnik, V.A. Kuzminykh, O. V Grigorchuk, V.I. Vasil, Analytical model of laminar flow electrodialysis with ion-exchange membranes, 133 (1997) 27–37.

[26] M. Demircioglu, N. Kabay, I. Kuricaovali, E. Ersoz, I. Kurucaovali, Demineralization by electrodialysis (ED) - separation performance and cost comparison of monovalent salts, Desalination. 153 (2003) 329–333.

[27] A. Lianou, K.P. Koutsoumanis, J.N. Sofos, Microbial Decontamination in the Food Industry, Elsevier, 2012. doi:10.1533/9780857095756.3.592.

[28] M. Sauer, D. Mattanovich, H. Marx, Microbial Production of Food Ingredients, Enzymes and Nutraceuticals, Elsevier, 2013. doi:10.1533/9780857093547.2.288.

[29] S.A. Survase, I.B. Bajaj, R.S. Singhal, Biotechnological production of vitamins, Food Technol. Biotechnol. 44 (2006) 381–396. http://0-search.ebscohost.com.library.uark.edu/login.aspx?direct=true&db=ffh&AN=2007-01-Bi0055&site=ehost-live.

[30] M. Moresi, E. Parente, Encyclopedia of Food Microbiology, Elsevier, 2014. doi:10.1016/B978-0-12-384730-0.00111-7.

[31] T.M. Potts, K. Durant, J. Hestekin, R. Beitle, M. Ackerson, Catalytic Production of 1-Octadecanol from Octadecanoic Acid by Hydrotreating in a Plug Flow Reactor, J. Am. Oil Chem. Soc. 91 (2014) 1643–1650. doi:10.1007/s11746-014-2501-7.

[32] G. Singh Dhillon, S. Kaur Brar, M. Verma, R.D. Tyagi, Recent Advances in Citric Acid Bio-production and Recovery, Food Bioprocess Technol. 4 (2010) 505–529. doi:10.1007/s11947-010-0399-0.

[33] A. Pandey, Production of Organic Acids by Solid-state Fermentation, Curr. Dev. Solid-State Ferment. (2009) 205–229.

[34] M. Gullo, E. Verzelloni, M. Canonico, Aerobic submerged fermentation by acetic acid bacteria for vinegar production: Process and biotechnological aspects, Process Biochem. 49 (2014) 1571–1579. doi:10.1016/j.procbio.2014.07.003.

[35] N. Saichana, K. Matsushita, O. Adachi, I. Frébort, J. Frébortová, Acetic acid bacteria: A group of bacteria with versatile biotechnological applications., Biotechnol. Adv. (2014). doi:10.1016/j.biotechadv.2014.12.001.

[36] T. Tanino, Y. Nara, T. Tsujiguchi, T. Ohshima, Coproduction of acetic acid and electricity by application of microbial fuel cell technology to vinegar fermentation., J. Biosci. Bioeng. 116 (2013) 219–23. doi:10.1016/j.jbiosc.2013.02.009.

[37] S.D. Pravasi, Encyclopedia of Toxicology, Elsevier, 2014. doi:10.1016/B978-0-12-386454-3.00216-5.

[38] K. Syngiridis, A. Bekatorou, P. Kandylis, C. Larroche, M. Kanellaki, A.A. Koutinas, Favouring butyrate production for a new generation biofuel by acidogenic glucose fermentation using cells immobilised on γ-alumina., Bioresour. Technol. 161 (2014) 118–23. doi:10.1016/j.biortech.2014.03.019.

[39] S. Baba, Y. Tashiro, H. Shinto, K. Sonomoto, Development of high-speed and highly efficient butanol production systems from butyric acid with high density of living cells of Clostridium saccharoperbutylacetonicum, J. Biotechnol. 157 (2012) 605–612. doi:http://dx.doi.org/10.1016/j.jbiotec.2011.06.004.

[40] S.E. López, J. Salazar, Trifluoroacetic acid: Uses and recent applications in organic synthesis, J. Fluor. Chem. 156 (2013) 73–100. doi:10.1016/j.jfluchem.2013.09.004.

[41] V. Guillard, V. Issoupov, A. Redl, N. Gontard, Food preservative content reduction by controlling sorbic acid release from a superficial coating, Innov. Food Sci. Emerg. Technol. 10 (2009) 108–115. doi:10.1016/j.ifset.2008.07.001.

[42] C. Hauser, J. Wunderlich, Antimicrobial packaging films with a sorbic acid based coating, Procedia Food Sci. 1 (2011) 197–202. doi:10.1016/j.profoo.2011.09.031.

[43] C. Phadungath, L.E. Metzger, Effect of sodium gluconate on the solubility of calcium lactate., J. Dairy Sci. 94 (2011) 4843–9. doi:10.3168/jds.2011-4549.

[44] S. Lo Presti, M. Moresi, Recovery of sodium gluconate from model solutions by reverse osmosis, J. Food Eng. 44 (2000) 109–117. doi:10.1016/S0260-8774(99)00172-7.

[45] D. Rothacker, C. Difigilo, I. Lee, A clinical trial of topical 10% trolamine salicylate in osteoarthritis, Curr. Ther. Res. 55 (1994) 584–597. doi:10.1016/S0011-393X(05)80190-0.

[46] H.-T. Wang, B. Luo, Y.-N. Huang, K.-Q. Zhou, L. Chen, Sodium salicylate suppresses serotonin-induced enhancement of GABAergic spontaneous inhibitory postsynaptic currents in rat inferior colliculus in vitro., Hear. Res. 236 (2008) 42–51. doi:10.1016/j.heares.2007.11.015.

[47] P. Thakur, B. Nehru, Modulatory effects of sodium salicylate on the factors affecting protein aggregation during rotenone induced Parkinson's disease pathology., Neurochem. Int. 75 (2014) 1–10. doi:10.1016/j.neuint.2014.05.002.

[48] T. Ghaffar, M. Irshad, Z. Anwar, T. Aqil, Z. Zulifqar, A. Tariq, et al., Recent trends in lactic acid biotechnology: A brief review on production to purification, J. Radiat. Res. Appl. Sci. 7 (2014) 222–229. doi:10.1016/j.jrras.2014.03.002.

[49] H. Quitmann, R. Fan, P. Czermack, Acidic Organic Compounds in Beverage, Food, and Feed Production, in: Biotechnol. Food Feed Addit., 2014: pp. 91–142.

[50] S. Ramachandran, P. Fontanille, A. Pandey, C. Larroche, Gluconic Acid : Properties , Applications and Microbial Production, 44 (2006) 185–195.

[51] J.A.L. Blinco, W.O.S. Doherty, Review of extraction technologies for organic acid production, Proc. Conf. Aust. Soc. Sugar Cane Technol. 27th (2005) 480–488.

[52] C.S. López-Garzón, A.J.J. Straathof, Recovery of carboxylic acids produced by fermentation., Biotechnol. Adv. 32 (2014) 873–904. doi:10.1016/j.biotechadv.2014.04.002.

[53] T. Magarifuchi, K. Goto, Y. Iimura, M. Tadenuma, G. Tamura, Effect of yeast fumarase gene (FUM1) disruption on production of malic, fumaric and succinic acids in sake mash, J. Ferment. Bioeng. 80 (1995) 355–361. doi:http://dx.doi.org/10.1016/0922-338X(95)94204-5.

[54] M.B. Arora, J. a. Hestekin, S.W. Snyder, E.J. St. Martin, Y.J. Lin, M.I. Donnelly, et al., The Separative Bioreactor: A Continuous Separation Process for the Simultaneous Production and Direct Capture of Organic Acids, Sep. Sci. Technol. 42 (2007) 2519–2538. doi:10.1080/01496390701477238.

[55] P. García-Fraile, L.R. Silva, S. Sánchez-Márquez, E. Velázquez, R. Rivas, Plums (Prunus domestica L.) are a good source of yeasts producing organic acids of industrial interest from glycerol., Food Chem. 139 (2013) 31–4. doi:10.1016/j.foodchem.2012.12.043.

[56] S. Yoshida, A. Yokoyama, Identification and characterization of genes related to the production of organic acids in yeast., J. Biosci. Bioeng. 113 (2012) 556–61. doi:10.1016/j.jbiosc.2011.12.017.

[57] M. Papagianni, Advances in citric acid fermentation by Aspergillus niger: biochemical aspects, membrane transport and modeling., Biotechnol. Adv. 25 (2007) 244–63. doi:10.1016/j.biotechadv.2007.01.002.

[58] A. Kutyła-Olesiuk, U.E. Wawrzyniak, P. Ciosek, W. Wróblewski, Electrochemical monitoring of citric acid production by Aspergillus niger., Anal. Chim. Acta. 823 (2014) 25–31. doi:10.1016/j.aca.2014.03.033.

[59] S. Yu, D. Huang, J. Wen, S. Li, Y. Chen, X. Jia, Metabolic profiling of a Rhizopus oryzae fumaric acid production mutant generated by femtosecond laser irradiation., Bioresour. Technol. 114 (2012) 610–5. doi:10.1016/j.biortech.2012.03.087.

[60] Z.Y. Zhang, B. Jin, J.M. Kelly, Production of lactic acid from renewable materials by Rhizopus fungi, Biochem. Eng. J. 35 (2007) 251–263. doi:10.1016/j.bej.2007.01.028.

[61] T. Hickey, D. Kreutzer, D.J. Burgess, F. Moussy, Dexamethasone/PLGA microspheres for continuous delivery of an anti-inflammatory drug for implantable medical devices., Biomaterials. 23 (2002) 1649–56. http://www.ncbi.nlm.nih.gov/pubmed/11922468.

[62] J. Du, A. McGraw, N. Lorenz, R.R. Beitle, E.C. Clausen, J. a. Hestekin, Continuous Fermentation of Clostridium tyrobutyricum with Partial Cell Recycle as a Long-Term Strategy for Butyric Acid Production, Energies. 5 (2012) 2835–2848. doi:10.3390/en5082835.

[63] M. Matsumoto, K. Mochiduki, K. Fukunishi, K. Kondo, Extraction of organic acids using imidazolium-based ionic liquids and their toxicity to Lactobacillus rhamnosus, Sep. Purif. Technol. 40 (2004) 97–101. doi:DOI: 10.1016/j.seppur.2004.01.009.

[64] F.S. Oliveira, J.M.M. Araujo, R. Ferreira, L. Rebelo Paulo N., I.M. Marrucho, Extraction of L-lactic, L-malic, and succinic acids using phosphonium-based ionic liquids, Sep. Purif. Technol. 85 (2012) 137–146. doi:10.1016/j.seppur.2011.10.002.

[65] D.G. Cherkasov, K.K. Il'in, Salting out of butyric acid from aqueous solutions with potassium chloride, Russ. J. Appl. Chem. 82 (2009) 920–924. doi:10.1134/S1070427209050346.

[66] D. Wu, H. Chen, L. Jiang, J. Cai, Z. Xu, P. Cen, Efficient Separation of Butyric Acid by an Aqueous Two-phase System with Calcium Chloride, Chinese J. Chem. Eng. 18 (2010) 533–537. doi:10.1016/S1004-9541(10)60255-8.

[67] Y. Wang, C. Huang, T. Xu, Which is more competitive for production of organic acids, ion-exchange or electrodialysis with bipolar membranes?, J. Memb. Sci. 374 (2011) 150–156. doi:10.1016/j.memsci.2011.03.026.

[68] A. Vertova, G. Aricci, S. Rondinini, R. Miglio, L. Carnelli, P. D'Olimpio, Electrodialytic recovery of light carboxylic acids from industrial aqueous wastes, J. Appl. Electrochem. 39 (2009) 2051–2059. doi:10.1007/s10800-009-9871-9.

[69] J.G. Zeikus, M.K. Jain, P. Elankovan, Biotechnology of succinic acid production and markets for derived industrial products, Appl. Microbiol. Biotechnol. 51 (1999) 545–552. doi:10.1007/s002530051431.

[70] R. Datta, M. Henry, Lactic acid : recent advances in products , processes and technologies – a review, 1129 (2006) 1119–1129. doi:10.1002/jctb.

[71] R.P. John, K.M. Nampoothiri, A. Pandey, Fermentative production of lactic acid from biomass: an overview on process developments and future perspectives., Appl. Microbiol. Biotechnol. 74 (2007) 524–34. doi:10.1007/s00253-006-0779-6.

[72] H. Dong, J. Wang, H. Lu, Recent progress in bipolar membrane electrodialysis, Huagong Jinzhan. 29 (2010) 217–222.

[73] K. Nijmeijer, S. Metz, Sustainable Water for the Future: Water Recycling versus Desalination, Elsevier, 2010. doi:10.1016/S1871-2711(09)00205-0.

[74] R.E. Pattle, Production of Electric Power by mixing Fresh and Salt Water in the Hydroelectric Pile, Nature. 174 (1954) 660.

[75] S. Loeb, R.S. Norman, Osmotic Power Plants, Science (80-.). 189 (1975) 654–655.

[76] G.Z. Ramon, B.J. Feinberg, E.M. V. Hoek, Membrane-based production of salinity-gradient power, Energy Environ. Sci. 4 (2011) 4423–4434. doi:10.1039/c1ee01913a.

[77] J.W. Post, J. Veerman, H.V.M. Hamelers, G.J.W. Euverink, S.J. Metz, K. Nymeijer, et al., Salinity-gradient power: Evaluation of pressure-retarded osmosis and reverse electrodialysis, J. Memb. Sci. 288 (2007) 218–230. doi:10.1016/j.memsci.2006.11.018.

[78] G.L. Wick, Power from salinity gradients, Energy. 3 (1978) 95–100. doi:10.1016/0360-5442(78)90059-2.

[79] G. Han, S. Zhang, X. Li, T.-S. Chung, High performance thin film composite pressure retarded osmosis (PRO) membranes for renewable salinity-gradient energy generation, J. Memb. Sci. 440 (2013) 108–121. doi:10.1016/j.memsci.2013.04.001.

[80] D. a Vermaas, D. Kunteng, M. Saakes, K. Nijmeijer, Fouling in reverse electrodialysis under natural conditions., Water Res. 47 (2013) 1289–98. doi:10.1016/j.watres.2012.11.053.

[81] D. a. Vermaas, E. Guler, M. Saakes, K. Nijmeijer, Theoretical power density from salinity gradients using reverse electrodialysis, Energy Procedia. 20 (2012) 170–184. doi:10.1016/j.egypro.2012.03.018.

[82] J.W. Post, C.H. Goeting, J. Valk, S. Goinga, J. Veerman, H.V.M. Hamelers, et al., Towards implementation of reverse electrodialysis for power generation from salinity gradients, Desalin. Water Treat. 16 (2010) 182–193.

[83] J. Veerman, M. Saakes, S.J. Metz, G.J. Harmsen, Electrical power from sea and river water by reverse electrodialysis: A first step from the laboratory to a real power plant, Environ. Sci. Technol. 44 (2010) 9207–9212. doi:10.1021/es1009345.

[84] J. Veerman, M. Saakes, S.J. Metz, G.J. Harmsen, Reverse electrodialysis: Performance of a stack with 50 cells on the mixing of sea and river water, J. Memb. Sci. 327 (2009) 136–144. doi:10.1016/j.memsci.2008.11.015.

[85] R. Audinos, Electric-power produced from 2 solutions of unequal salinity by reverse electrodialysis, Indian J. Chem. 31 (1992) 348–354.

[86] J. Veerman, M. Saakes, S.J. Metz, G.J. Harmsen, Reverse electrodialysis: A validated process model for design and optimization, Chem. Eng. J. 166 (2011) 256–268. doi:10.1016/j.cej.2010.10.071.

[87] J.W. Post, H.V.M. Hamelers, C.J.N. Buisman, Energy recovery from controlled mixing salt and fresh water with a reverse electrodialysis system, Environ. Sci. Technol. 42 (2008) 5785–5790. doi:10.1021/es8004317.

[88] D. a Vermaas, M. Saakes, K. Nijmeijer, Doubled power density from salinity gradients at reduced intermembrane distance., Environ. Sci. Technol. 45 (2011) 7089–95. doi:10.1021/es2012758.

[89] B.E. Logan, M. Elimelech, Membrane-based processes for sustainable power generation using water., Nature. 488 (2012) 313–9. doi:10.1038/nature11477.

[90] J. Veerman, J.W. Post, M. Saakes, S.J. Metz, G.J. Harmsen, Reducing power losses caused by ionic shortcut currents in reverse electrodialysis stacks by a validated model, J. Memb. Sci. 310 (2008) 418–430. doi:10.1016/j.memsci.2007.11.032.

[91] P. Dlugolecki, J. Dabrowska, K. Nijmeijer, M. Wessling, Ion conductive spacers for increased power generation in reverse electrodialysis.pdf, J. Memb. Sci. 347 (2010) 101–107.

[92] D. a. Vermaas, M. Saakes, K. Nijmeijer, Power generation using profiled membranes in reverse electrodialysis.pdf, J. Memb. Sci. 385-386 (2011) 234–242.

[93] E. Güler, R. Elizen, M. Saakes, K. Nijmeijer, Micro-structured membranes for electricity generation by reverse electrodialysis, J. Memb. Sci. 458 (2014) 136–148. doi:10.1016/j.memsci.2014.01.060.

[94] E. Güler, R. Elizen, D. a. Vermaas, M. Saakes, K. Nijmeijer, Performance-determining membrane properties in reverse electrodialysis, J. Memb. Sci. 446 (2013) 266–276. doi:10.1016/j.memsci.2013.06.045.

[95] D.A. Vermaas, M. Saakes, K. Nijmeijer, Early detection of preferential channeling in reverse electrodialysis, Electrochim. Acta. 117 (2014) 9–17. doi:10.1016/j.electacta.2013.11.094.

[96] S. Pawlowski, P. Sistat, J.G. Crespo, S. Velizarov, Mass Transfer in Reverse Electrodialysis: Flow Entrance Effects and Diffusion Boundary Layer Thickness, J. Memb. Sci. 471 (2014) 72–83. doi:10.1016/j.memsci.2014.07.075.

[97] J. Liu, G.M. Geise, X. Luo, H. Hou, F. Zhang, Y. Feng, et al., Patterned ion exchange membranes for improved power production in microbial reverse-electrodialysis cells, J. Power Sources. 271 (2014) 437–443. doi:10.1016/j.jpowsour.2014.08.026.

III. Separation of Organic Acids from Water using Ionic Liquid Assisted Electrodialysis

Separation of Organic Acids from Water using
Ionic Liquid Assisted Electrodialysis

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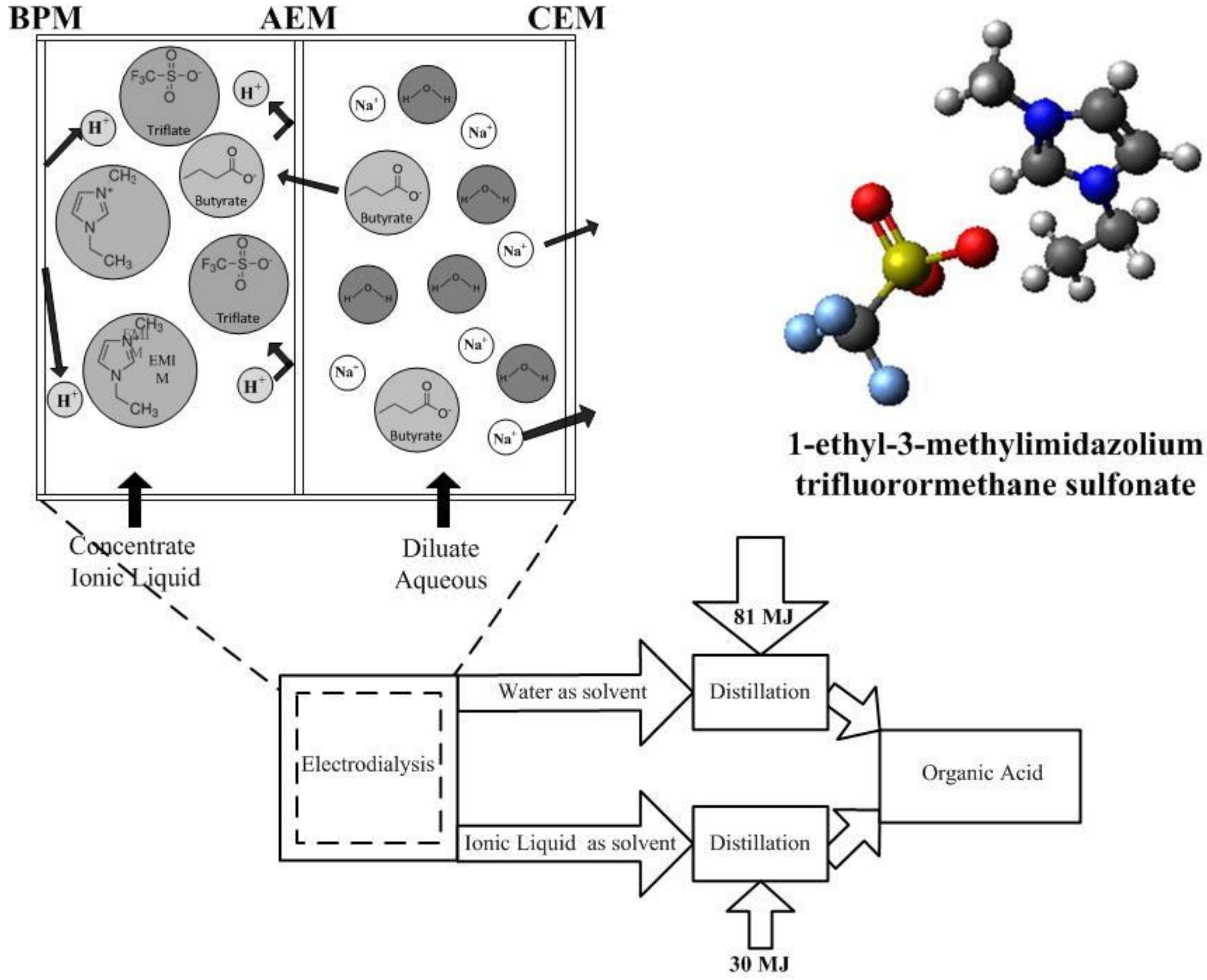
Abstract

In this study, we present a system capable of concentrating, acidifying, and removing organic salts from aqueous solution through the use of ionic liquids in an electrodialysis stack. This system used a bipolar electrodialysis stack operating in batch mode with ionic liquids in the concentrate stream and an aqueous solution containing organic salts in the diluate stream. Sodium butyrate was used as our model organic salt. The desired organic product was successfully transferred from an aqueous phase to an ionic liquid phase through electrodialysis and then recovered from the ionic liquid. Bipolar electrodialysis produced butyric acid which allowed separation through distillation. Since ionic liquids possess no measurable vapor pressure, this process was able to recover organic acid at a recovery rate of 99% and recycle the ionic liquid back into the electrodialysis stack. This system also reduced separation energy requirements by 60% when compared to distillation from aqueous solution. The research presented has the potential to significantly improve upon current organic acid purification techniques by eliminating costly dehydration steps following fermentations and other typical organic acid production methods. By combining the versatility of ionic liquids with the energy efficiency of electrodialysis, a simple low-cost organic acid purification method has been developed.

Keywords: Electrodialysis, Ionic Liquid, Butyric acid, Bipolar Electrodialysis

Graphical Abstract



Introduction

Organic acids are a vital commodity in the chemical industry. Their use ranges from the food industry to pharmaceuticals. Typical organic acid production involves fermentation and acid neutralization to produce organic salts. These salts are then treated with concentrated sulfuric acid to create desired organic acid products. Products are then separated from solution and the waste acid is neutralized. This process is well understood and efficient; however, it requires large quantities of acid and produces large amounts of waste [1]. Additionally, purification of organic acids from aqueous solutions requires multi-step distillation, an energy intensive and costly procedure [2]. In order to reduce the costs associated with acid and waste treatment, a novel separation technique using electrodialysis in conjunction with ionic liquids has been developed for the purification of organic acids.

Electrodialysis (ED) is a process in which ions are transferred from a dilute stream into a concentrate stream through semi-permeable membranes by the application of an electric field. ED has traditionally been used to remove ions from solutions, most often the desalination of brackish water [3]. The development of bipolar membranes has allowed salt concentration and acidification to occur simultaneously in an ED cell. Bipolar membrane electrodialysis (BPED) has been used for a broad range of applications from de-acidification of fruit juices to the synthesis and recovery of acids and bases [4-6]. Recovery of light carboxylic acids through ED has already been tested and successfully performed [7]. However, recovery of concentrated organic acids from aqueous solution can be difficult and energy intensive [8, 9]. Azeotropes and high boiling points make traditional distillation techniques cost ineffective. Use of liquid-liquid extraction requires separation from ternary mixtures, which results in low extraction efficiencies [10]. Wu *et al*. [11] and Cherkasov *et al*. [12] demonstrated an organic acid salting technique using calcium chloride and potassium chloride respectively. However, maximum purity of samples obtained after separation were only 80% acid with the remaining solution being water and salt. Additionally, obtaining the organic acid solution required additional separation steps in order to remove the remaining salt and water. Therefore, a simple and cost-effective method for purifying organic acids from aqueous solution is needed for organic acid production. Modification of electrodialysis technologies through dialyzing ions into an ionic liquid solvent may be a solution to this difficult chemical separation.

Ionic liquids hold the potential to drastically improve the ED industry by becoming an ideal solvent for concentrating solutions as their low volatility allows for easy separation and unique solvent properties allow for expanded applications. Ionic liquids are liquid salts and have a wide variety of applications such as catalysis, extraction, crystallization, and gas absorption [13, 14]. Recently, Nobel *et al*. investigated the use of ionic liquids in membrane systems and designed supported liquid membranes using ionic liquids for gas separation applications [15, 16]. Their work demonstrated the advantages and versatility that ionic liquids possess in the development of membrane separation technology. Ionic liquids possess many unique properties such as non-flammability, low toxicity, and are considered "green solvents" due to their recyclability. However, recent studies suggest that some ionic liquids are difficult to decompose, indicating that not all varieties can be considered environmentally friendly [17]. Ionic liquids are also considered designer solvents due to the ability to change the cation and anion components of the liquid. This allows researchers to synthesize ionic liquids with specific chemical properties to suit the needs of a given application. These designer solvents are considered non-volatile, allowing volatile components to be separated easily from ionic liquids through vaporization in flash systems [18]. Research into the use of ionic liquids in ED has been conducted, but mostly for ionic liquid synthesis and purification purposes [19-22]. For example Himmler *et al*. used BPED to isolate an ionic liquid cation to design and develop new ionic liquids [19]. Additionally Haerens *et al*. produced low concentrations of the ionic liquid choline dicyanamide from salt solutions using ED [21]. Research into the use of organic and mixed solvents for ED has also been conducted [23-25]. Li *et al*. used a methanol solution for BPED in the production of methyl methoxyacetate [24]. This studies' approach to non-aqueous media in ED allowed novel synthesis and separation methods to be developed. Yet, to our knowledge, this is the first study investigating the use of ionic liquids as a concentration medium in ED and BPED.

Ionic liquids are ideal for ED and BPED electrodialysis due to their potential to assist in the separation of organic acids, salts, and other desirable products from aqueous solution [26, 27]. Since ionic liquids possess no vapor pressure, organic acids are easily separated from an ionic liquid solvent through distillation with a significant reduction in energy requirements when compared to distillation in an aqueous phase [13]. A major drawback to using ionic liquid solvents is the large cost associated with producing the ionic liquids. Significant research into the use of ionic liquids in ED has focused on the synthesis and purification of ionic liquids to reduce this high cost [21, 27]. Preliminary results show that research efforts in the improvement of ionic liquid production techniques are promising in that ionic liquids will soon be produced in large quantities at a much lower cost (50 USD per kg versus current prices of >1000 USD per kg) [28]. With these cost-reductions in ionic liquid synthesis, we believe that ionic liquids have the capability of improving ED techniques as a novel solvent for concentrating and purifying organic products.

The purpose of this study was to determine the feasibility of using an ionic liquid as the concentrate medium for ED of organic salts. Figure 1 shows how ions can be transported from an aqueous phase into an ionic liquid solution through ED and/or BPED. Our hypothesis was that ionic liquids can be used to remove organic salts from an aqueous phase into an ionic liquid phase with minimal interaction between the two phases. Since ionic liquids can support ionization, a completely water free separation is possible. For this study, sodium butyrate (NaBu) was used as a model organic salt. Butyrate salts can be synthesized via fermentation systems and are similar to other organic salts (acetic, formic, propionic). Additionally, focus on butanol biofuels has led research into the enhanced production of precursor molecules, i.e. butyrate and butyric acid. This study also investigated the feasibility of acidifying salt solutions through the use of bipolar membranes. Ionic liquids' low vapor pressures allow extracted butyric acid to be recovered through conventional distillation at a much lower energy cost compared to aqueous phase distillation [13]. Additionally, ionic liquids' designable physicochemical properties make them ideal for organic acid recovery. Fadeev and Meagher investigated the use of imidazolium based ionic liquids in the extraction of butanol from aqueous solutions [27]. Ha *et al*. has studied liquid-liquid extraction of organic solvents using a wide variety of ionic liquids [10]. However, ED and BPED have never been reported with a two phase aqueous/ionic liquid configuration. We hypothesize that through BPED, we can transfer organic salts from fermentation broth into an ionic liquid in an acidified form, resulting in the development of a simple and cost-effective method for organic acid purification.

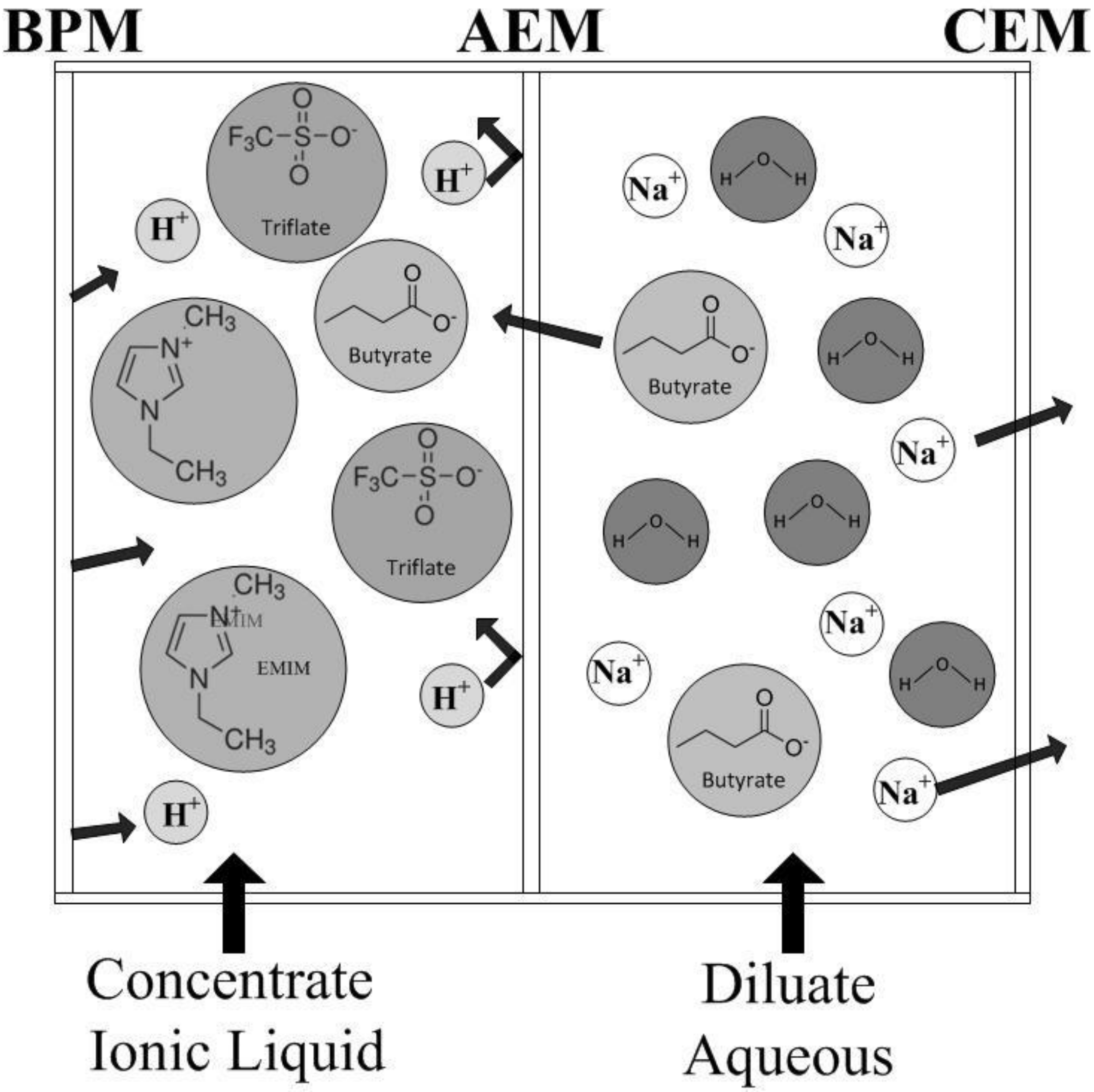


Figure 1. Ionic Liquid Assisted Electrodialysis. EMIM – 1-ethyl-3-methyl imidazolium Triflate – trifluoromethanesulfonate H^+ – Hydrogen Na^+ – Sodium HOH – Water BPM – Bipolar Membrane AEM – Anion Exchange Membrane CEM – Cation Exchange Membrane Note: For conventional electrodialysis, A cation exchange

Experimental

2.1 Chemical and Membrane Information

The ionic liquid used during experimentation was 1-ethyl-3-methylimidazolium-triflouromethansulfonate obtained from Sigma-Aldrich and produced by BASF. This ionic liquid was chosen due to its availability and ideal chemical and physical characteristics. For this process the ionic liquid needed to be a stable liquid at room temperature, non-volatile at temperatures greater than 165 °C (boiling point of butyric acid), and possess a high butyrate/butyric acid solubility and ionic conductivity. Table 1 lists some of the key properties of the ionic liquid, indicating why it is an ideal first candidate. Deionized water was obtained from a Millipore Milli-Q Water System. Sodium butyrate and butyric acid were of analytical grade (>98%) and were purchased from Alfa Aesar. Tokuyama CMX cation and AMX anion exchange membranes were purchased from Electrolytica and bipolar membranes were purchased from Ameridia. Chemicals and membranes were used in experiments as received.

Table 1. Properties of Ionic Liquid

Melting Point	**-13 °C**
Boiling Point	**350 °C**
Molecular Mass	**260.24 g/mol**
Density	**1.387 g/cm^3**
Electrical Conductivity	**7.61 mS/cm**
Viscosity	**52 cP @ Room Temperature**
Water Solubility	**Soluble**

2.2 ED/BPED Configuration

Batch electrodialysis operations were performed using Mityflex 913 peristaltic pumps to move fluid through a PCCell ED 64-4 electrodialysis stack in a four chamber, single cell configuration. DC power was supplied by a Gwinstek GPR-3060P power supply. Table 2 shows the specifications of the electrodialysis stack which had a single diluate and concentrate stream. The concentrate and diluate wells contained 250 mL of a 2 weight % sodium butyrate solution and the rinse well contained 500 mL of a 0.1N sodium sulfate solution. During ionic liquid experiments, 20g/L butyrate was present in the concentrate stream initially unless otherwise specified. Samples were taken every half hour for 3 hours then every hour afterwards. Experiments continued until system voltage reached 5.0 V at which point constant current could no longer be maintained. Cell internal leakage of our system is rated for operation between 3-30 mL/h and for our purposes leakage was maintained below 7 mL/hr. This is considered acceptable leakage for a small ED stack.

Table 2. Technical features of the Electrodialysis Stack

Anode	**Titanium, Pt/Ir coating**
Cathode	**Titanium, Pt/Ir coating**
Cell Frame	**Polypropylene**
Tubes	**Polypropylene**
Anion Membrane	**NEOSEPTA CMS of Tokuyama Corp.**
Cation Membrane	**NEOSEPTA AFX of Tokuyama Corp.**
Bipolar Membrane	**NEOSEPTA BP-1E of ASTOM Corp.**
Effective Membrane Area	**64 cm^2**

2.3 Analysis of diluate and concentrate solutions

High pressure liquid chromatography (HPLC) was used to analyze butyrate and ionic liquid concentrations of the diluate and concentrate streams. The HPLC system consisted of a Waters 717 plus autosample injector, a Waters 1525 binary HPLC pump, an IC-Pak™ ion-exclusion column (7.8mm x 150mm), and a Waters 2414 refractive index detector. The solvent used during analysis was 0.5 mM/L sulfuric acid at a flowrate of 1.0 mL/min. A Mettler-Toledo DL31 Karl-Fischer titrator was used to analyze water leakage into the ionic liquid during ED experiments. A drying oven was used to determine the concentration of butyric acid present in ionic liquid samples. Gas chromatography was also used to confirm the presence of butyric acid in samples using a Shimadzu chromatograph. The column chosen was a Phenomenex Zebron

FFAP, 30 m x .32 mm x .25 µm. The oven temperature was set at a 40-230 °C ramp with the injector and detector set at a temperature of 250 °C.

2.4 Current Efficiency and Product Yield Calculations

The current efficiency, η, was calculated according to Equation 1:

$$\eta = \frac{zQF(C_{di}-C_{do})}{NI} \tag{1}$$

where z is the ionic valence of the acid, Q is the diluate flow rate, F is Faraday's constant, C_{di} is the inlet diluate solute concentration, C_{do} is the outlet diluate solute concentration, N is the number of cell pairs, and I is the current.

For our experiments, the ionic valence and number of cells pairs were both one. The equation was modified for long term runs where samples were taken at regular time intervals instead of constant monitoring of the inlet and outlet concentrations. The adapted equation for current efficiency is given as Equation 2.

$$\eta = \frac{VF(C_f-C_i)}{tIM} \tag{2}$$

In equation 2, V is the volume of the diluate, C_f is the diluate solute concentration at time t, C_i is the initial diluate solute concentration, M is the organic salt molecular mass, I is the system current, and t is experimental run time. The recovery ratio of samples and ED power consumption was determined using Equations 3 and 4 respectively

$$\frac{Butyric\,acid\ recovered\ (g)}{Total\ Butyric\ acid\ (g)} * 100 = RR \tag{3}$$

$$P = \frac{1.52VI}{\eta} \tag{4}$$

where V is the system voltage, I is the system current, and η is the current efficiency [11].

2.5 Process Simulation of Organic Acid Separation

In order to obtain an estimation of the power requirements for organic acid separation from fermentation system, a process simulation was created using CHEMCAD® software. This software was used to simulate the separation steps required for purifying butyric acid from a fermentation broth. For simplicity, additional by-products were not inserted into the simulation and the expected butyric acid yield from fermentation steps was 20 g/L with a final target purity of approximately 95 weight percent. Distillation, electrodialysis, and flash separations were considered during the simulation and power requirements were determined and compared.

Results & Discussion

3.1 Electrodialysis of Sodium Butyrate with Aqueous Concentration Stream.

Electrodialysis experiments of butyrate from water solvents were carried out in order to determine the salt removal rate and current efficiency obtained from a traditional electrodialysis procedure. Multiple trials were conducted for the initial removal rate up to 3 hours of operation, and a single long term trial of seven hours was conducted. The long term trial was conducted until the limiting current density was reached as evidenced by a decrease in electrical conductivity from 3.67 mS/cm to 300 μS/cm in 2 hours and a spike in the output voltage. The results of these experiments are shown in Figure 2. The concentration of sodium butyrate increased in the concentrate stream during experimentation at a rate of approximately 2.2 g/L-hr. Final concentration of butyrate in the diluate was <0.01% in the long term study. The average current efficiency during ED operation was 82% with a maximum current efficiency obtained of 98% while power requirements were approximately 1 kwh/kg for butyrate concentration. Current efficiency and power requirements for butyrate removal were similar to results obtained by Wang *et al*. of 2.15-2.88 kwh/kg and 90% for process power and current efficiency respectively [5].

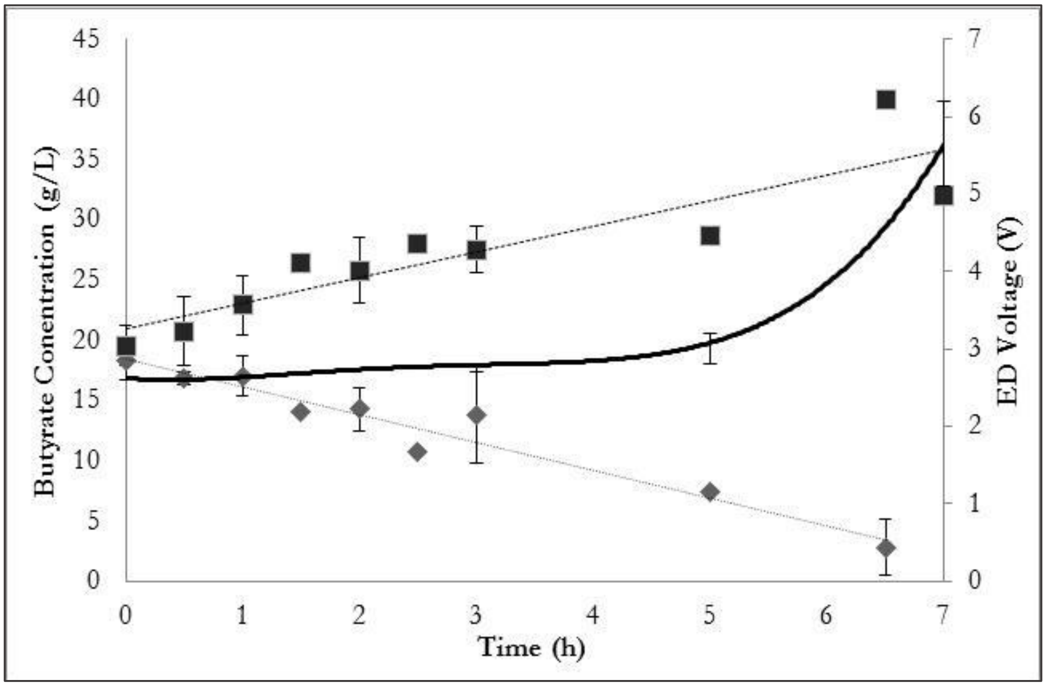


Figure 2. Electrodialysis of Sodium Butyrate using Water as concentrate solvent. ◆: Diluate ■ : Concentrate. η ≈ 86% Solid line denotes system voltage. Constant current was not maintained after 5 hours due to system switch over to constant voltage at 5 V.

3.2 Electrodialysis of Sodium Butyrate with Ionic Liquid Concentration Stream.

Electrodialysis of butyrate experiments using an ionic liquid as the concentrate stream solvent was conducted. Sodium butyrate was added at 16 g/L to the concentrate stream compared to 20 g/L in the feed stream. This concentration was allowed separation at high conductivity without running into solubility problems. The results of this study are shown in Figure 3. The average current efficiency was 30% with the maximum current efficiency obtained of 37%. This corresponds to a butyrate removal rate of 0.98 g/L h. This experiment demonstrates two things. First, that we can use a “neat” ionic liquid to separate organic acid and second that although it is significantly lower current efficiency than water, it is still high enough to be reasonable. Li *et al*. conducted bipolar electrodialysis in a methanol solution with current efficiencies ranging between 2.7-15.4% [24]. Additionally, mixed solvent electrodialysis was conducted by Gartner *et al*. using an ethylene glycol and water mixture with current efficiencies ranging from 78-100%, demonstrating that water content in ED streams significantly effects electrical resistance and current efficiency [29].

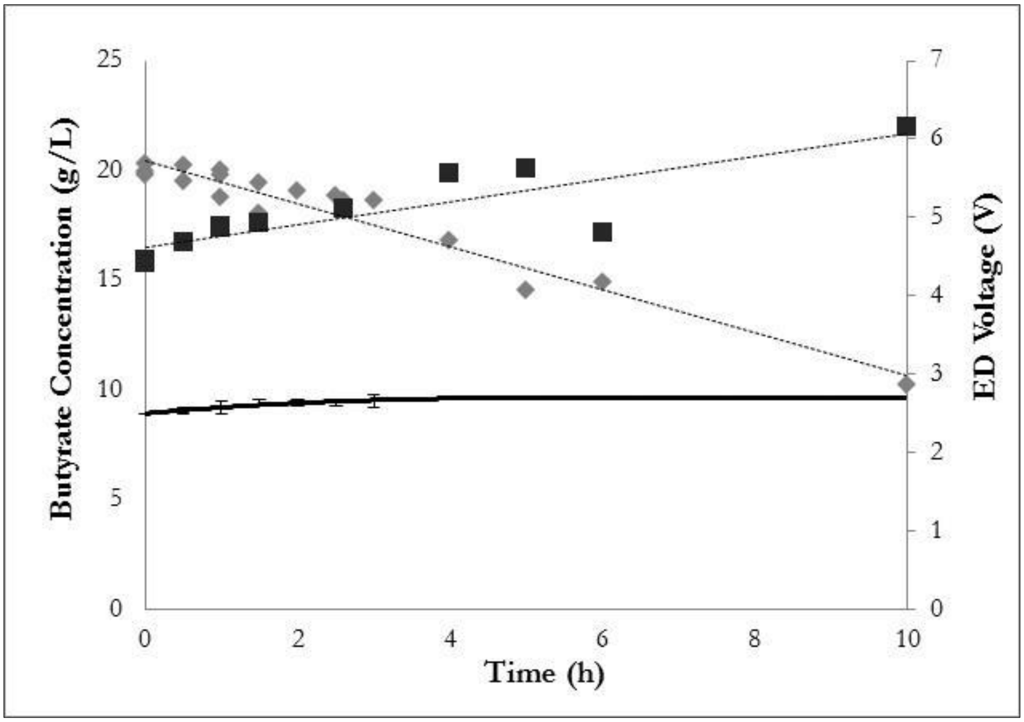


Figure 3. Electrodialysis of Sodium Butyrate using Ionic Liquid as concentrate solvent. ◆: Diluate ■ : Concentrate. η ≈ 33% Solid line denotes system voltage.

3.3 Bipolar Electrodialysis of Sodium Butyrate with Aqueous Concentrate Stream.

In a fermentation broth, organic products will be in the salt form due to pH control required for organism growth. However, in order to boil these products, it must be in the acid form and thus ED technology can be used to separate the organic salt and convert it to the acid form. Bipolar electrodialysis experiments resulted in conversion of sodium butyrate to butyric acid with accumulation in the concentrate compartment. Figure 4 shows the results of BPED experiments using and aqueous solution in the concentrate stream. Power requirements for BPED of sodium butyrate were comparable to ED experiments. GC analysis of samples after BPED operation confirmed the presence of butyric acid in the concentrate stream. Butyric acid concentration was approximately 1.3 weight % or 13 g/L after 7 hours of ED operation and flash separations to recover generated butyric acid from ionic liquid solution. Final butyrate concentration (salt and acid form) in solution was 3 weight % or 30 g/L. System current efficiency was approximately 95%. Both diluate and concentrate pH decreased from approximately 7.8 to 4.8. The rinse solution pH increased from 8.1 to 12.5. These pH changes are expected due to the bipolar membrane forming hydroxide ions in the rinse solution and hydronium ions in the concentrate solution. Additionally, a decrease in butyrate concentration in the diluate stream was expected as confirmed by the Henderson-Hasselbalch equation.

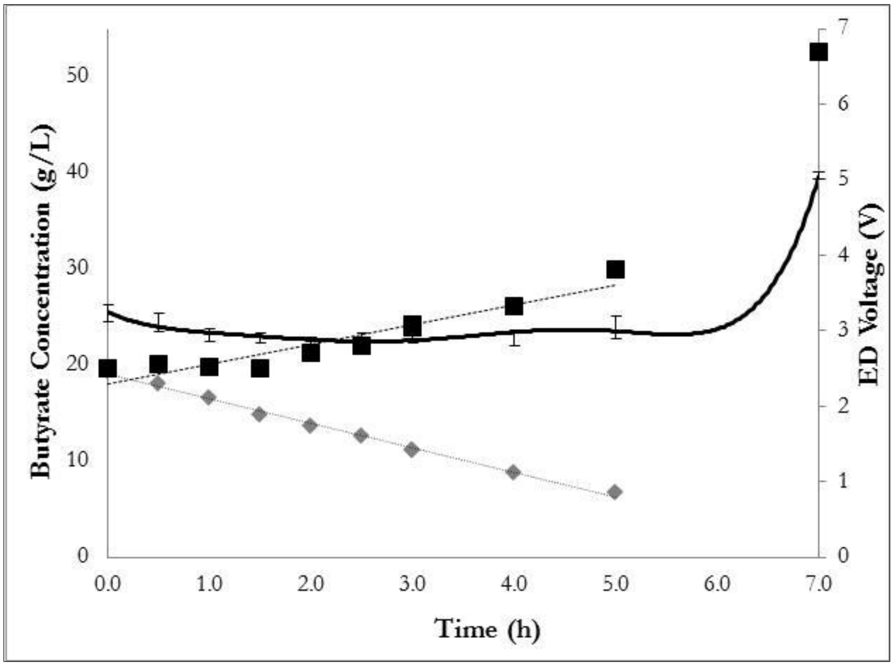


Figure 4. Bipolar Electrodialysis of Sodium Butyrate using Water as concentrate solvent. ◆ : Diluate ■ : Concentrate. η ≈ 97% Solid line denotes system voltage.

3.4 Bipolar Electrodialysis of Sodium Butyrate with Ionic Liquid Concentration Stream.

The use of an ionic liquid solvent in BPED would allow the removal of desired organic salts from an aqueous solution. Further, the use of bipolar membranes allows acidification of organic salts to organic acids to occur, resulting in a trifecta of phenomenon occurring in the BPED stack: salt removal from aqueous solution, salt concentration, and salt acidification. BPED using ionic liquids resulted in successful transfer of sodium butyrate. Pure ionic liquid with no added butyrate was used for this experiment. The results of these experiments are shown in Figure 5. Comparison of Figures 3 and 5 showed that current efficiency diminished upon use of the bipolar membranes due to additional power required for water splitting in the bipolar membrane. Sodium butyrate concentrations in the concentrate compartment were unquantifiable until 3 hours of ED system operation. After 3 hours, the concentration slowly increased, leading to a system current efficiency of approximately 11%. The addition of the bipolar membrane allowed conversion of sodium butyrate into butyric acid in the ionic liquid. Generated acid was then separated from the ionic liquid through evaporation where it was collected and analyzed via gas chromatography. GC analysis showed recovered butyric acid concentrations of approximately 0.7 weight % or 7 g/L after 10 hours of ED operation. Although only 3 g/L was recovered from electrodialysis, the flash separation was able to concentrate the recovered butyric acid further to 7 g/L by separating the acid from the ionic liquid solution. This demonstrated the benefit of using ionic liquids in that flash separations can further enhance the purification of organic acids via solvent extraction.

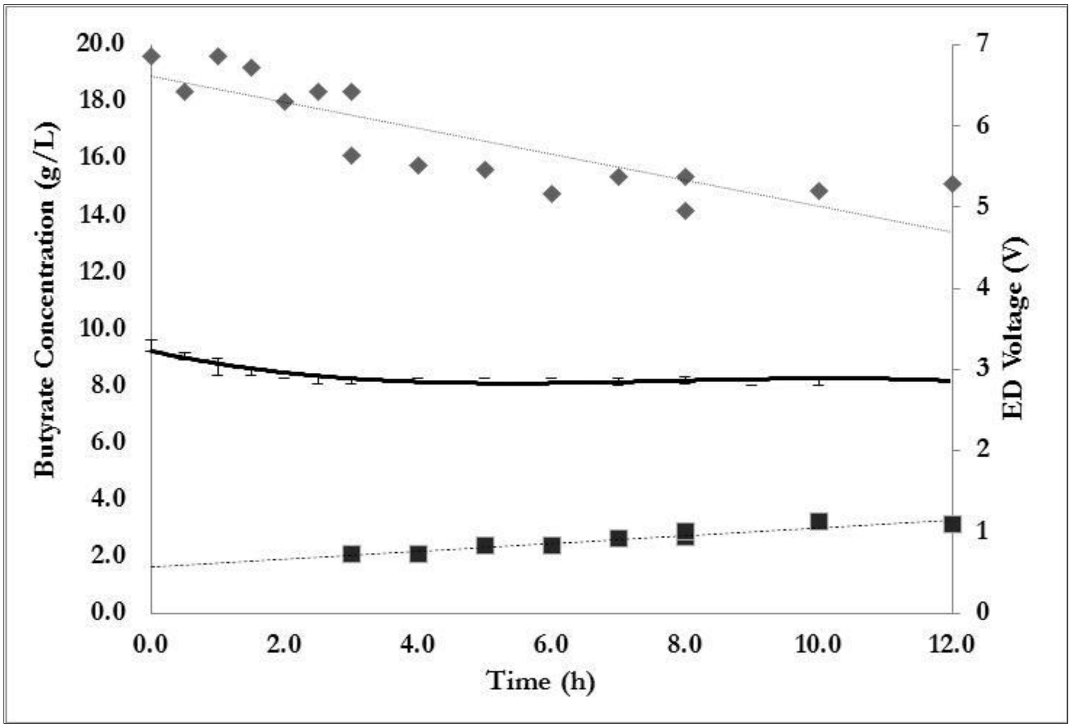


Figure 5. Bipolar Electrodialysis of Sodium Butyrate using Ionic Liquid as concentrate solvent. ◆ : Diluate ■ : Concentrate. η ≈ 11% Solid line denotes system voltage.

3.5 Butyric acid extraction efficiency and power consumption through ED and BPED

Butyric acid produced from experiments was separated from ionic liquid using a TurboVap® 500 closed cell concentrator. Butyric acid concentrations are shown in Table 2 below. The extraction efficiency for butyric acid was approximately 99% when concentrated solutions of butyric acid in ionic liquid were flashed at 160 °C. This demonstrates that we are capable of separating butyric acid completely from ionic liquid. Table 3 compares this efficiency with other separation methods researched for butyric acid, butanol, and other organic acid production methods. LLE offers fairly high extraction efficiencies. However, multiple steps are often required for adequate separation, and ternary mixtures can often lead to complications in industrial separations. Ionic liquids have been incorporated into LLE techniques for organic acid removal, but water contamination is an issue which complicates acid purification [30]. Salting techniques has been used to produce butyric acid [11, 12], but large amounts of waste are produced as a byproduct of salt removal. BPED with ionic liquids offers high extraction efficiency without by-products making it a viable candidate for industrial production.

The power consumption to transport butyric acid into ionic liquids was comparable to current power consumption levels of other ED separations. Table 4 shows the power consumption of ionic liquid assisted electrodialysis compared with other ED techniques. The low current efficiency was the largest contributor to the power costs for this technique. Fortunately, current efficiency improvements will have a drastic effect on reducing the power costs of BPED with IL. The power costs can also be reduced by determining another ionic liquid that will reduce water contamination in the concentrate and improve the selectivity of the process.

Table 3. Butyric acid Recovery from Concentrate Solution

Experiment Type	**Butyric Acid Generation Rate (g/L h)**	**Final Butyric Acid Concentration (g/L)**
BPED Water	**1.0**	**10.1**
BPED Water	**1.4**	**13.6**
BPED Water	**1.4**	**13.7**
BPED IL	**0.6**	**7.23**
BPED IL	**0.09**	**0.86**

Table 4. Comparison of Butyric acid recovery rates based on method of separation

Separation Method	**Study**	**Recovery Ratio**
LLE	**Ha (2010)** **Oliviera (2012)**	**81%** **52-98%**
Salting Technique	**Wu (2010)**	**86%**
ED & Flash	**This study**	**99%**

Table 5. Comparison of Separation Power Requirements

ED Type	**Study**	**Power Consumption**
BPED	**Wang (2010)**[1]	**2.15 – 2.88 kWh/kg** **η = 91-131%**
BPED	**Timbuntam (2008)**[2]	**1.58 – 5.87 kWh/kg** **η = 65-86%**
BPED	**This study**	**0.91 – 1.14 kWh/kg** **η = 80-95%**
BPED & IL	**This study**	**2.38 – 8.02 kWh/kg** **η = 11-37%**

3.6 Analysis of multi-solvent ED and BPED transport mechanism through conductivity and product solubility.

Through the course of experiments, a significant decrease in current efficiency and overall butyric acid transport was observed when using the ionic liquid solvent. Possible reasons for this loss could include an increase in stack resistance resulting in lower transport rates, counter-ions preferentially transporting across the membrane instead of butyrate, internal water splitting within the ED cell, back diffusion, water leakage, or a combination of these occurring. In order to understand this issue in greater detail, experiments were conducted to determine which factors were affecting ion transport. Electrical conductivity readings during experiments showed that ionic liquid solutions had a greater electrical conductivity than aqueous solutions. This implies that resistivity in the concentrate stream is improved when using ionic liquids. However, it is evident that ion transport is diminished, so the resistivity was not the main cause of reduced current efficiency. Solubility studies were conducted to determine the maximum organic salt concentration obtainable in the chosen ionic liquid. Salts were added to water, ionic liquid, and a mixture of solvents to determine the effects of water contamination on organic salt dissolution. The results of this study are summarized in Figure 6. Experiments with water showed a linear increase in electrical conductivity with addition of organic salt and complete dissolution of butyrate to a concentration of 40 g/L. This indicates that the butyrate salt is all in the ionized form and correlates well with the ED results showing high current efficiency except when ionic concentration in the diluate was extremely low. Ionic liquid showed a negligible change of electrical conductivity with addition of butyrate with some of the salt remaining in the solid form above 3 g/L. This demonstrates that in earlier experiments (Figure 2) small amounts of water were necessary to add butyric acid and butyrate salt into the ionic liquid solution, showing that water content was important in solubilization (which we saw > 16 g/L). Thus, although we have a nearly “neat” ionic liquid, the small amount of water in the solution was important in ionization and solubility. This may not be the case for all ionic liquids but it was the case in the one tested in these experiments.

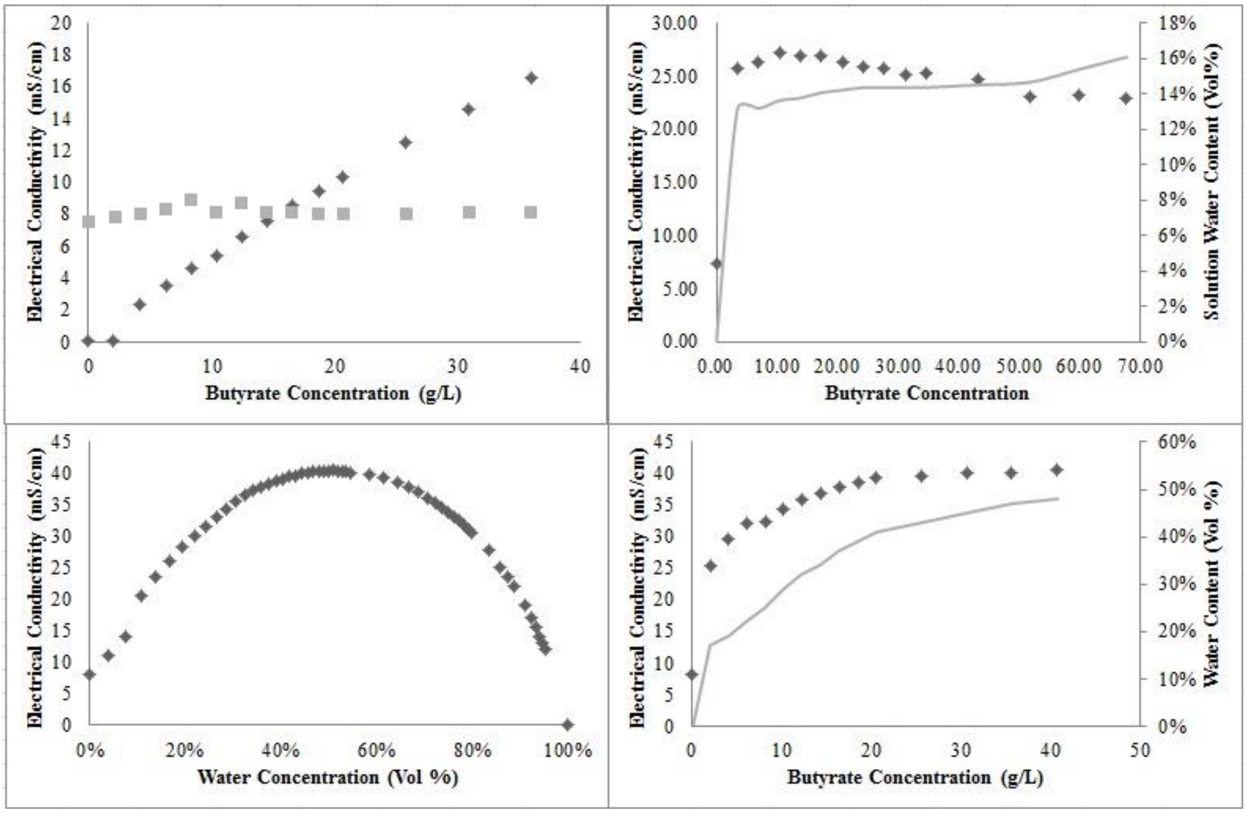


Figure 6. Electrical Conductivity of Water and Ionic Liquid Solutions. Top Left— Conductivity vs. Salt concentration for Water and Ionic Liquid Solutions ◆ : Water ■ : Ionic Liquid Top Right— Conductivity vs Salt concentration for Ionic Liquid Water solutions at low water concentrations ◆ : Ionic Liquid and Water Mix ▬ Water Content Bottom Left— Conductivity vs. Water concentration for Ionic Liquid solutions Bottom Right— Conductivity vs Salt concentration for Ionic Liquid Water solutions at moderate water concentrations ◆ : Ionic Liquid and Water Mix ▬ Water Content

3.7 Analysis of organic acid purification energy costs.

A simulation of organic acid purification from a diluate fermentation stream was conducted using CHEMCAD® software. Two cases were analyzed for comparison purposes: one case where electrodialysis without ionic liquids was followed by distillation and a second case where electrodialysis with ionic liquids was followed by flash separations. The basis for separations was 1 kg of butyrate and the current efficiency for electrodialysis separations ranged from 95 to 80% and 33 to 11% for water and ionic liquid respectively. From these two simulations, the minimal energy input required for separations was determined. The energy requirements for butyrate purification are shown in Figure 7. Electrodialysis inputs were lower in the pure water case; however, the large energy demand and complexity of distillation makes this case very uneconomical. It is this secondary separation step that makes the use of ionic liquids in electrodialysis advantageous when compared to other separation techniques. However, it is important to note that commercial production of organic acids rely on precipitation of organic salts and re-acidification of organic salts to facilitate water removal. The energy requirements of salting out desired organic products were lower than ionic liquid separation techniques; however, the extra raw materials needed and waste produced from this process makes it undesirable. We believe that through further design of ionic liquids we can lower the cost of the overall process such that it will be economical to produce organic acids through ionic liquid assisted electrodialysis.

Organic acid concentration is important in determining the cost of aqueous organic acid recovery. However, since the butyric acid is going to be recovered by distillation by flashing the minor component (the butyric acid) rather than the major component (the water or ionic liquid), concentration of butyric acid should not directly affect the overall cost of separation. If a high concentration butyric acid stream is required, work by Du *et al*. [31] has shown that butyric acid can be concentrated to levels greater than 180 g/L. In this case the separation would be limited by solubility of butyric acid in ionic liquid. If new ionic liquids can be tested and developed with higher solubility’s, concentrations greater than 100 g/L will be possible.

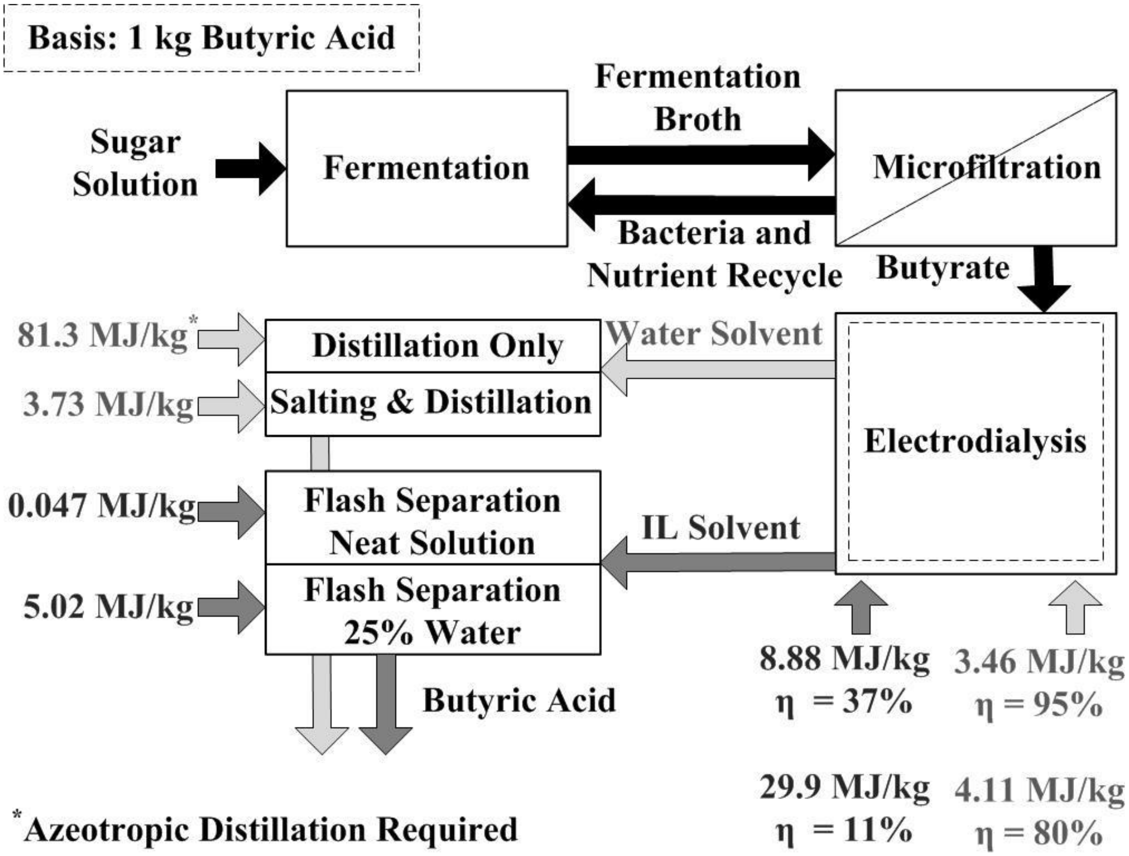


Figure 7. Block Diagram with Power Requirements for Organic Acid Separation. Dark Grey – ED with Ionic Liquids Light Grey – ED without Ionic Liquids

Conclusion

In this work we demonstrated that ionic liquids can be used in electrodialysis to remove organic salts and acids from an aqueous phase. We also showed that bipolar membrane electrodialysis can be used with our developed method to concentrate, acidify, and phase-change valuable organic products. Electrodialysis with ionic liquids generated sodium butyrate with a current efficiency of approximately 30%. Bipolar membrane electrodialysis generated butyric acid with a current efficiency of approximately 11%. Butyric acid was recovered from our ionic liquid solvent with a 99% recovery rate, producing a 1% solution of butyric acid. Water contamination was the greatest factor for the dilution of our recovered acid. Results from experimentation indicated that solvent interaction could not be avoided. Further research will investigate other ionic liquids to reduce water contamination in the concentrate stream and improve current efficiency and ion selectivity. Initial simulations of organic acid separations appear promising with improvements to overall current efficiency resulting in a decrease in energy and production costs. A hydrophobic ionic liquid that reduces interaction with water but still demonstrates a high solubility for organic acids and salts would be the ideal solvent. With subsequent research, a simple technique for purifying organic acids can be developed.

Acknowledgments

This research was conducted at the Ralph E. Martin Department of Chemical Engineering the University of Arkansas in Fayetteville, Arkansas. The authors would like to acknowledge the University of Arkansas Graduate School for providing fellowship funding. This material is based upon work supported by the National Science Foundation Graduate Research Fellowship under Grant No. DGE-0957325.

Nomenclature

AEM	Anion Exchange Membrane
BPED	Bipolar Membrane Electrodialysis
BPM	Bipolar Membrane
CEM	Cation Exchange Membrane
C_{di}	Sodium Butyrate Concentration in Diluate Inlet (g/L)
C_{do}	Sodium Butyrate Concentration in Diluate Outlet (g/L)
C_f	Final Sodium Butyrate Concentration in Diluate Compartment (g/L)
C_i	Initial Sodium Butyrate Concentration in Diluate Compartment (g/L)
ED	Electrodialysis

F	Faradays Constant (C/mol)
I	Current (mA)
LLE	Liquid-Liquid Extraction
IL	Ionic Liquid
M	Molecular Mass (g/mol)
N	Number of cells
Q	Volumetric Flow rate (mL/min)
t	Time (h)
V	Compartment Volume (mL)
z	Ion valence
η	Current Efficiency

References

[1] C. Huang, T. Xu, Y. Zhang, Y. Xue, G. Chen, Application of electrodialysis to the production of organic acids: State-of-the-art and recent developments. J. Membrane Sci. 288 (2007) 1-12.

[2] J.A.L. Blinco, W.O.S. Doherty, Review of extraction technologies for organic acid production. Proceedings of the Conference of the Australian Society of Sugar Cane Technologists. 27 (2005) 480-488.

[3] S.K. Adhikary, P.K. Narayanan, S.K. Thampy, N.J. Dave, D.K. Chauhan, V.K. Indusekhar. Desalination of brackish water of higher salinity by electrodialysis. Desalination. 84 (1991) 189-200.

[4] L. Bazinet, F. Lamarche, D. Ippersiel, Bipolar-membrane electrodialysis: Applications of electrodialysis in the food industry. Trends in Food Science & Technology, 9 (1998) 107-113.

[5] Y. Wang, X. Zhang, T. Xu, Integration of conventional electrodialysis and electrodialysis with bipolar membranes for production of organic acids. J. Membrane Sci. 365 (2010) 294-301.

[6] H. Dong, J. Wang, H. Lu, Recent progress in bipolar membrane electrodialysis. Huagong Jinzhan, 29 (2010) 217-222.

[7] A. Vertova, G. Aricci, S. Rondinini, R. Miglio, L. Carnelli, P. D'Olimpio, Electrodialytic recovery of light carboxylic acids from industrial aqueous wastes. J. Appl. Electrochem. 39 (2009) 2051-2059.

[8] M.B. Arora, J.A. Hestekin, S.W. Snyder, E.J.S. Martin, Y.J. Lin, M.I. Donnelly, C.S. Millard, The separative bioreactor: A continuous separation process for the simultaneous production and direct capture of organic acids. Sep. Sci. Technol. 42 (2007) 2519-2538.

[9] V.M. Bhandari, T. Yonemoto, V.A. Juvekar, Investigating the differences in acid separation behavior on weak base ion exchange resins. Chem. Eng. Sci. 55 (2000) 6197-6208.

[10] S.H. Ha, N.L. Mai, Y. Koo, Butanol recovery from aqueous solution into ionic liquids by liquid-liquid extraction. Process Biochem. 45 (2010) 1899-1903.

[11] D. Wu, H. Chen, L. Jiang, J. Cai, Z. Xu, P. Cen, Efficient separation of butyric acid by an aqueous two-phase system with calcium chloride. Chinese J. Chem. Eng. 18 (2010) 533-537.

[12] D.G. Cherkasov, K.K. Il'in, Salting out of butyric acid from aqueous solutions with potassium chloride. Russian J. Appl. Chem. 82 (2009) 920-924.

[13] H. Li, H. Meng, C. Li, L. Li, Competitive transport of ionic liquids and impurity ions during the electrodialysis process. Desalination 245 (2009) 349-356.

[14] M. Matsumoto, K. Mochiduki, K. Fukunishi, K. Kondo, Extraction of organic acids using imidazolium-based ionic liquids and their toxicity to *lactobacillus rhamnosus*. Sep. Purif. Technol. 40 (2004) 97-101.

[15] J.E. Bara, C.J. Gabriel, T.K. Carlisle, D.E. Camper, A. Finotello, D.L. Gin, R.D. Noble, Gas separations in fluoroalkyl-functionalized room-temperature ionic liquids using supported liquid membranes, Chem. Eng. J. 147 (2009) 43-50.

[16] R.D. Noble, D.L. Gin, Perspective on ionic liquids and ionic liquid membranes, J. Membrane Sci. 369 (2011) 1-4.

[17] T.P. Thuy Pham, C. Cho, Y. Yun, Environmental fate and toxicity of ionic liquids: A review. Water Res. 44 (2010) 352-372.

[18] A.B. Pereiro, J.M.M. Araújo, J.M.S.S. Esperança, I.M. Marrucho, L.P.N. Rebelo, Ionic liquids in separations of azeotropic systems – A review. J. Chem. Thermodyn. 46 (2012) 2-28.

[19] S. Himmler, A. Koenig, P. Wasserscheid, Synthesis of [EMIM]OH via bipolar membrane electrodialysis - precursor production for the combinatorial synthesis of [EMIM]-based ionic liquids. Green Chem. 9 (2007) 935-942.

[20] H. Meng, H. Li, C. Li, L. Li, Synthesis of ionic liquid using a four-compartment configuration electrodialyzer. J. Membrane Sci. 318 (2008) 1-4.

[21] K. Haerens, P. De Vreese, E. Matthijs, L. Pinoy, K. Binnemans, B. Van der Bruggen, Production of ionic liquids by electrodialysis. Sep. Sci. Technol. 97 (2012) 90-95.

[22] H. Li, H. Meng, C. Li, L. Li, L. Competitive transport of ionic liquids and impurity ions during the electrodialysis process. Desalination 245 (2009) 349-356.

[23] L. Chaabane, G. Bulvestre, C. Innocent, G. Pourcelly, B. Auclair, Physicochemical characterization of ion-exchange membranes in water-methanol mixtures. Eur. Polym. J. 42 (2006) 1403-1416.

[24] Q. Li, C. Huang, C., T. Xu, Bipolar membrane electrodialysis in an organic medium: Production of methyl methoxyacetate. J. Membrane Sci. 339 (2009) 28-32.

[25] S. Sridhar, C. Feldmann, Electrodialysis in a non-aqueous medium: A clean process for the production of acetoacetic ester. J. Membrane Sci. 124 (1997) 175-179.

[26] M. Blahušiak, S. Schlosser, J. Marták, Extraction of butyric acid by a solvent impregnated resin containing ionic liquid. React Funct. Polym. 71 (2011) 736-744.

[27] A.G. Fadeev, M.M. Meagher, Opportunities for ionic liquids in recovery of biofuels. Chem. Commun. 3 (2001) 295-296.

[28] BASF. (2013) Frequently Asked Questions. Accessed May 25th 2012. Retrieved from http://www.intermediates.basf.com/chemicals/ionic-liquids/faq

[29] R.S. Gartner, F.G. Wilhelm, G.J. Witkamp, M. Wessling, Regeneration of mixed solvent by electrodialysis: Selective removal of chloride and sulfate. J. Membrane Sci. 250 (2005) 113-133.

[30] F.S. Oliveira, J.M.M. Araujo, R. Ferreira, L. Rebelo, N. Paulo I.M. Marrucho, Extraction of L-lactic, L-malic, and succinic acids using phosphonium-based ionic liquids. Sep. Purif. Technol. 85 (2012) 137-146.

[31] J. Du, N. Lorenz, R. Beitle, J.A. Hestekin. Application of Wafer-Enhanced Electrodeionization in a Continuous Fermentation Process to Produce Butyric Acid with Clostridium tyrobutyricum. Sep. Sci. Technol. 47 (2012) 43-51.

Appendix

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IV. Improved Organic Acid Purification through Wafer Enhanced Electrodeionization Utilizing Ionic Liquids

Improved Organic Acid Purification through Wafer Enhanced Electrodeionization Utilizing Ionic Liquids

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Ralph E. Martin Department of Chemical Engineering, University of Arkansas

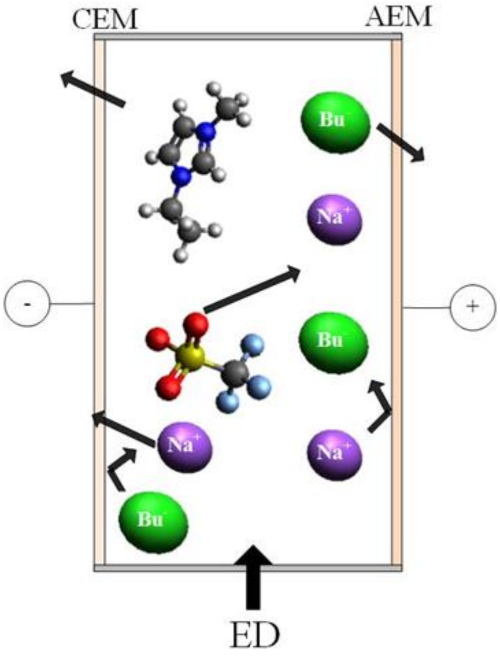
Abstract

Purification of organic acids through electrodialysis has been studied extensively over the past two decades; however, little work has been done on attempting to utilize electrodialysis for solvent replacement for improved acid recovery. This study presents the use of ionic liquids as a secondary electrodialysis solvent in order to transport organic acids from a water phase into an ionic liquid phase. Specifically, the use of wafer enhanced electrodeionization (WE-EDI) techniques with ionic liquids is investigated to improve system performance. Incorporation of ionic liquids allows continuous separation with high solvent recyclability and low operation hazards. Through wafer technology, current efficiencies reached 37-90% with energy consumption rates of approximately 1.25-2.80 kWh/kg acid recovered. Improved separation efficiencies were due to improved electrical conductance of the solutions provided by addition of the resin wafer into the cell compartments. The influence of solution conductivity and current density on separation performance was also studied. It was found that high current densities resulted in higher ion and water transport. Solubility of products, ionic liquid solution characteristics, and water contamination were also found to have a significant impact on current efficiency and power consumption. Through this project, separation of organic acids into ionic liquids with low energy requirements and high separation efficiencies was achieved.

Keywords: Organic Acids, Electrodeionization, Ionic Liquids, Ion Exchange Membranes

Graphical Abstract

Electrodialysis with Ionic Liquids
2.38 – 8.02 kWh/kg
η = 11-37%



Electrodeionization with Ionic Liquids
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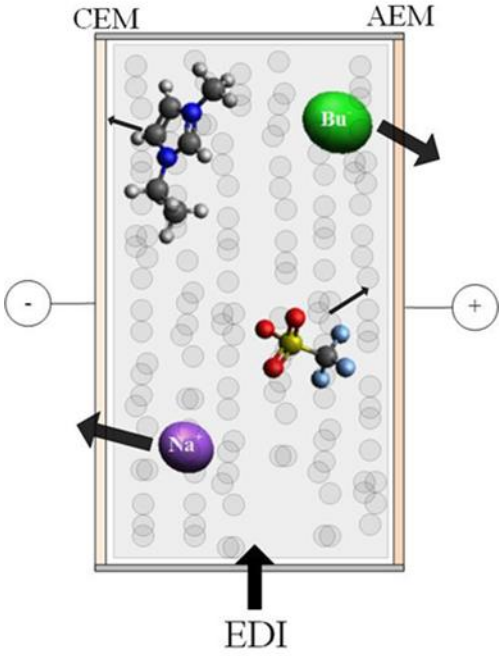

Wafer-Electrodeionization resulted in improved separation efficiency of organic products, lowering overall energy requirements.

Introduction

Organic acids are valuable products that are used in a multitude of industries. Purification of these products often requires significant energy and solvent requirements, opening the way for novel and sustainable separation processes [1–3]. Current separation techniques employ liquid-liquid extraction, or a salting out process, which requires large amounts of solvent and produces waste [4,5]. Liquid-liquid also often results in complex separations and non-ideal extraction efficiencies [6,7]. Ion exchange has also been employed and is generally a prime choice when acidifying organic salts due to low cost; however, the resins used require periodic regeneration resulting in waste produced [8,9]. A more sustainable method is needed to further enhance the efficiency of the production of organic acids. An ideal separation procedure would use a recyclable solvent, have low energy requirements, and a reduced carbon footprint. One such procedure would be the incorporation of novel recyclable solvents in electrodeionization (EDI). This study investigates the possibility of this process through the use of ionic liquids with wafer enhanced EDI.

Membrane separation techniques have been developed to purify organic acids, with significant promise in electrodialysis and EDI [2,10–14]. Electrodialysis (ED) is a charged based separation in which a current is applied to facilitate ion transport from one solution to another. ED allows the manipulation of charged species in a solution while maintaining the integrity of non-ionic molecules. This allows ions to be added or removed when necessary. ED is most commonly used in industry for the desalting of brackish water and de-ashing of whey in the dairy industry [15–17]. The limitations of ED are that as ions are reduced in a solution, more power is needed to move current through that solution resulting in larger power requirements for solutions of low salt content [11,18]. Additionally, conductivity requirements limit the extent of how many ions you can remove before ED becomes inoperable (limiting current density), thus new methods are needed for complete ion removal [19]. EDI is capable of concentrating high value products down to extremely low concentrations [20,21]. This occurs through the use of ion exchange resins within solution compartments that enhance solution conductivity and ion transport. Through EDI, ion removal can progress well beyond the limiting current density found in ED and high recovery of ionic products can be obtained [20,22]. Examples of EDI's use in industry are through metal contamination removal and the development of ultrapure water for electronics and pharmaceutical manufacturing [21]. The limitations of EDI are that pretreatment steps are needed to ensure fouling of membranes is negligible often resulting in complex and costly shielding and anti-fouling measures to ensure proper membrane performance [23,24].

Arora *et al*. and others developed methods for creating ion exchange wafers from resins [22,25,26]. These wafers can be used to enhance electrical conductivity in solutions similar to EDI processes. The main difference using this technique is that the ion exchange resins are bound together using a polymer. The benefit to using a wafer is that electrode cells can be much thinner, and regeneration of the resin can occur within the cell through water splitting, resulting in a lower overall resistance in the electrodialytic stack. Previous research has been focused on the recovery of organic acids using wafer EDI techniques [25]; however, this technique has yet to be combined with ionic liquid assisted ED [27]. Ionic liquids are desirable in electrodialytic separations because of the versatility of these solvents. Ionic liquids are non-flammable, recyclable, possess low vapor pressure, and can easily be separated from organic acid via flash separations [28–30]. Use of ionic liquids instead of water reduces the energy required for downstream processing while allowing the ionic liquid solvent to be recycled back into the EDI stack.

The use of non-aqueous solvents in ED and EDI has been previously studied. Kameche *et al*. investigated the effects of water-ethanol solutions on the acidification of organic salts in order to improve overall organic solubility [31]. Sridhar and Feldmann performed experiments on water-methanol mixtures for the production of sodium methoxide and acetoacetic ester using bipolar membranes in ED and found methoxide formation was possible but with low yield [32,33]. Xu *et al*. also conducted work in the use of organic/aqueous mixtures in ED for the production of organic acids [34]. The main results from these studies using non-aqueous solutions was that addition of organics resulted in lower solution conductivities, implying more energy was needed to produce the desired ionic products. Further, water was included to some degree, typically at 50 vol. %, in order to ensure reasonable ionic transport. Therefore, this research conducted is novel in that experiments performed were conducted using a neat ionic liquid solution that contained no water initially to determine if wafer EDI could overcome the transport limitations caused by non-aqueous solutions.

This study investigated the use of wafer EDI processes for the recovery of organic acids using ionic liquids as a recovery solvent. In this process, ionic liquids were circulated through the concentrate side of the EDI stack while an aqueous feed solution containing the desired organic product was circulated in the diluate stack. Figure 1 shows how the EDI cell was constructed. Since most organic acids exist as ionized salts in fermentation broth, organic salts were used in lieu of acids. Previous research demonstrated the feasibility of this process with organic salts and acids; however, significant ion transport resistance resulted in non-ideal current efficiencies [27]. Through the use of ion exchange resin wafer, higher ion transport can be achieved, improving the separation process and lowering power requirements over traditional ED and bipolar ED techniques.

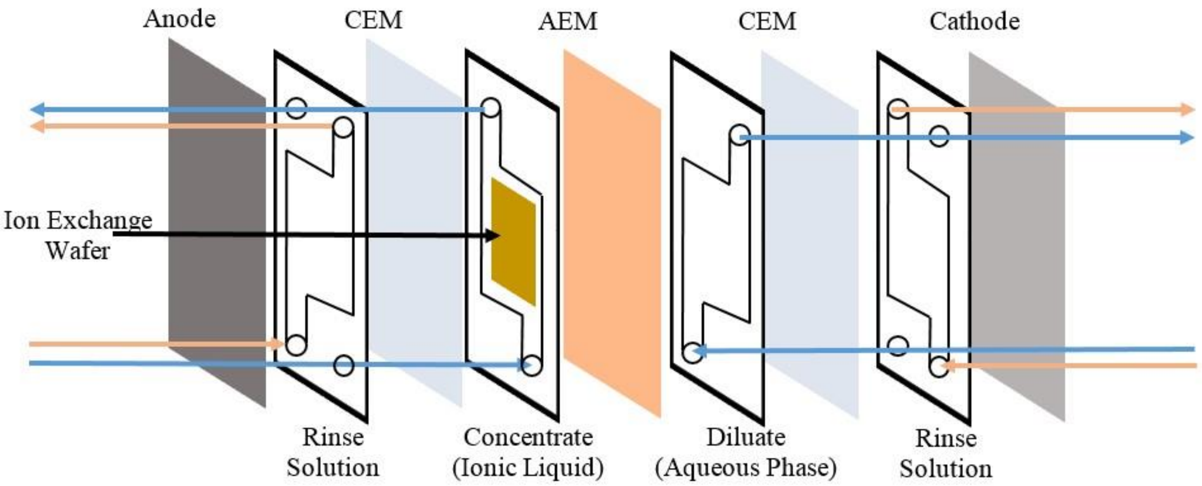

Figure 1. Wafer Electrodeionization with Ionic Liquids Experimental Set-up

Experimental

2.1 Characteristics of Membranes and Chemicals used for Experimentation

Sodium butyrate and acetate were used as model organic salts and obtained from Alfa-Aesar. Amberlite IRA-400 chloride form and Amberlite IR-120 plus were the resins used in construction of ion exchange wafers and obtained from Sigma-Aldrich. Polysulfone and sucrose used during wafer construction were obtained from VWR. Membranes used for EDI were NEOSEPTA AMX and CMX obtained from Tokuyama America. These membranes were chosen due to their wide availability and their robust nature to a wide variety of solvents. The ionic liquids used during experimentation were 1-ethyl-3-methylimidazolium-trifluourmethansulfonate (EMIM-OTIF) and 1-butyl-3-methylimidazolium acetate (BMIM-ACE) obtained from Sigma-Aldrich and produced by BASF. These ionic liquids were chosen due to their hydrophilicity, stable operating temperature range, and expected affinity for the organic products. Table 1 summarizes the importance physical and chemical characteristics of the ionic liquids and membranes used during experiments as well as the solubilities of the chosen organic salts in the ionic liquids.

Table 1. Membrane and Ionic Liquid Properties

	NEOSEPTA AMX	NEOSEPTA CMX	EMIM-OTIF	BMIM-ACE
Thickness (mm)	0.14	0.17	-	-
Resistance (Ω cm^2)	2.4	3.0	Varied	Varied
pH	0-8	0-10	0-14	0-14
Temperature (°C)	≤ 40	≤ 40	$\leq 113^*$	$\leq 153^*$
Density (g/cm^3)	-	-	1.387	1.055
Molecular Weight (g/mol)	-	-	260.23	198.26
Butyrate Solubility (g/kg)	-	-	2.1	10.2
Acetate Solubility (g/kg)	-	-	-**	>400
Butyric Acid Solubility	-	-	Soluble	Soluble
Acetic Acid Solubility	--	-	Soluble	Soluble

*Ionic Liquid Flash Points

**Dissolution of sodium acetate crystals did not occur in EMIM-OTIF

2.2 Wafer Construction and Electrodeionization Operation

Ion exchange wafers were produced by combining anion and cation exchange resin with polysulfone and sucrose in a (2.3:2.3:1:1.5) weight ratio respectively as established by Ho *et al.* [22]. Once combined, the mixture was spread into a metal mold where it was placed in a pneumatic press and heated to 237 °F at 10,000 psi for 90 minutes. After heating, the wafer was air cooled for 15 minutes, cut to fit the EDI stack, and soaked in deionized water for 20 minutes to dissolve the sucrose in the mixture. This provides porosity to the wafer which allows water to flow in and around the wafer during EDI operation. Wafers were placed in the diluate and concentrate compartment of the stack replacing the turbulence mesh typically found in a cell. The EDI stack used was a Micro Flow Cell purchased from ElectroCell North America, Inc. Table 2 lists the dimensions and operating conditions of the stack. Experiments were conducted with a 2 wt. % solution of organic salt (butyrate or acetate) in water on the dilute side. The concentrate compartment consisted of ionic liquid with no added organic salt due to solubility limitations. Rinse compartment consisted of 5 wt. % sodium sulfate solution. Experiments were conducted in a batch system operating in a constant current mode to ensure linear ion depletion in the diluate compartment.

Table 2. Experimental Conditions of Electrodeionization Stack

	EDI (EMIM-OTIF)	EDI (BMIM-ACE)	EDI (EMIM-OTIF)	EDI (BMIM-ACE)
Salt	Acetate	Acetate	Butyrate	Butyrate
Number of Cells	1	1	1	1
Current (A)	0.05	0.1-0.5	0.05	0.05
System Voltage (V)	3.0-6.0	3.0-5.5	3.0-5.0	3.0-4.5
Operation Time (h.)	7-10	7-10	10-24	7-12

2.3 Solution Analysis and System Performance Elevation

High pressure liquid chromatography (HPLC) was used to analyze butyrate and acetate concentrations of the diluate and concentrate streams. The HPLC system consisted of a Waters 717 plus autosampler injector, a Waters 1525 binary HPLC pump, an IC-Pak™ ion-exclusion column (7.8mm x 150mm), and a Waters 2414 refractive index detector. The solvent used during analysis was 5 mM/L sulfuric acid at a flowrate of 1.0 mL/min. A Mettler-Toledo DL31 Karl-Fischer and Brinkmann 701 KF Titrino titrator were used to analyze water leakage into the ionic liquid during ED experiments.

2.4 EDI Current Efficiency and Power Consumption

System performance was measured primarily by current efficiency and power consumption for product recovery. Equation 1 denotes how current efficiency was calculated.

$$\eta = -\frac{zFV(C_f - C_i)}{tIM} \qquad (1)$$

where z is the ionic valence of the acid, V is the volume of the diluate compartment, F is Faraday's constant, C_f is the final salt concentration in the diluate compartment, C_i is the initial salt concentration in the diluate compartment , N is the number of cell pairs, I is the current, and t the system operation time. Once current efficiency was obtained, the power consumption for organic salt recovery was calculated from equation 2.

$$P_r = \frac{V_t I t}{(C_i - C_f)\eta} \qquad (2)$$

Results and Discussion

3.1 Electrodeionization of Ionic Liquid Solutions

ED was performed initially with water in both compartments to ensure proper stack configuration. Once the wafer-EDI cell was optimized, ionic liquid was placed in the concentrate compartment while a 2 wt. % sodium butyrate solution was placed in the dilute compartment, and the system was operated for 7-10 hours. Each experiment was duplicated to ensure accuracy of results and integrity of the EDI stack. Samples were taken, analyzed by HPLC, and the results are shown in Figure 2. Use of wafer-EDI resulted in an average current efficiency of 60% for EMIM-OTIF and 37% for BMIM-ACE. When sodium acetate was used, average current efficiencies were 75% for EMIM-OTIF and 63% for BMIM-ACE. The results from these experiments are presented in Figure 3. Experiments using sodium acetate and EMIM-OTIF resulted in a maximum current of 110%. This is a result of high ion diffusion during the initial hour of the experiment which occurred in conjunction with ion transport due to applied current. In Figure 3 only the diluate concentration for BMIM-ACE is shown due to high concentrations of acetate in the ionic liquid. Current efficiencies lower than ideal (> 90%) were caused by the ionic liquid’s consumption of applied current during operation. Since the solution is ionic, the applied current causes ionic movement of the solvent species, consuming part of the applied current in the process. Fortunately, this bulky nature of the anion and cation species of the ionic liquids limits their movement and transport to other solution compartments within the cell.

BMIM-ACE’s lower separation was attributed to its lower ion conductivity and ion affinity for the organic products tested as compared to EMIM-OTIF. When compared with a previous study using traditional ED and bipolar ED techniques, current efficiencies have improved significantly [27]. The system performance has been improved due to the improved electrical conductivity provided by using ion exchange wafers in the cell.

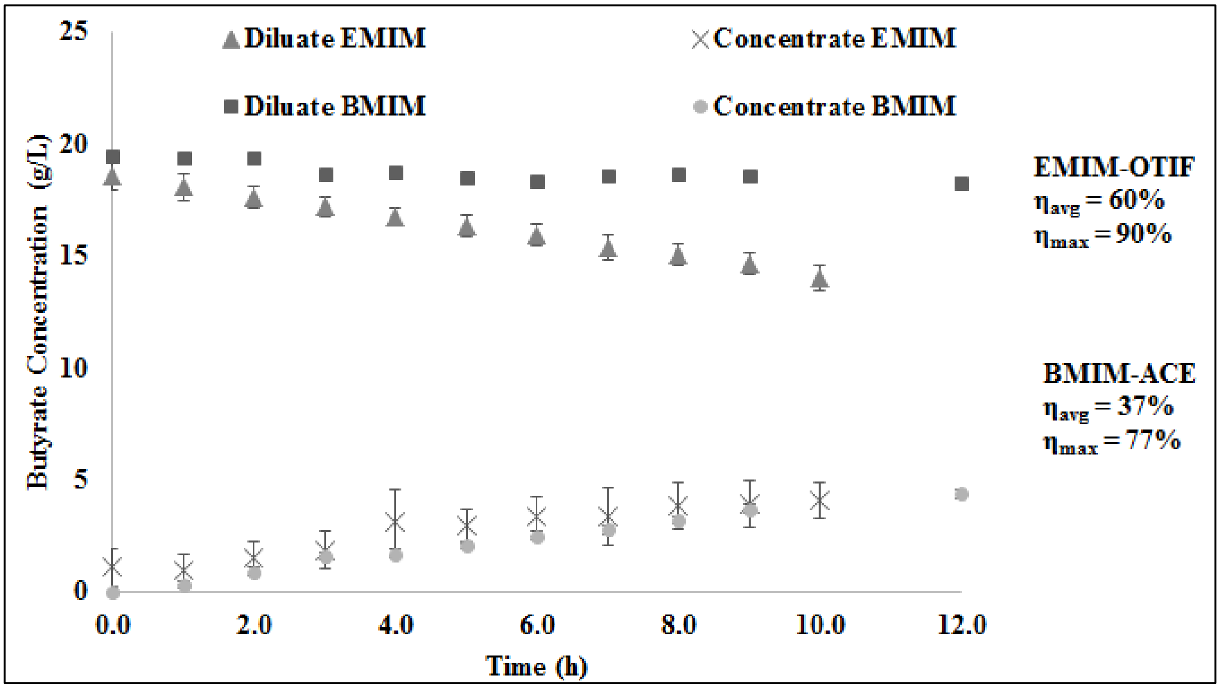

Figure 2. Electrodeionization of Sodium Butyrate with EMIM-OTIF and BMIM-ACE

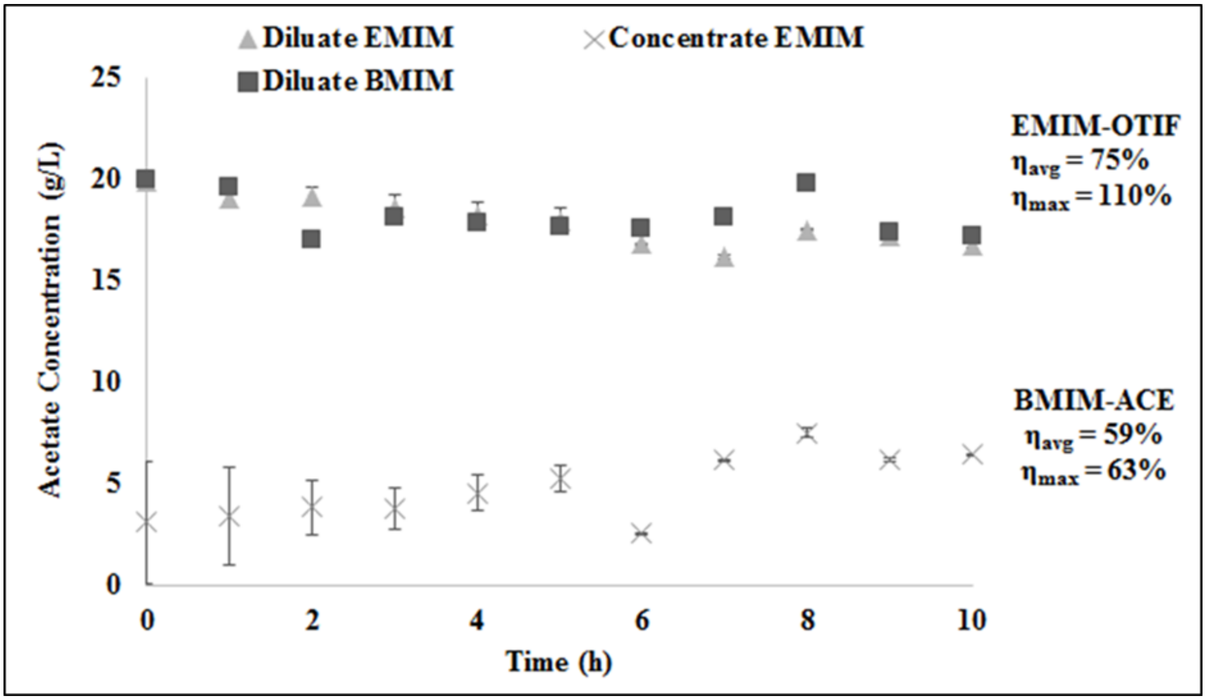

Figure 3. Electrodeionization of Sodium Acetate with EMIM-OTIF and BMIM-ACE

3.2 Water Transport and Influence on EDI Performance

When conducting EDI in non-aqueous solutions, it is important to determine the degree of water transport during system operation. Water contamination results in increased power consumption during downstream purification of the organic products. Figure 4a shows the water content in ionic liquids during experimentation. As the experiments progress, water content increased linearly with time as a function of ion transport rate. The average water transport rate during operation was approximately 21.8g/h for EMIM-OTIF and 10.5 g/h for BMIM-ACE. Initial water concentrations were greater than zero due to mixing with entrained water present within the cell after cleaning between experiments. This is further evidenced by the increase in water transport rate at higher current densities as shown in Figure 4b. Limitation of water transport is crucial to minimize the power requirements and complexity of downstream processing. Unfortunately, current ion exchange membranes are incapable of limiting water co-transport with ion removal. Future studies will consider methods of limiting water transport through the use of more selective membranes and hydrophobic ionic liquid solutions.

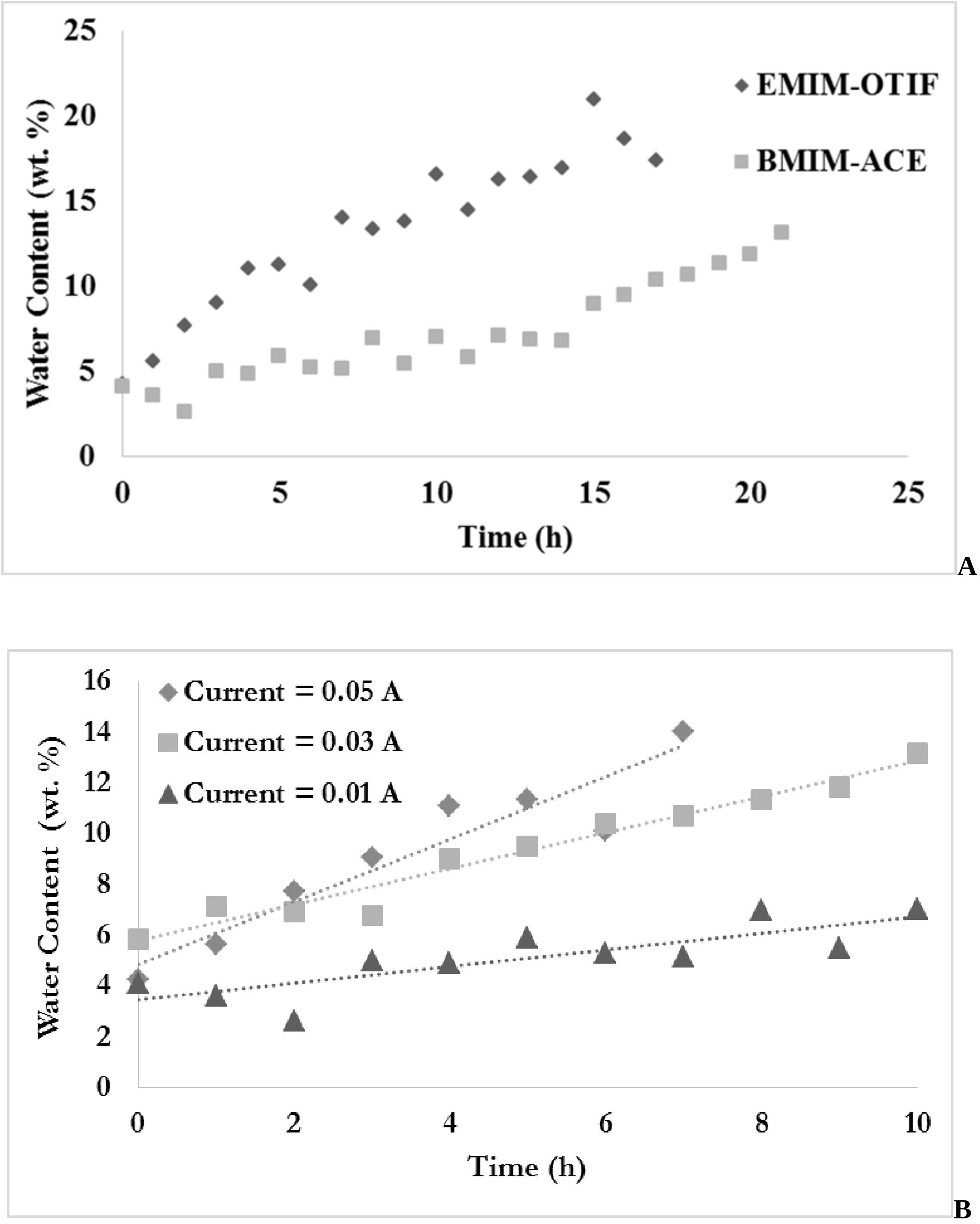

Figure 4. Water Influence on Electrodeionization Performance

3.3 Effects of Ionic Liquid and Acid Structure on EDI Performance

The ionic liquids used in this study display varying characteristics and affinities towards the organic products. Table 1 shows the solubility of the organic acids in the ionic liquids, suggesting that BMIM-ACE would outperform EMIM-OTIF during testing. However, the electrical conductivity and flow characteristics overshadowed the improvements expected. Figure 5 presents a comparison of the ionic liquids when recovering butyrate and acetate. BMIM-ACE had a high viscosity and was difficult to flow through solution, resulting in issues with water contamination and ion transport. This led to lower than expected current efficiencies for the ionic liquid. EDI did improve the performance of both ionic liquids; however, results indicate that other factors such as solution viscosity, water solubility, and product affinity in addition to electrical conductivity are important when recovering these organic products.

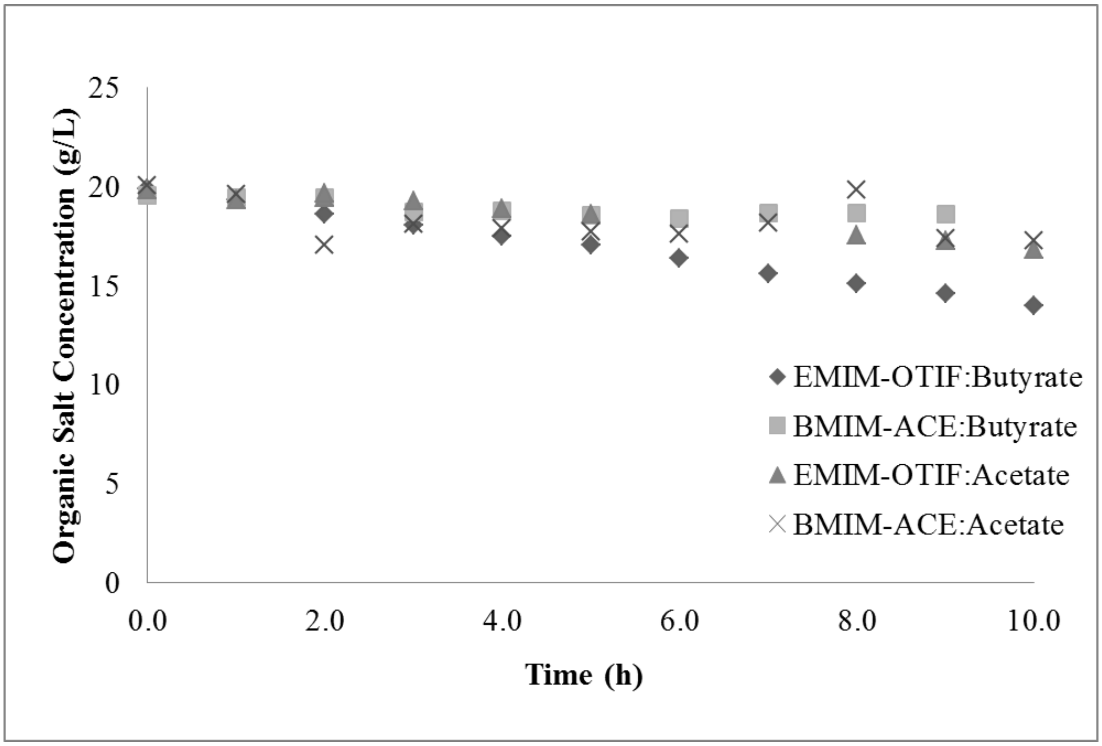

Figure 5. Effect of Ionic Liquid Structure on EDI Performance

3.4 Process Improvements through Ideal Solvent Selection

The use of wafer-EDI techniques has significantly improved the separation performance of ionic liquids in the recovery of organic salts, yet there are many other factors to consider when determining the ideal conditions for product recovery. Transport of co-ions and water has a direct impact on the overall complexity and energy requirements for product recovery. However, water contamination ionic liquid results in lower power consumption in the EDI system due to increased electrical conductivity of the solution. Figure 6 shows how electrical conductivity is influenced by water content in the ionic liquids. As water is added to the ionic liquid, conductivity is increased until water begins to solvate the ionic liquid (approximately 50 vol. %). After this point, the conductivity begins to drop due to lower ion concentrations in solution. What is important to note is that initially water can dramatically improve electrical conductivity in the solution which may be advantageous in EDI with ionic liquids. Figure 7 shows the effect of ionic liquids at various water concentrations on product requirements for organic acid recovery. Initially, total power consumption decreases with increasing water content due to the increase of conductivity of solution. Over time the increase in energy requirements for downstream processing dominates and power consumption increases linearly with water content. This data suggests that hydrophilic ionic liquids with small traces of water can recover organic acid products with lower overall energy requirements over neat ionic liquids. The main drawback is with water contamination; the final product would still need dewatering if high purity is desired, but through this process the majority of the water is removed allowing a much smaller dewatering step. Membrane development with a strong focus on limiting water transport during ED and EDI would dramatically improve the applicability of this process.

Table 3 presents the power consumption for each of the four process methods tested. Through the use of wafer-EDI, power consumption for organic acid recovery utilizing ionic liquids has been reduced to levels below 2 kWh/kg. This reduction of power consumption in EDI is the lowest reported energy requirements for organic acid products to date, and the developed procedure requires the same power consumption as applications where only aqueous solutions are used. Further improvements to below 1kWh/kg are ideal. Nevertheless, the reduction of energy achieved during this study is suitable for advancement to pilot-scale testing.

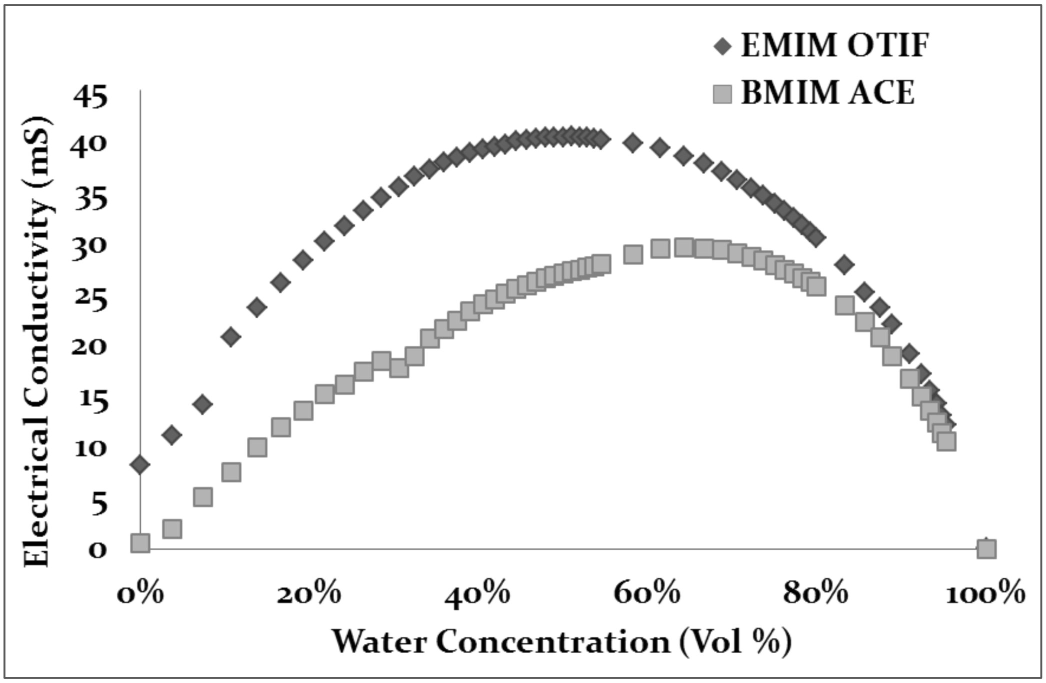

Figure 6. Electrical Conductivity of Water Ionic Liquid Solutions

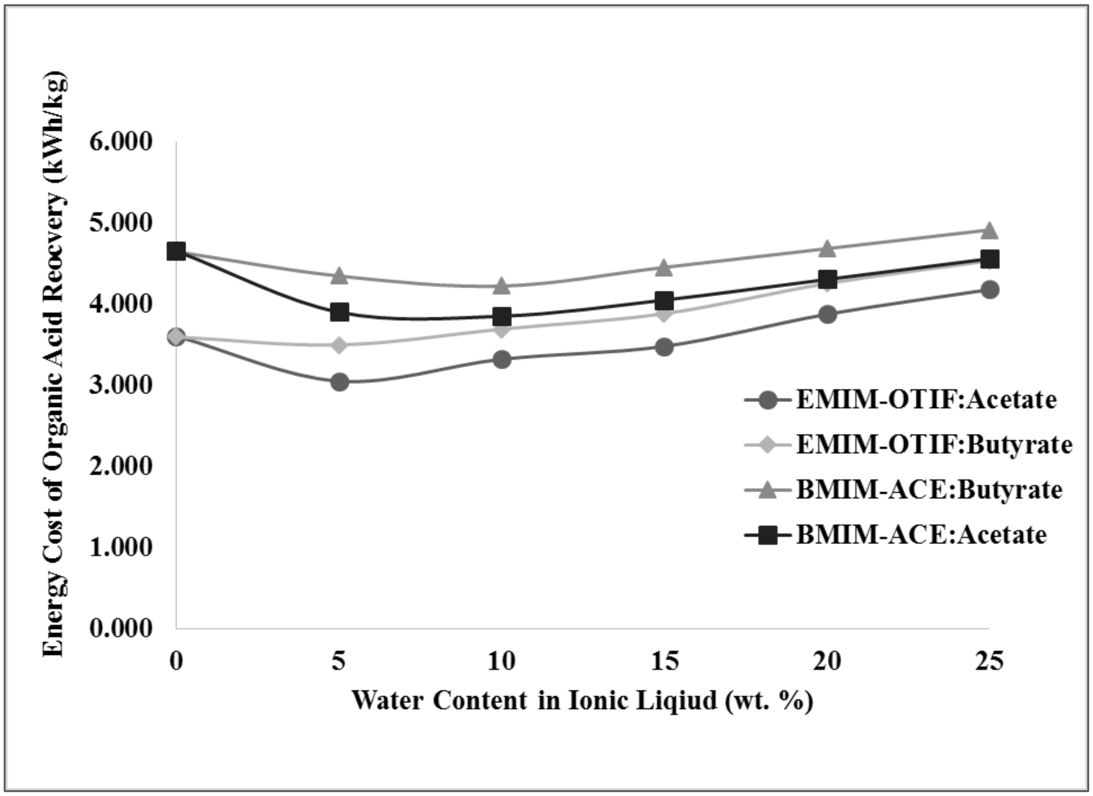

Figure 7. Power Consumption for Organic Product Recovery as a Function of Water Content.

Table 3. Power Requirements for Organic Product Recovery

Separation Method	Study	Energy Requirements (kWh/kg)
BPED	Wang (2010) [10]	2.15 – 2.88 η = 95-131%
BPED	Timbuntam (2008) [41]	1.58 – 5.87 η = 65-86%
EDI	Boontawan (2011) [13]	15.58-30.22
BPED & IL EMIM-OTIF	Previous study [27]	2.38 – 8.02 η = 11-37%
EDI & IL EMIM-OTIF/Butyrate	Current study	1.25 – 1.88 η = 60-90%
EDI & IL BMIM-ACE/Butyate	Current Study	1.34 – 2.80 η = 37-77%
EDI & IL EMIM-OTIF/Acetate	Current Study	1.40 – 2.06 η = 75-110%
EDI & IL BMIM-ACE/Acetate	Current Study	2.45 – 2.62 η = 59-63%

Conclusion

This study investigated the use of ionic liquids for organic salt transport using EDI techniques. Sodium butyrate and acetate were used as model organic salts and transported into two ionic liquids in order to determine ion transport rate, current efficiency, and product recovery power consumption. EDI techniques resulted in improved current efficiencies for both ionic liquids tested. Power consumption decreased as a result of wafer addition, and power consumption values are in the range of similar recoveries using water solutions. Comparison of the ionic liquids showed that EMIM-OTIF outperformed BMIM-ACE for recovery of both products. Additionally, the investigation determined that higher current densities resulted in increased ion and water transport with negligible effect on current efficiency. Manipulation the water content within the ionic liquid may lead to lower energy requirements for organic product recovery as long as the water content stays below 10 wt. %. At these levels, results suggest that slight water contamination may improve EDI operation; however, ramifications of water addition to downstream product recovery need further investigation. Future studies will investigate the use of hydrophobic ionic liquids on product recovery, ion transport, and productivity as well as the effects of flow characteristics on EDI performance.

Acknowledgments

This research was conducted at the Ralph E. Martin Department of Chemical Engineering the University of Arkansas in Fayetteville, Arkansas. The authors would like to acknowledge the University of Arkansas Graduate School for providing fellowship funding. This material is based upon work supported by the National Science Foundation Graduate Research Fellowship under Grant No. DGE-0957325.

Nomenclature

AEM	Anion Exchange Membrane
BMIM-ACE	1-butyl-3-methylimidazolium acetate
CEM	Cation Exchange Membrane
Cf	Final Sodium Butyrate Concentration in Diluate Compartment (g/L)
Ci	Initial Sodium Butyrate Concentration in Diluate Compartment (g/L)
ED	Electrodialysis
EDI	Electrodeionization
EMIM-OTIF	1-ethyl-3-methylimidazolium trifluoromethane sulfonate
F	Faradays Constant (C/mol)
I	Current (mA)
IL	Ionic Liquid
M	Molecular Mass (g/mol)
N	Number of cells
Pr	Product Recovery (kwh/kg)
t	Time (h)
V	Compartment Volume (L)
Vt	System Voltage (V)
z	Ion valence
ΔC	Overall Ion Depletion (g/L)
η	Current Efficiency

References

[1] J.A.L. Blinco, W.O.S. Doherty, Review of extraction technologies for organic acid production, Proc. Conf. Aust. Soc. Sugar Cane Technol. 27th (2005) 480–488.

[2] A. Vertova, G. Aricci, S. Rondinini, R. Miglio, L. Carnelli, P. D’Olimpio, Electrodialytic recovery of light carboxylic acids from industrial aqueous wastes, J. Appl. Electrochem. 39 (2009) 2051–2059. doi:10.1007/s10800-009-9871-9.

[3] L. Vidal, J. Parshintsev, K. Hartonen, A. Canals, M.-L. Riekkola, Ionic liquid-functionalized silica for selective solid-phase extraction of organic acids, amines and aldehydes., J. Chromatogr. A. 1226 (2012) 2–10. doi:10.1016/j.chroma.2011.08.075.

[4] D.G. Cherkasov, K.K. Il’in, Salting out of butyric acid from aqueous solutions with potassium chloride, Russ. J. Appl. Chem. 82 (2009) 920–924. doi:10.1134/S1070427209050346.

[5] D. Wu, H. Chen, L. Jiang, J. Cai, Z. Xu, P. Cen, Efficient Separation of Butyric Acid by an Aqueous Two-phase System with Calcium Chloride, Chinese J. Chem. Eng. 18 (2010) 533–537. doi:10.1016/S1004-9541(10)60255-8.

[6] M. Matsumoto, K. Mochiduki, K. Fukunishi, K. Kondo, Extraction of organic acids using imidazolium-based ionic liquids and their toxicity to *Lactobacillus rhamnosus*, Sep. Purif. Technol. 40 (2004) 97–101. doi:DOI: 10.1016/j.seppur.2004.01.009.

[7] S.H. Ha, N.L. Mai, Y.M. Koo, Butanol recovery from aqueous solution into ionic liquids by liquid–liquid extraction, Process Biochem. 45 (2010) 1899–1903. doi:10.1016/j.procbio.2010.03.030.

[8] Y. Wang, C. Huang, T. Xu, Which is more competitive for production of organic acids, ion-exchange or electrodialysis with bipolar membranes?, J. Memb. Sci. 374 (2011) 150–156. doi:10.1016/j.memsci.2011.03.026.

[9] C.S. López-Garzón, A.J.J. Straathof, Recovery of carboxylic acids produced by fermentation., Biotechnol. Adv. 32 (2014) 873–904. doi:10.1016/j.biotechadv.2014.04.002.

[10] Y. Wang, X. Zhang, T. Xu, Integration of conventional electrodialysis and electrodialysis with bipolar membranes for production of organic acids, J. Memb. Sci. 365 (2010) 294–301. doi:10.1016/j.memsci.2010.09.018.

[11] C. Huang, T. Xu, Y. Zhang, Y. Xue, G. Chen, Application of electrodialysis to the production of organic acids.pdf, J. Memb. Sci. 288 (2007) 1–12.

[12] G. Liu, H. Luo, H. Wang, B. Wang, R. Zhang, S. Chen, Malic acid production using a biological electrodialysis with bipolar membrane, J. Memb. Sci. 471 (2014) 179–184. doi:10.1016/j.memsci.2014.08.014.

[13] P. Boontawan, S. Kanchanathawee, A. Boontawan, Extractive fermentation of l-(+)-lactic acid by *Pediococcus pentosaceus* using electrodeionization (EDI) technique, Biochem. Eng. J. 54 (2011) 192–199. doi:10.1016/j.bej.2011.02.021.

[14] I. Widiasa, P. Sutrisna, I. Wenten, Performance of a novel electrodeionization technique during citric acid recovery, Sep. Purif. Technol. 39 (2004) 89–97. doi:10.1016/j.seppur.2003.12.020.

[15] M. Fidaleo, M. Moresi, Electrodialysis applications in the food industry., Adv. Food Nutr. Res. 51 (2006) 265–360. doi:10.1016/S1043-4526(06)51005-8.

[16] H.M.N. AlMadani, Water desalination by solar powered electrodialysis process, Renew. Energy. 28 (2003) 1915–1924. doi:10.1016/S0960-1481(03)00014-4.

[17] E. Korngold, L. Aronov, N. Daltrophe, Electrodialysis of brine solutions discharged from an RO plant, Desalination. 242 (2009) 215–227. doi:10.1016/j.desal.2008.04.008.

[18] H. Strathmann, Electrodialysis, a mature technology with a multitude of new applications, Spec. Issue to Honour Previous Ed. Miriam Balaban. 264 (2010) 268–288. doi:10.1016/j.desal.2010.04.069.

[19] V. Geraldes, M.D. Afonso, Limiting current density in the electrodialysis of multi-ionic solutions, J. Memb. Sci. 360 (2010) 499–508. doi:10.1016/j.memsci.2010.05.054.

[20] L.L. Alvarado, A. Chen, Electrodeionization Principles, strategies and applications.pdf, Electrochim. Acta. 132 (2014) 583–597. doi:10.1016/j.electacta.2014.03.165.

[21] Ö. Arar, Ü. Yüksel, N. Kabay, M. Yüksel, Various applications of electrodeionization (EDI) method for water treatment—A short review, Desalination. 342 (2014) 16–22. doi:10.1016/j.desal.2014.01.028.

[22] T. Ho, A. Kurup, T. Davis, J. Hestekin, Wafer Chemistry and Properties for Ion Removal by Wafer Enhanced Electrodeionization, Sep. Sci. Technol. 45 (2010) 433–446. doi:10.1080/01496390903526709.

[23] K.I. Dermentzis, A.E. Davidis, A.S. Dermentzi, D. Chatzichristou, An electrostatic shielding-based coupled electrodialysis/electrodeionization process for removal of cobalt ions from aqueous solutions, Water Sci. Technol. 62 (2010) 1947–1953. doi:10.2166/wst.2010.547.

[24] W. Su, R. Pan, Y. Xiao, X. Chen, Membrane-free electrodeionization for high purity water production, Desalination. 329 (2013) 86–92. doi:10.1016/j.desal.2013.09.013.

[25] M.B. Arora, J. a. Hestekin, S.W. Snyder, E.J. St. Martin, Y.J. Lin, M.I. Donnelly, *et al.*, The Separative Bioreactor: A Continuous Separation Process for the Simultaneous Production and Direct Capture of Organic Acids, Sep. Sci. Technol. 42 (2007) 2519–2538. doi:10.1080/01496390701477238.

[26] A.S. Kurup, T. Ho, J. A. Hestekin, Simulation and Optimal Design of Electrodeionization Process: Separation of Multicomponent Electrolyte Solution, Ind. Eng. Chem. Res. 48 (2009) 9268–9277. doi:10.1021/ie801906d.

[27] A.M. Lopez, J. A. Hestekin, Separation of organic acids from water using ionic liquid assisted electrodialysis, Sep. Purif. Technol. 116 (2013) 162–169. doi:10.1016/j.seppur.2013.05.028.

[28] R.D. Noble, D.L. Gin, Perspective on Ionic liquids and ionic liquid membranes, J. Memb. Sci. 369 (2011) 1–4.

[29] A.H. Mohammad Fauzi, N.A.S. Amin, An overview of ionic liquids as solvents in biodiesel synthesis, Renew. Sustain. Energy Rev. 16 (2012) 5770–5786. doi:10.1016/j.rser.2012.06.022.

[30] T.P. Thuy Pham, C.-W. Cho, Y.-S. Yun, T.P.T. Pham, C.-W. Cho, Y.-S. Yun, Environmental fate and toxicity of ionic liquids: a review., Water Res. 44 (2010) 352–72. doi:10.1016/j.watres.2009.09.030.

[31] M. Kameche, F. Xu, C. Innocent, G. Pourcelly, Electrodialysis in water-ethanol solutions: Application to the acidification of organic salts, Desalination. 154 (2003) 9–15. doi:10.1016/S0011-9164(03)00203-0.

[32] S. Sridhar, Electrodialysis in a non-aqueous medium: production of sodium methoxide, J. Memb. Sci. 113 (1996) 73–79. doi:10.1016/0376-7388(95)00217-0.

[33] S. Sridhar, C. Feldmann, Electrodialysis in a non-aqueous medium: A clean process for the production of acetoacetic ester, J. Memb. Sci. 124 (1997) 175–179. doi:10.1016/S0376-7388(96)00221-9.

[34] F. Xu, C. Innocent, P. Gerald, Electrodialysis with Ion exchange membranes in organic media, Sep. Purif. Technol. 43 (2005) 17–24.

[35] W. Timbuntam, K. Sriroth, K. Piyachomkwan, Y. Tokiwa, Application of bipolar electrodialysis on recovery of free lactic acid after simultaneous saccharification and fermentation of cassava starch, Biotechnol. Lett. 30 (2008) 1747–1752. doi:10.1007/s10529-008-9771-9.

V. Improvements in Extracting Electrical Power Using Reverse Electrodialysis during Water Recycling at Hydraulic Fracturing Operations

Improvements in Extracting Electrical Power Using Reverse Electrodialysis during Water Recycling at Hydraulic Fracturing Operations

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Abstract

Reverse electrodialysis is the extraction of usable energy from the Gibbs free energy of mixing two liquids of different salinities. Current research efforts have been focused on the improvement of power density through higher voltages, large cell numbers, and overall reduction of stack resistance, yet problems associated with power generation still persist. We have improved this technology by incorporating ion exchange wafers in each cell, shortening the diffusion pathways and thus decreasing their electrical resistance. We also studied the effects of applying reverse electrodialysis in hydraulic fracturing operations, the first study where direct industrial applications are considered. We developed an innovative resolution to high resistance levels through the use of ion exchange wafers, and have obtained gross power densities of approximately 1.06 W/m^2. This is the first study incorporating electrodeionization techniques in reverse electrodialysis systems. Additionally, overall stack resistance decreased an order of magnitude upon inclusion of ion exchange wafers into the reverse electrodialysis stack. This study also investigated the use of reverse electrodialysis in hydraulic fracturing. This technology could be utilized for processing of flowback water from hydraulic fracturing operations to provide some of the power used at the well site with no greenhouse gas emissions. Using reverse electrodialysis at fracking sites, an industrial process that has been mired by environmental concerns can take positive steps toward developing and adopting sustainable practices.

Keywords Reverse electrodialysis, Ion Exchange Membranes, Hydraulic Fracturing, Membrane Science

Introduction

Recently, marine-based energy sources have become competitive options in the alternative energy sector [1,2]. Salinity-gradient energy, or “blue energy” [3], is defined as the energy available from mixing two aqueous solutions of different salinities, and has a total global potential for power production of 1.4-2.6 TW or as many as 3,000 coal fired power plants [2,4–10]. When “produced water” from fracking is returned to the surface, it contains a high concentration of salts and thus, when it is mixed with fresh water for later reuse, a significant potential to extract usable power exists from Gibbs free energy of mixing [11–13]. However, no studies have been conducted relating this energy potential to the fracking industry. The fracking industry is an ideal application for reverse electrodialysis (RED) because brine solutions and freshwater are found in large quantities at each well site. Not only does our research focus on augmenting the RED process for improved power production, but also it takes this a step further by providing a sustainable solution some environmental hydraulic fracturing concerns.

1.1 Reverse Electrodialysis

RED is an electrochemical process driven by the concentration difference between feed streams (diluate and concentrate) that are separated by ion selective membranes, creating an ion flux as cations and anions diffuse across the membranes [1,3,14]. Through a series of oxidation-reduction reactions at each electrode, this ion flux is converted directly into an electric current [3,15]. Several designs for RED systems have been considered, generally consisting of alternating cation and anion exchange membranes separated by spacers and terminated with an electrode at each end [14–16]. In stacks consisting of multiple cells, a serial configuration is used to maximize power generation [17]. Homogeneous ion exchange membranes are used for their high permselectivity for ions with opposing charge while repelling ions with like charge [18].

Previous research has found solutions to some limitations in RED including those for the spacer shadow effect [19–21], fouling [6], and resistance [10].

In a traditional RED setup, the environment of the diluate chamber is non-conductive, providing limited ionic diffusion. As a result, the resistance here is the dominant restriction [22,23], and no research to date has effectively solved this problem. Therefore, the focus of this research is to provide a working solution to limited ion diffusion by applying principles of Wafer Enhanced-Electrodeionization (WE-EDI) [24–26] in hopes of greatly reducing this resistance. A wafer is made by binding ion exchange resins with polyethylene [24], and will be used as a spacer in each chamber to stimulate ionic transport. The largest reported experimental power density is 2.2 W/m^2 using a stack composed of five cells, spacer thickness of 100 μm, and specially manufactured ultra-thin membranes (30-40 μm thick) [7]. However, power densities an order of magnitude above this level are possible, evidenced by theoretical calculations with minimal system resistances.

1.2 Technology Implications for Produced Water from Hydraulic Fracturing

Hydraulic fracturing has become widely utilized as a means for extracting unconventional natural gas and oil. Each well site is horizontally drilled, and injected with 12-16 million liters of "fracking fluid" (water with sand and chemical additives), under high pressure to crack the formation thus increasing the permeability of the surrounding rock enabling enhanced gas and oil flow to the well [27]. Following the fracturing process, fluid returns to the surface as produced water containing contaminants, mainly dissolved salts, with recovery rates ranging from 20 to 100% [11,27]. The most common method of produced water disposal is deep-well injection, however, it is suspected that this has contributed to recent seismic events in addition to permanently removing water from the ecosystem [28–30]. As a result, the need for devising an alternative method for handling produced water has become both environmentally and economically pressing.

To begin water recovery, a series of pretreatment regimens are implemented in order to remove contaminants and foulants. Once these have been removed, RED technology can be used to harness the Gibbs free energy of mixing between this partially treated produced water and a freshwater feed with the purpose of replenishing the water that could not be recovered from water clean-up. This extracted energy can then be used to power ongoing processes or stored in a battery for later use in subsequent fracking process when needed. The resulting water solution output from the RED system can then be recycled back into the hydraulic fracturing process. This revolutionary approach allows for the recycle of water and production of energy.

Materials and Methods

We designed an innovative RED system that utilized WE-EDI techniques to minimize system resistance. This system was tested with varying numbers of cell pairs. Membranes were separated by custom hybrid spacer-gaskets to minimize cell length. Each one measured 500 microns in thickness. Fumatech FKS-30 and FAS homogeneous ion exchange membranes were used for experimentation. A schematic of the general system configuration is shown below in Figure 1.

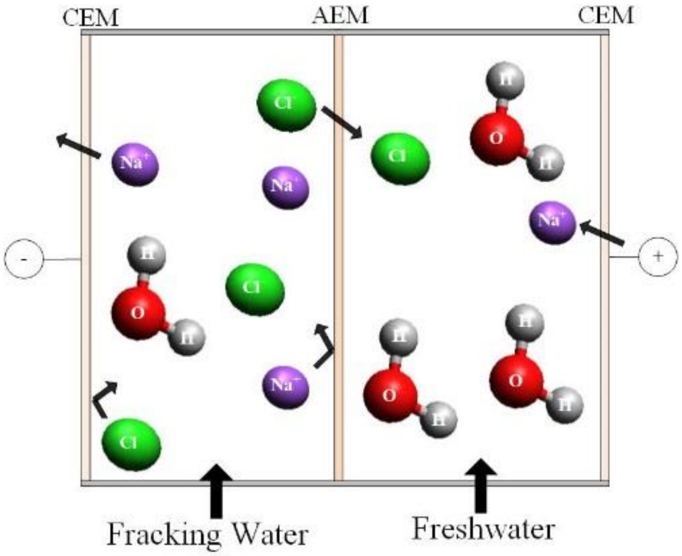

Figure 1: Diagram of RED Cell. Membranes are spaced within the cell, and compartments alternate between freshwater and fracking/brackish water.

2.1 Wafer Casting

Ion exchange wafers used in experimentation were composed of both anion and cation exchange resins (Amberlite® IRA-400(Cl) and Amberlite® IR120 Na+ form ion exchange resins), polymer (Polyethylene powder, 500 µm), and sucrose. A custom iron cast was constructed that measured 127x 127cm in diameter. Each batch of wafer ingredients were mixed in a 46:15:10 gram ratio of resin, sugar, and polymer developed in a previous study [24]. The composition was then mixed at a rate of 300 rpm for 5 seconds using a FlackTek Inc. SpeedMixerTM (model: DAC 150 SP) to ensure uniformity. Wafer material was placed in the cast, and then inserted into a Carver press (model 3851-0 at 10,000 psi and 237°F for 90 minutes, followed by a 20 minute cooling period via pressurized air treatment. After cooling, the cast was removed, and wafer carefully extracted. Figure 2 shows an image of the resulting wafer structure. The resin and sucrose become bound by the polymer, and following a soak in a water solution, the sucrose dissolves leaving a porous wafer. This allows the RED solutions to flow around and through the wafer similar to a turbulence spacer in traditional systems. The novelty of our wafer comes from its improvement of ion transport through a drastically reduced diffusion path length for ions. At voltages above 1.5 V, water splitting will occur within the RED system, and the generated ions eliminate the potential for surface attachment of other mono and divalent ions in solution, improving ion mobility and diffusion rates.

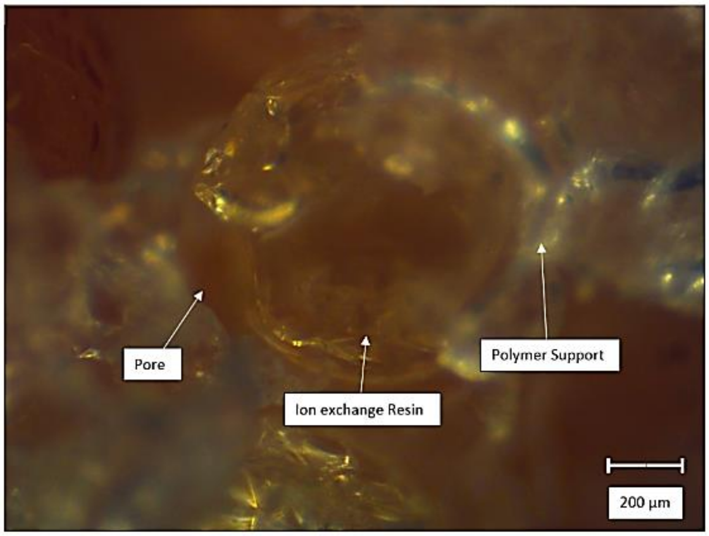

Figure 2. Microscopic Image of Resin Wafer used in Electrodeionization. Spherical resin partially encased by polymer binder. Active area should be maximized to ensure proper wafer activity.

2.2 Feed Water Concentrations

Experiments were conducted with simulated saltwater and freshwater feeds. For each experiment, a 3% NaCl concentration was used for rinse feeds. All feed waters were pumped through the cell using peristaltic pumps, and varying flow rates were tested. Initial and final conductivities of concentrate and diluate feed streams were measured in addition to the open circuit voltage potential. Experiments were also conducted using fracking water obtained from an Oklahoma well site. All hydraulic fracturing simulations performed were based on voltages obtained in these tests.

2.3 Analytical Measurements: Electrochemical

Voltage and current readings were taken for both traditional RED conditions and our wafer-enhanced design. These were obtained using both a digital multimeter (Klein Tools) and potentiostat (Amel model 2053). Once the RED stack was set up for a specific set of conditions, fluid was pumped through the stack, and voltage readings were measured directly from the multimeter with fluid flow being the only source of ionic movement. Once an average voltage was obtained per cell pair from a single cell stack, the potentiostat was used to simulate process scale-up. A range of voltages were applied to the stack, and current measurements were obtained. It was then possible to calculate the system resistance and the overall power density capability of the stack.

2.4 Mathematical Theory

To simulate the process scale-up, the following equations were used to obtain the resistance of each cell pair and electrode at a specified voltage:

$$R_{cell} + R_{electrode} = R_{total} \qquad 1$$

where R_{cell} was the resistance of a single cell and $R_{electrode}$ was the combined resistance of the electrodes. Once these were obtained, it was necessary to find the number of cell pairs needed to generate a given voltage. This was determined using equation 2.

$$\frac{V_{applied}}{V_{cell\ pair}} = N_{cells} \qquad 2$$

where the V_{cell} pair was the voltage obtained from a single cell pair using RED and $V_{applied}$ was the theoretically generated voltage through applying it to the RED system. The cell pair voltage was identified from the multimeter data, and the applied voltage was varied from 0.2-4.5 V using the potentiostat. This number was multiplied by R_{cell} to obtain the total resistance per stack. Power density was then calculated from equation 3.

$$P = \frac{V_{applied}^{2}(R_{load})}{2(R_{total}+R_{load})^{2}} = \frac{V_{applied}^{2}}{8R_{total}} \qquad 3$$

Previous studies have demonstrated that the maximum power generated from an RED stack occurs when a load applied the system equals the stack resistance [5]. To find power density in units of W/m^2, the last expression is divided by the total active membrane area, found by multiplying the number of membranes used by the active area. For this research, the active area was 10 cm^2.

Results and Discussion

3.1 Voltage Potential

Once focus for this project was directed towards implications in the hydraulic fracturing industry, experimental conditions were tailored for simulating the fluid properties of produced water. During pretreatment, produced water from hydraulic fracking entering the RED apparatus had undergone nanofiltration pretreatment to remove all divalent ions from the water, maximizing voltage potential. This set of experiments was performed using a single-cell RED stack, and run with simulated fracking solution of 14% NaCl and 0.1% NaCl salt solution in the concentrate/rinse feed streams and diluate feed stream respectively. Additionally, water from an Oklahoma fracking site was used to confirm the voltage output from this application. It was found that an average of 181 mV was produced per cell pair on a single-cell stack. When simulated seawater at 3% NaCl was tested with 0.1% NaCl solution, the output voltage was 150 mV. These values were later used for power density calculations.

3.2 Gross Power Density

In order to obtain gross power density, several sets of experiments were performed to simulate a multi-stack design for high voltage operation ranging from 0.2 to 5 volts. Further, direct power measurement was conducted in a single-cell traditional RED setup (i.e. no wafers used), single-cell wafer-enhanced RED setup, 6-cell traditional RED setup, and 6-cell wafer-enhanced RED setup. Current and power density calculations were then carried out and corrected for non-ohmic behavior caused by the presence of the ion exchange wafers [25,31]. Figure 3 shows the gross power density obtained for both traditional and wafer-enhanced conditions. The highest power generation was 1.06 W/m^2 for the wafer enhanced system using fracking solutions while simulated seawater resulted in a power density of 0.68 W/m^2. When no wafers were used, the power density obtained was 0.46 W/m^2. For voltages below 1.5 V, power output was very low (< 0.05 W/m^2). When 1.5 V was reached, wafer activation occurred and significant increases in gross power density were observed. Membrane performance also improved, leading to increased observed power densities in non-wafer systems. The improvement in power density is thought to be mainly a result of the wafer activation. This is the first known study where EDI is shown to increase the power density in a reverse electrodialysis system.

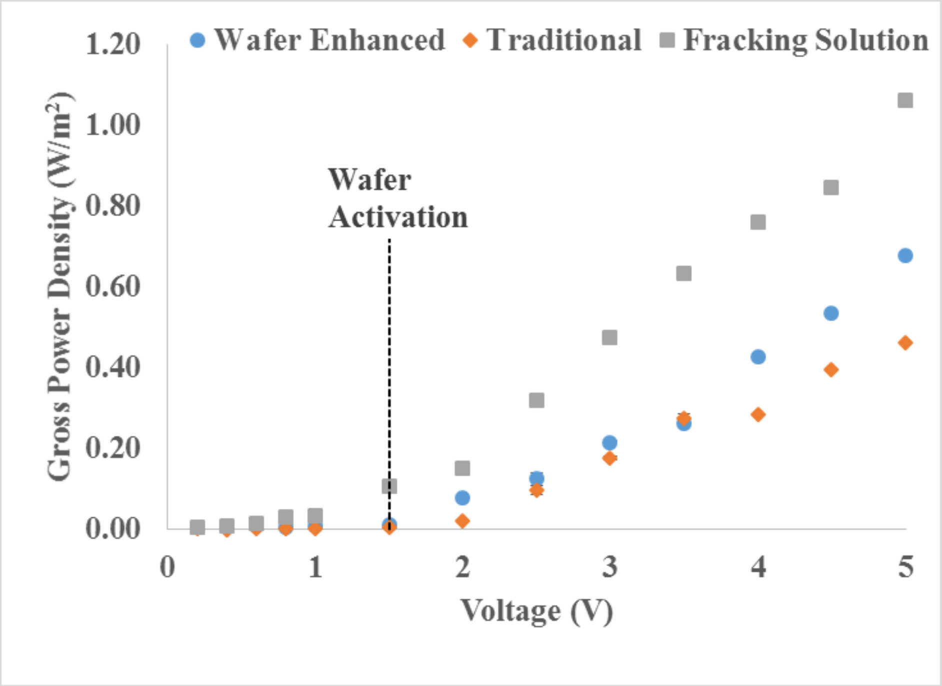

Figure 3. Gross Power Density. Gross power density of the RED stack for traditional and wafer-enhanced RED conditions.

Overall it is shown that the use of ion-exchange wafers had a moderate effect on gross power densities for RED, and that optimum conditions exist greater than 1.5 V. In the higher voltage regions (i.e. > 1.5 V), a phenomenon known as "water splitting" has a large effect on the process; conversely, below 1.5 V, the ion-exchange wafer is inactive and water splitting does not occur. Thus, each ion has passive diffusion throughout the cell, resulting in higher resistances. When the wafers activate at voltages above 1.5 V, water molecules rapidly break apart and form hydrogen and hydroxide ions. Faster diffusion is promoted when these H^+ and OH^- ions force counter-ions through the cells, dramatically decreasing resistances through facilitated diffusion. Simulated power densities for the traditional system show an ideal case; however, there are several system hindrances that would result in lower than expected power yield with traditional RED. At low voltages, ion diffusion is limited by the high resistance of the freshwater stream, so reaching a high voltage potential can be very difficult due to the large resistance inherent to the system. This resistance limitation is shown in Figure 4. The increase in resistance between 1-2 V for the traditional system occurred for every experimental trial conducted. Also in high voltage systems, water splitting can result in severe damage to the ion exchange membranes in traditional RED; however, the wafer enhanced case prevents membrane damage and promotes wafer regeneration [24,25,31].

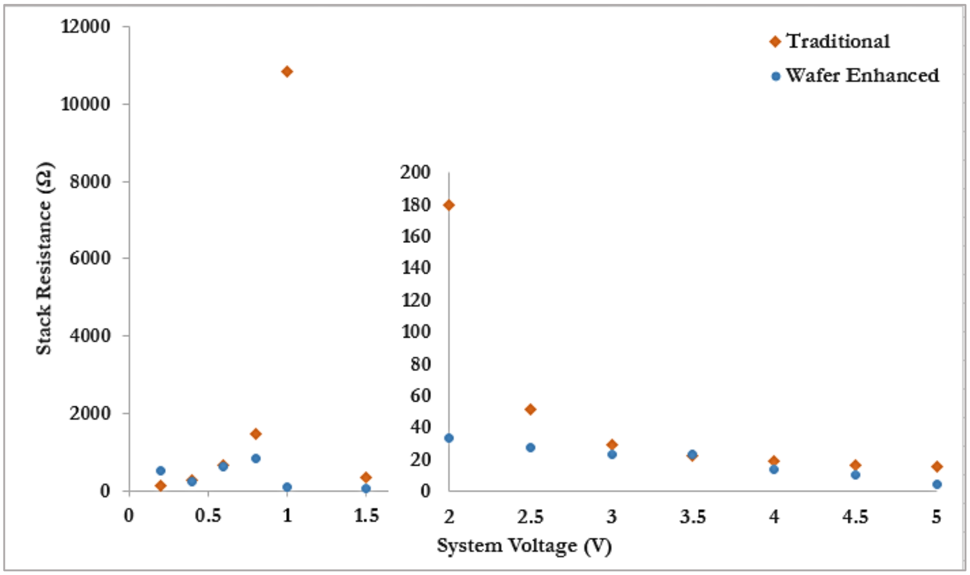

Figure 4. RED Stack Resistance Comparison of resistances between traditional and wafer-enhanced conditions.

3.3 Net Power Density

For an accurate representation of possible power density output, power consumption due to pumping losses, wafer regeneration, and passive current added during testing must be considered. Passive current was determined by testing the system for power output when no salinity gradient was present. The resulting current and power output at the no gradient case were calculated for each applied voltage. Wafer regeneration requires a degree of water splitting to occur within the system. This requires approximately 0.5 V per cell pair for maximum wafer regeneration and ion transport. Subtracting these values from gross power density numbers yields the net power density, or what would be generated for use in practical applications. Figure 5 show the effect of passive current correction and water splitting on gross power density.

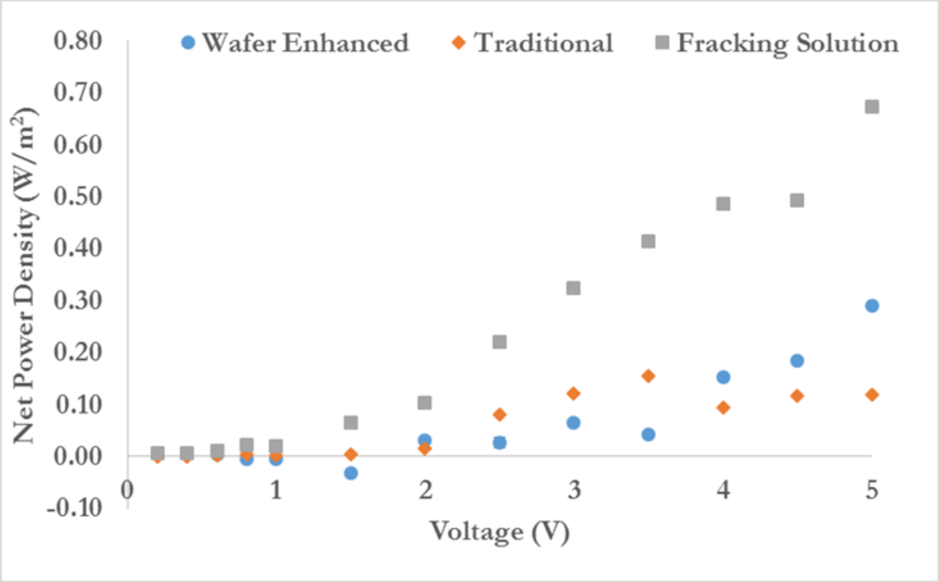

Figure 5. Net power density of wafer enhanced and traditional RED systems correcting for passive current added during testing.

The net power density was 0.67 W/m^2 for the wafer enhanced system running with fracking water and 0.29 W/m^2 for the wafer enhanced system simulated seawater was used. The traditional system had a net power density of 0.12 W/m^2. At voltages below 1.5 V, low power output is observed as seen in Figure 3 above. At the onset of water splitting, we observe a negative power density for the wafer enhanced system resulting from the power required for wafer regeneration. At higher voltages, the wafer enhanced system outperforms the traditional RED system. This is a result of wafer performance and a decrease in traditional system performance directly resulting from increased water splitting. Taking into account the total pressure drop across the system, the power losses due to pumping were 1.6 W/m^2 for all tests.

Unfortunately in small lab scale testing, this exceeds the amount of gross power, meaning that little to no useful power can be recovered on the scale tested. Pumping power is difficult to consider in small systems because the flow and power used is often designed for larger systems and pressure drops fluctuate during testing as noted by others [7,32]. In addition, the spacers and membranes used were much thicker than desired and much larger than other systems used in other studies [7]. In order to obtain useful power larger systems as well as thinner membranes and solution spacers are needed. As power density increases, losses due to pumping become less significant. Theoretical predictions based on lab data suggest that realistic maximum power densities of 2-5 W/m^2 are possible with an optimized system. Therefore, we conclude that power densities approaching 5 W/m^2 can be achieved and would be a tremendous sustainable and financial incentive to the industry. Coupling this technology with water recycle, the hydraulic fracturing industry can reduce the amount of energy and resources required for oil and natural gas extraction.

3.4 Implications for the Fracking Industry

Research investigating the treatment and recycle of this produced water for re-use at other well sites has been conducted [33,34]. In one case, a nanofiltration process was used to recycle produced water and then freshwater was reintroduced to the process through RED. Through nanofiltration and RED, water recoveries greater than 80% and 40 J/gallon of produced water are possible. Calculations show an average increase in revenue of approximately 2 million dollars a year per well making the technology environmentally friendly and economically attractive. A diagram of the proposed treatment cycle is shown in Figure 6 below.

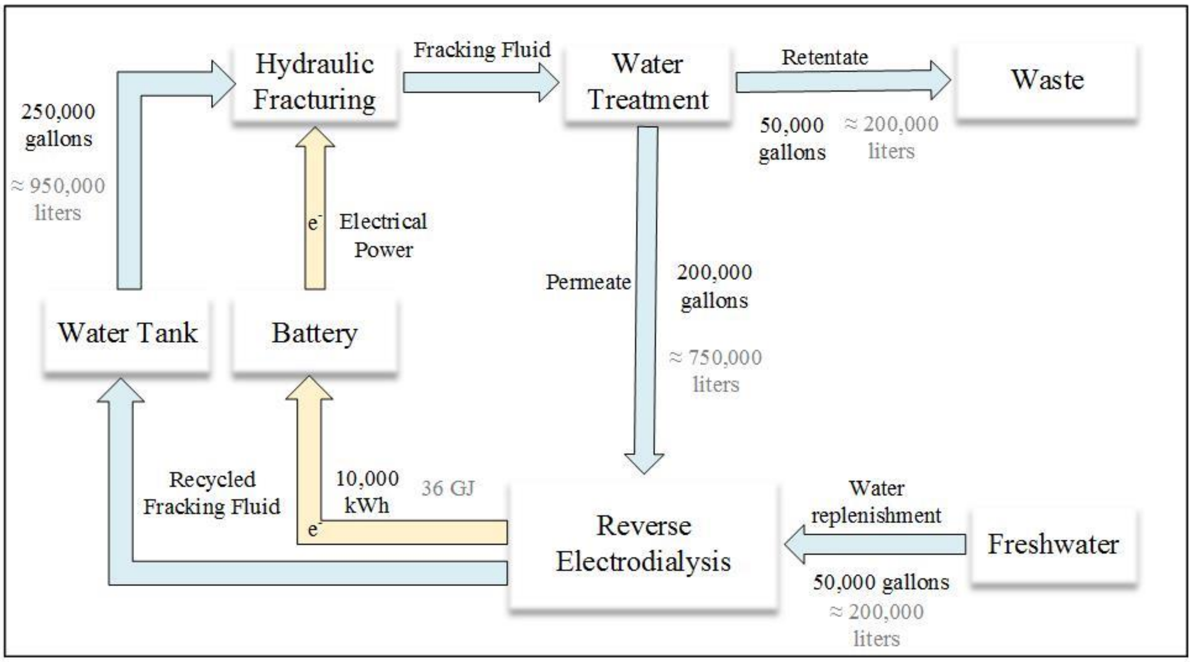

Figure 7. Enhanced Produced Water Treatment Cycle. Treatment cycle consisting of both traditional and advanced pretreatment techniques, while implementing RED technology.

The process water leaving the hydraulic fracturing system will be treated for recycle. However, some of the water cannot be recovered and requires replacement. By controlling the mixing of this freshwater feed with the treated fracking water, RED systems can be implemented to provide useful power for fracking operations. The resulting water energy recovered can then be used in additional hydraulic fracking operations, reducing the overall water and energy demands.

Conclusion

Salinity-gradient energy is one of the most promising untapped potentials in the alternative energy sector, with reverse electrodialysis as a front-runner among the extraction technologies currently being explored. Through this research the limitations in RED caused by high stack resistance have been mitigated. With the use of ion-exchange wafers in RED, system resistance is dramatically decreased, and thus a substantial increase in power density is observed.

This technology also serves as a bridge to close the gap between lab-scale and practical applications. It allows for the system to operate effectively at higher voltages, and uses the effects of water-splitting that occur to an advantage. The dominant economic factor of using RED as an alternative energy source is the price of the membranes. With this improved application for wafer technology in the reverse electrodialysis process, it is possible to reach power densities in the range of 2-5 W/m^2 depending on the system configuration, water quality, and other constraints. Finally, this study considered incorporating RED technology into hydraulic fracturing. Using RED, energy can be produced for fracking operations with water recycle systems for a more environmentally friendly and economic hydraulic fracking process.

Acknowledgements

The authors would like to acknowledge the Ralph E. Martin Department of Chemical Engineering at the University of Arkansas for their support on this project. Support was also provided by the Arkansas SURF. This material is based upon work supported by the National Science Foundation Graduate Research Fellowship under Grant No. 12259. Any opinion, findings, and conclusions or recommendations expressed in this material are those of the authors(s) and do not necessarily reflect the views of the National Science Foundation.

Nomenclature

N_{cell}	Number of Cells
RED	Reverse Electrodialysis
R_{cell}	Cell Resistance
$R_{electrode}$	Electrode Resistance
R_{load}	Load Resistance
R_{total}	Total Stack Resistance

$V_{applied}$	Applied Voltage
$V_{cell\ pair}$	Voltage Generated per Cell Pair
WE-EDI	Wafer-Enhanced Electrodeionization

References

[1] J.W. Post, J. Veerman, H.V.M. Hamelers, G.J.W. Euverink, S.J. Metz, K. Nymeijer, *et al.*, Salinity-gradient power: Evaluation of pressure-retarded osmosis and reverse electrodialysis, J. Memb. Sci. 288 (2007) 218–230. doi:10.1016/j.memsci.2006.11.018.

[2] N.Y. Yip, M. Elimelech, Thermodynamic and energy efficiency analysis of power generation from natural salinity gradients by pressure retarded osmosis., Environ. Sci. Technol. 46 (2012) 5230–9. doi:10.1021/es300060m.

[3] J.W. Post, Blue Energy : electricity production from salinity gradients by reverse electrodialysis, Wageningen University, 2009.

[4] J.W. Post, H.V.M. Hamelers, C.J.N. Buisman, Energy recovery from controlled mixing salt and fresh water with a reverse electrodialysis system, Environ. Sci. Technol. 42 (2008) 5785–5790. doi:10.1021/es8004317.

[5] G.Z. Ramon, B.J. Feinberg, E.M. V. Hoek, Membrane-based production of salinity-gradient power, Energy Environ. Sci. 4 (2011) 4423–4434. doi:10.1039/c1ee01913a.

[6] D.A. Vermaas, D. Kunteng, M. Saakes, K. Nijmeijer, Fouling in reverse electrodialysis under natural conditions., Water Res. 47 (2013) 1289–98. doi:10.1016/j.watres.2012.11.053.

[7] D.A. Vermaas, M. Saakes, K. Nijmeijer, Doubled power density from salinity gradients at reduced intermembrane distance., Environ. Sci. Technol. 45 (2011) 7089–95. doi:10.1021/es2012758.

[8] J. Veerman, M. Saakes, S.J. Metz, G.J. Harmsen, Electrical power from sea and river water by reverse electrodialysis: A first step from the laboratory to a real power plant, Environ. Sci. Technol. 44 (2010) 9207–9212. doi:10.1021/es1009345.

[9] P. Długołęcki, A. Gambier, K. Nijmeijer, M. Wessling, Practical potential of reverse electrodialysis as process for sustainable energy generation, Environ. Sci. Technol. 43 (2009) 6888–6894. doi:10.1021/es9009635.

[10] J. Veerman, M. Saakes, S.J. Metz, G.J. Harmsen, Reverse electrodialysis: Performance of a stack with 50 cells on the mixing of sea and river water, J. Memb. Sci. 327 (2009) 136–144. doi:10.1016/j.memsci.2008.11.015.

[11] R.D. Vidic, S.L. Brantley, J.M. Vandenbossche, D. Yoxtheimer, J.D. Abad, Impact of shale gas development on regional water quality., Science. 340 (2013) 1235009. doi:10.1126/science.1235009.

[12] M. Elimelech, W.A. Phillip, The future of seawater desalination: energy, technology, and the environment., Science. 333 (2011) 712–717. doi:10.1126/science.1200488.

[13] H.R. Acharya, C. Henderson, H. Matis, H. Kommepalli, B. Moore, H. Wang, Cost effective recovery of low-TDS frac flowback water for re-use, US Dep. Energy Washington, DC. (2011).

[14] S. Pawlowski, P. Sistat, J.G. Crespo, S. Velizarov, Mass Transfer in Reverse Electrodialysis: Flow Entrance Effects and Diffusion Boundary Layer Thickness, J. Memb. Sci. 471 (2014) 72–83. doi:10.1016/j.memsci.2014.07.075.

[15] J. Veerman, R.M. de Jong, M. Saakes, S.J. Metz, G.J. Harmsen, Reverse electrodialysis: Comparison of six commercial membrane pairs on the thermodynamic efficiency and power density, J. Memb. Sci. 343 (2009) 7–15. doi:10.1016/j.memsci.2009.05.047.

[16] R.D. Cusick, Y. Kim, B.E. Logan, Energy Capture from Thermolytic Solutions in Microbial Reverse-Electrodialysis Cells, Science (80). 335 (2012) 1474–1477. doi:10.1126/science.1219330.

[17] K.S. Kim, W. Ryoo, M.-S. Chun, G.Y. Chung, Simulation of enhanced power generation by reverse electrodialysis stack module in serial configuration, Desalination. 318 (2013) 79–87. doi:10.1016/j.desal.2013.03.023.

[18] R. Banan Sadeghian, O. Pantchenko, D. Tate, A. Shakouri, Miniaturized concentration cells for small-scale energy harvesting based on reverse electrodialysis, Appl. Phys. Lett. 99 (2011) 99–101. doi:10.1063/1.3656279.

[19] P. Dlugolecki, J. Dabrowska, K. Nijmeijer, M. Wessling, Ion conductive spacers for increased power generation in reverse electrodialysis.pdf, J. Memb. Sci. 347 (2010) 101–107.

[20] D. a. Vermaas, M. Saakes, K. Nijmeijer, Power generation using profiled membranes in reverse electrodialysis, J. Memb. Sci. 385-386 (2011) 234–242.

[21] J. Liu, G.M. Geise, X. Luo, H. Hou, F. Zhang, Y. Feng, *et al*., Patterned ion exchange membranes for improved power production in microbial reverse-electrodialysis cells, J. Power Sources. 271 (2014) 437–443. doi:10.1016/j.jpowsour.2014.08.026.

[22] P. Długołecki, B. Anet, S.J. Metz, K. Nijmeijer, M. Wessling, Transport limitations in ion exchange membranes at low salt concentrations, J. Memb. Sci. 346 (2010) 163–171. doi:10.1016/j.memsci.2009.09.033.

[23] P. Długołecki, P. Ogonowski, S.J. Metz, M. Saakes, K. Nijmeijer, M. Wessling, On the resistances of membrane, diffusion boundary layer and double layer in ion exchange membrane transport, J. Memb. Sci. 349 (2010) 369–379. doi:10.1016/j.memsci.2009.11.069.

[24] T. Ho, A. Kurup, T. Davis, J. Hestekin, Wafer Chemistry and Properties for Ion Removal by Wafer Enhanced Electrodeionization, Sep. Sci. Technol. 45 (2010) 433–446. doi:10.1080/01496390903526709.

[25] A.S. Kurup, T. Ho, J. a. Hestekin, Simulation and Optimal Design of Electrodeionization Process: Separation of Multicomponent Electrolyte Solution, Ind. Eng. Chem. Res. 48 (2009) 9268–9277. doi:10.1021/ie801906d.

[26] S. Datta, Y.J. Lin, D.J. Schell, C.S. Millard, S.F. Ahmad, M.P. Henry, *et al.*, Removal of acidic impurities from corn stover hydrolysate liquor by resin wafer based electrodeionization, Ind. Eng. Chem. Res. 52 (2013) 13777–13784. doi:10.1021/ie4017754.

[27] B.G. Rahm, J.T. Bates, L.R. Bertoia, A.E. Galford, D. a. Yoxtheimer, S.J. Riha, Wastewater management and Marcellus Shale gas development: Trends, drivers, and planning implications, J. Environ. Manage. 120 (2013) 105–113. doi:10.1016/j.jenvman.2013.02.029.

[28] W.L. Ellsworth, Injection-Induced Earthquakes, Science (80-.). 341 (2013) 1–7.

[29] W. Gan, C. Frohlich, Gas injection may have triggered earthquakes in the Cogdell oil field, Texas., Proc. Natl. Acad. Sci. U. S. A. 110 (2013) 18786–91. doi:10.1073/pnas.1311316110.

[30] N. van der Elst, H.M. Savage, K.M. Keranen, G.A. Abers, Enhanced Remote Earthquake Triggering at Fluid-Injection Sites in the Midwestern United States, Science (80-.). 341 (2013) 164–167.

[31] H. Meng, C. Peng, S. Song, D. Deng, Electro-regeneration mechanism of ion-exchange resins in electrodeionization, Surf. Rev. Lett. 11 (2004) 599–605.

[32] D.A. Vermaas, E. Guler, M. Saakes, K. Nijmeijer, Theoretical power density from salinity gradients using reverse electrodialysis, Energy Procedia. 20 (2012) 170–184. doi:10.1016/j.egypro.2012.03.018.

[33] B. Freeman, Engineers improve recycling system used in fracking to save water and energy, Membr. Technol. 2013 (2013) 7.

[34] D.J. Miller, X. Huang, H. Li, S. Kasemset, A. Lee, D. Agnihotri, *et al.*, Fouling-resistant membranes for the treatment of flowback water from hydraulic shale fracturing: A pilot study, J. Memb. Sci. 437 (2013) 265–275. doi:10.1016/j.memsci.2013.03.019.

VI. Conclusion

Electrodialysis and Electrodeionization for Novel Solutions for Complex Separations

In this dissertation, electrodialysis (ED) and electrodeionization (EDI) were investigated for use in the recovery of organic acid products using novel ionic liquid solvents. ED and EDI have been used in a wide variety of applications in the chemical industry. The introductory chapter discussed the concepts and motivation for research into ED, EDI, and RED. Chapter 2 divulged greater detail on the use of ED, EDI, and RED as well as the major mathematical theory, state-of-the-art performance, and major researchers in each subject area. In Chapter 3, proof-of-concept experiments for the use of ED with ionic liquids were studied. The results showed that ionic liquid assisted ED successfully transfers organic salts into an ionic liquid phase. With bipolar membranes, organic salts were converted into organic acids which can then be separated from the ionic liquid via flash separation with no loss of ionic liquid solvent. Water contamination was a major issue and had a significant impact on expected power requirements for downstream processing. The power requirements for organic acid purification from ED were determined and the impact of ionic liquids and water on overall product purity was discussed.

Chapter 4 discussed the improvements that EDI and WE-EDI can have on ionic liquid assisted ED and other ED separations where non-aqueous solutions can be useful. Implementation of ion exchange resin wafers resulted in significant improvements over the previous ED study. Though WE-EDI, ionic liquids can be used in ED and EDI separations with power requirements competitive with other separation techniques. Through this research, WE-EDI can allow other organic solvents to be considered for product recovery through reduction of ionic conductivity limitations and improvements of ion transfer rates.

Reverse electrodialysis with Ion exchange Wafers for Improved Power Generation

Salient gradient energy holds tremendous potential for the sustainable production of usable power worldwide. RED and PRO are the leading technologies for power generation from salient gradient energy. PRO generates power through osmotic pressure from separating freshwater and saltwater through a water permeable membrane whereas RED generates power by separating freshwater and saltwater by ion permeable membranes. PRO is limited by fouling, pressure generation, and turbine efficiencies, and RED is limited by fouling, solution conductivity, and system electrical resistance. Currently, PRO and RED boast similar maximum power densities, yet RED is the only technology where pilot operations have been implemented.

Chapter 5 discussed the performance of a carefully designed RED stack for power generation using wafer enhanced electrodeionization (WE-EDI) techniques. Wafers resulted in lower cell resistances as compared to traditional RED techniques. Gross power densities of 0.64 W/m^2 were obtained; however, correcting for the passive current applied during testing lowered the gross power density to 0.29 W/m^2. Accounting for the pumping energy and wafer regeneration resulted in no usable power from experiments, implying that large scale systems would be needed determine if wafer RED could be feasible. Theoretical predictions indicated that application of RED to the hydraulic fracturing industry may provide beneficial power to the industry, reducing the overall energy and cost of the fracking process. In order for RED technologies to be implemented in industry, larger systems must be design which focus on minimizing system resistances which ensuring the maximum voltage potential is maintained.

Future Work

Following the completion of these studies, there exist a multitude of experiments and research investigations that can be pursued in order to further the science created and improved by the research described previously. Figure 1 presents possible research that may be pursued based on the work described in this dissertation. Each topic represents a new research area that can be pursued in the development of improved ED, EDI and RED technology. Several research projects can impact multiple areas as described below.

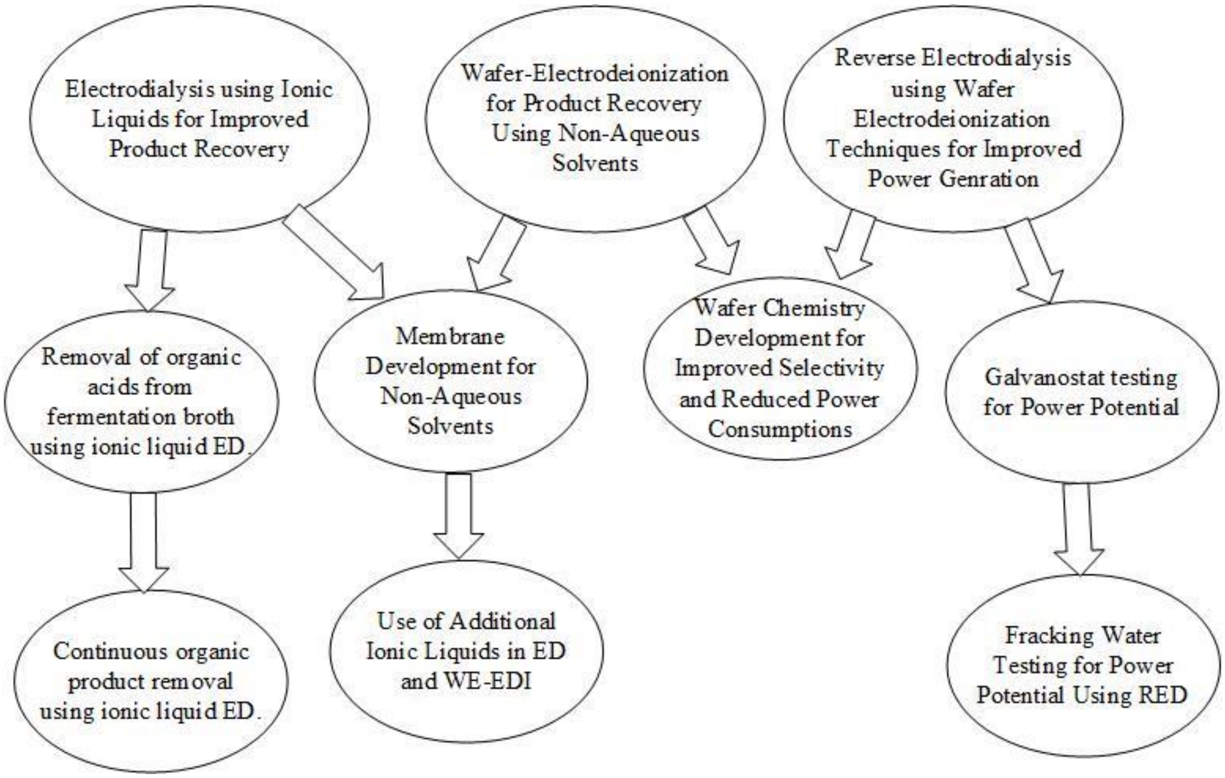

Figure 1. Future outlook of completed research progress. The top ovals indicate the work presented in chapters 3-5. Each oval below this level briefly describes subsequent research projects that can develop as a result of the work accomplished.

Research into the development of membranes specifically designed for ED and EDI in non-aqueous solutions would improve separation efficiencies and broaden the applications these techniques in which they are used. The main limitations caused by use of organic solvents in ED are the reduction of ion mobility and the water co-transport. EDI techniques can solve the issues of ion mobility, yet there still exists the water co-transport. The development of membrane that limit water co-transport would result in higher purity products and greater longevity of organic solvents in ED and EDI. This research could occur through membrane modification of existing ion exchange membranes or by synthesis of purely novel membranes designed for increased interaction with organic solutions.

Improving the research of ionic liquid assisted electrodialysis can occur in several ways. Investigations into different ionic liquids with unique properties may provide greater insight into better solvents for ED and EDI. Ideally, modeling of ionic liquid parameters in a computerized ED cell may allow screening of large quantities of ionic liquids in a short amount of time. Further, running systems with real fermentation broth can result in information concerning selectivity and fouling. Continuous operation of ED, EDI, and product removal would be beneficial in terms of determining ionic liquid longevity and impacts of heating on ED systems.

A study into the development of wafers specifically designed for RED may lead to higher power densities. Current wafer technology requires 1-1.5 V per cell pair to initiate water splitting. Investigations in new wafer chemistries and ion exchange resin may lead to a reduction of required energy for water splitting and enhance the monovalent ion transfer during power production. Additional research into RED could look into determining power potential of wafer RED by means of galvantostat measurements. Previous research in RED looked at manipulation of current densities using a galvanostat and determined power densities through output voltages. Application of this measurement technique may provide additional insight into the potential of wafer enhanced RED for power generation. Finally, research into using real riverwater, seawater, and industrial solutions can provide detail on the effects of fouling and divalent ions on maximum power potential. Fracking solutions would be ideal in that a direct comparison and model for RED systems in the fracking industry can be developed.

Summary

This dissertation described the development of novel solutions to existing industrial problems using ED, EDI, and RED. Ionic assisted ED and EDI is capable of separating organic acid products with separation efficiencies meeting current state-of-the-art standards. Incorporation of wafers in RED decreased system resistances. Unfortunately, power densities obtained did not meet the desired benchmark of 5 W/m^2, an indication that much more research must be done. Limitations to this work included the energy required for water splitting and the system resistances continue to plague the power potential of RED systems. Through the work described, insight into the performance of non-aqueous solutions in electrochemical systems was gained.