

ON DEMAND ELECTROCHEMICAL PRODUCTION OF REAGENTS TO MINIMIZE RESUPPLY OF EXPENDABLES

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ABSTRACT

The electrosynthesis of expendable reagents including acids, bases, and oxidants from simple salts or salt mixtures has been demonstrated using a variety of electrochemical cells. A five chambered electrodiolytic water splitting (EDWS) cell with bipolar membranes was utilized to efficiently convert sodium sulfate, sodium chloride, potassium nitrate, and potassium chloride to conjugate acids and bases. With the same cell, selective segregation of cations and anions from mixed salt solutions occurred, resulting in relatively pure acids and bases. These results suggest that pure acids and bases can be produced from composite spacecraft brines. Chemical oxidants such as sodium and ammonium persulfate were also synthesized with high current efficiencies by the electrooxidation of salts and acids in a two chambered electrochemical cell. This demonstration of the electrosynthesis of useful reagents from simple and mixed salts provides opportunities to eliminate expendables and bring inorganic material balances nearer to closure in future manned space missions. The current technology is capable of producing reagents suitable for the pretreatment of urine, control of pH and nutrient levels in bioreactor and hydroponics solutions, hydrolysis of biomass, and treatment of acidic or basic incinerator exhaust gases.

INTRODUCTION

The development of the next generation of Advanced Life Support System (ALSS) technology will focus on reductions of size and weight, minimization of power usage, and most importantly, the elimination of expendables. Ideally, such systems will need only energy to provide life support resources within a spacecraft. Strong acids and bases, and oxidizers are examples of expendables required for routine ALSS

operation and scientific experimentation aboard the International Space Station (ISS). UMPQUA Research Company has demonstrated novel methods for the production of expendable reagents such as acids, bases, and oxidants by membrane based electrochemical processes using simple salts and electrical energy. Hydrochloric and sulfuric acids, sodium and potassium hydroxides, and oxidizers such as peroxydisulfuric acid, sodium persulfate, and ammonium persulfate are expendable reagents that have been synthesized in this manner. These reagents are applicable to current life support processes such as urine pretreatment and future ALSS processes such as biomass hydrolysis¹ and hydrogen peroxide²⁻⁴ generation. Importantly, the capability for "on demand" reagent production can mitigate risks associated with storage of dangerous chemicals, and provide the basis for separation and reuse of salts produced by future ALSS technologies that will be required to close the material balance during long term manned space missions.

Two different electrochemical cells were utilized to efficiently generate a multiplicity of acids, bases, and chemical oxidizers from salt solutions. The electrodiolytic water splitting (EDWS) cell utilizes cation, anion, and bipolar membranes in a multichambered arrangement. Water is electrodiolytically split into hydronium and hydroxide ions which recombine with counter ions that have been separated from the salt solution to form acids and bases. Cation and anion membranes mediate the separation of counter ions, while bipolar membranes are the basis for efficient, electrodiolytic water splitting. The electrooxidation cell consists of anode and cathode compartments separated by a hydrogen ion conducting membrane. This design separates the cell into two chambers and prevents the reduction of newly formed oxidant species at the cathode. A variety of electrodes, membranes, and operating conditions were investigated for both cells, and

their performance characterized.

Acids, bases, and oxidants were efficiently synthesized in the two electrochemical cells. Hydrochloric, sulfuric, and nitric acids were formed from NaCl, Na₂SO₄, and KNO₃ salt solutions, respectively. Sodium hydroxide was formed from NaCl and Na₂SO₄ salt solutions, while potassium hydroxide was formed from KCl and KNO₃ salt solutions. Similar concentrations of acids and bases were also produced from mixed salt solutions that were designed to represent ALSS brines such as would be generated by urine processing. The electrooxidation cell produced various persulfate (S₂O₈⁼) salts starting from ammonium sulfate, sulfuric acid, and a mixture of sodium sulfate and sulfuric acid precursors. The currently accepted method of urine pretreatment utilizes S₂O₈⁼ as a strong oxidant for sterilization.⁵ These results demonstrate the efficacy of producing acids, bases, and strong oxidants from simple salt solutions. In addition, by changes in the electrochemical cell configuration and the starting salts, many other reagents can be produced.

ELECTRODIALYTIC CELL WITH BIPOLAR MEMBRANES

BIPOLAR MEMBRANES

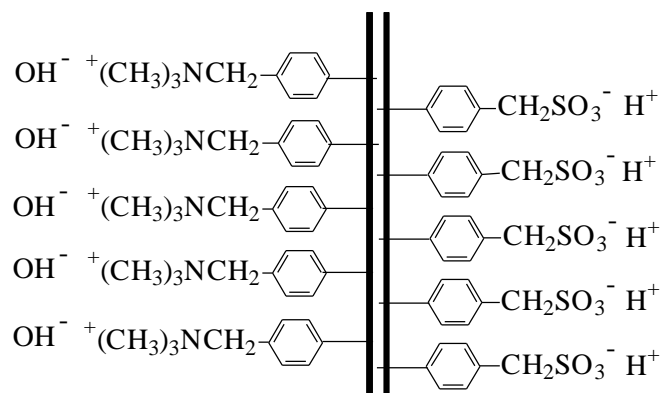


Figure 1. Generalized Bipolar Membrane Structure.

The efficiency of the EDWS cell depends on the unique properties of bipolar membranes to separate hydronium and hydroxide ions. As the name suggests, such membranes contain both anion and cation functionality. Figure 1 represents a typical bipolar membrane in which sulfonic acid groups fill one side of the membrane and quaternary amines the other. When these functional groups are aligned with the external electric field, hydroxide and hydronium ions are continuously transferred towards the anode and cathode, respectively. Dissociation of water within the polymeric matrix provides a continuous source of ions by the reaction shown in Eq.1,



Since ions continually move into chambers adjacent to the bipolar membrane, ionization reactions within the bipolar membrane are required to maintain the ionic current. Water that is lost due to the electrodiolytic transfer of these ions out of the bipolar membrane is continuously replaced by water that readily diffuses through membrane. The production of hydroxide and hydronium ions by migration following dissociation requires much less energy than is needed to produce the same ionic flux by the direct electrolysis of water.

CELL CONFIGURATION

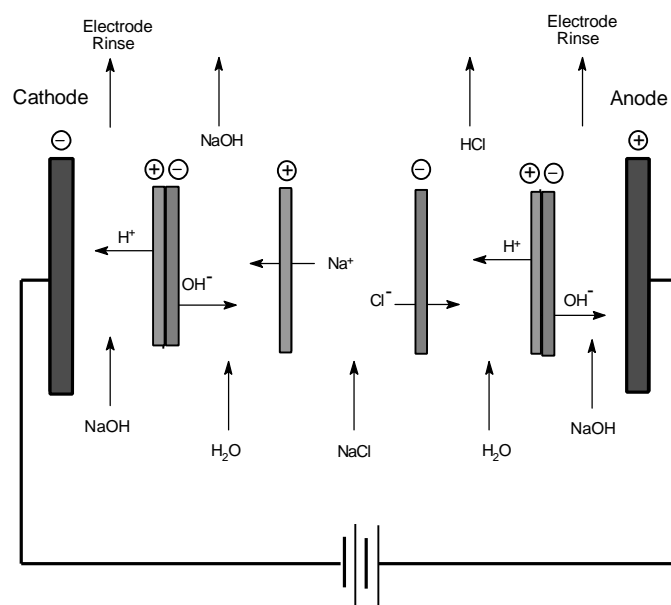


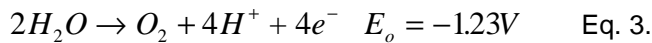
Figure 2. Five Compartment Electrodiolytic Water Splitting (EDWS) Cell for Acid and Base Production.

The production of strong acids and bases from salts in the EDWS cell is illustrated schematically in Figure 2.⁶ The five compartments of this cell from left to right are: 1) an electrode rinse compartment formed between the cathode and the first bipolar membrane; 2) a base stream compartment formed between the first bipolar membrane and a cation exchange membrane; 3) a salt stream compartment formed between two cation exchange membranes; 4) an acid stream compartment formed between an anion exchange membrane and the second bipolar membrane, and; 5) a second electrode rinse compartment formed between the second bipolar membrane and the anode. During separation of sodium chloride, anions and cations move in opposite directions through different membranes to form hydrochloric acid and sodium hydroxide.

Upon application of the electric field, sodium and hydronium ions move towards the cathode through the cation exchange membrane and the cation half of the bipolar membrane. Charge balance is maintained by the flow of chloride and hydroxide ions in the opposite

direction. The movement of these ions forms sodium hydroxide and hydrochloric acid in the base and acid stream compartments, respectively. To complete the circuit, hydronium and hydroxide ions also move into the left and right hand electrode rinse streams, respectively. Excluding electrode reactions and loss of ions through membranes, the net result of the flow of two moles of charge through the cell is the creation of one mole of acid and one mole of base. In addition, one mole of sodium chloride disappears and one mole of water is transferred from the bipolar membrane to the electrode rinse solution. The transfer of water is reversible due to the high permeability of water through the bipolar membranes.

Parasitic membrane processes that can decrease the current efficiency include: 1) the transfer of sodium hydroxide across the first bipolar membrane or the cation exchange membrane; 2) the transfer of hydrochloric acid across the second bipolar membrane or the anion exchange membrane; 3) the transfer of chloride ions across the cation exchange membrane, and; 4) the transfer of sodium ions across the anion exchange membrane. Potential unwanted electrode reactions are given by Eq. 2 and 3.



These reactions waste energy and produce unwanted hydrogen and oxygen. The use of a sodium hydroxide electrode rinse inhibits the production of hydrogen gas. In practice, the number of compartments in the EDWS cell shown in Figure 2 can be increased in increments of three with common feeds to salt, acid, and base streams. This approach reduces the relative importance of electrode reactions, since additional acid and base compartments are formed; however as the electrode separation increases, higher voltages are needed to achieve equivalent current, and eventually, the electrode potentials cause the reactions shown in Eq. 2 and 3 to predominate.

ELECTRODES AND MEMBRANES

Platinum plated titanium and Ebonex[®] were evaluated as electro dialysis electrodes. Ebonex[®] is a substoichiometric titania (Ti₄O₇) that is highly conductive, relatively inert, and exhibits high overpotentials for evolution of oxygen and hydrogen gas, which helps to reduce parasitic electrode processes. The platinum plated titanium electrode was found to be the most energetically efficient electrode for the EDWS cell.

Two bipolar membranes were tested in the five compartment cell, the Tokuyama Soda BP-1 and Aqualytics BP membranes. Only the Aqualytics membrane generated significant acid and base

concentrations. In each case, the five compartment EDWS cell configuration was assembled with two Aqualytics bipolar membranes and an Ionics AR204SXZR412 anion membrane. Three cation membranes were investigated including Nafion[®] 117, CR67 HMR, and CR61 CMP. The Ionics CR67 HMR cation membrane provided the best stability, selectivity, and efficiency for the production of acids and bases with the five chambered EDWS cell.

The resulting five compartment electro dialytic cell configuration consists of: 2 platinum plated titanium electrodes, 2 Aqualytics bipolar membranes, 1 Ionics CR67 HMR cation membrane, and 1 Ionics AR204SXZR412 anion membrane.

ASSEMBLY OF EDWS CELL COMPONENTS

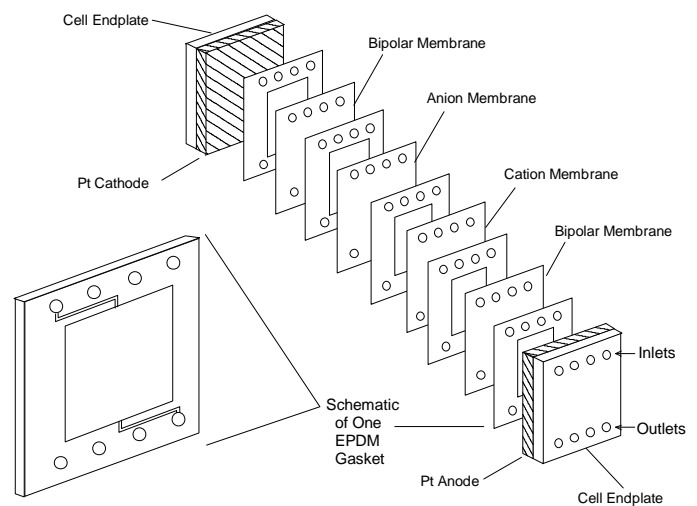


Figure 3: Schematic of Preassembled EDWS Cell Components.

A schematic of the EDWS cell components is shown in Figure 3. The five compartments are formed from a sequence of four membranes located between two electrodes. The key elements include from left to right: an endplate, the platinized titanium cathode, an electrode rinse chamber, a bipolar membrane, the base stream compartment, a cation exchange membrane, the salt stream compartment, an anion exchange membrane, the acid stream compartment, a second bipolar membrane, a second common electrode rinse compartment, the platinized titanium anode, and a second endplate. A cutout in an ethylene propylene rubber (EPDM) gasket forms each compartment. The endplates extend beyond the gasketed area. Bolts through the endplates holds the cell together. Access to the internal flow is made at one endplate through tubing connectors. Each stream is recirculated through the cell from separate reservoirs, with the exception of the electrode rinse stream which is combined in a common reservoir and then recirculated.

OPERATION OF THE EDWS CELL

Four streams (i.e., acid, base, salt, and electrode rinse streams) are recirculated through the five compartments of the EDWS cell. The recirculating system consists of a four channel peristaltic pump, connecting tubing, and four reservoirs. Each reservoir serves as a calibrated volumetric to determine net gain or loss of water due to osmotic and electroosmotic water flux. At the start of each run, the acid, base, and salt streams contained 500 mL of 0.1 M salt solution to reduce the initial resistance of these chambers and the electrode rinse reservoir contained 400 mL of 1.0 M sodium hydroxide. The concentrations of acid and base were determined by pH electrodes in each reservoir. These sensors were situated between the inlet at the top and outlet at the bottom of each reservoir. The conductivity of the salt stream was also monitored to determine loss of ions from the salt stream.

All flow paths were initially filled with the appropriate solution and purged of gas. Due to the permeability of water through the membranes that separate each compartment, the water flux between each chamber was also initially fixed by establishing a balance between hydrostatic and osmotic pressures. During operation, electroosmosis complicates water flux and some adjustment of hydrostatic pressure is needed.

After voltage is applied to the EDWS cell, the synthesis of acids and bases is initiated. The power supply was operated in a constant current mode so that the voltage was adjusted to maintain one of three current densities, 7.32, 9.47, or 11.63 mA/cm². The active area of all membranes was 232 cm². The pH of the acid and base streams, and the conductivity of the salt stream were recorded during each electro dialysis run. In addition, the volumes of each reservoir were periodically monitored and the gas evolved from the anode determined.

EDWS RESULTS

A wide variety of salt solutions were investigated using the five compartment EDWS cell. The electro dialytic production of acids and bases from salt solutions, including: sodium chloride, sodium sulfate, potassium chloride, and potassium nitrate, was investigated for several different membrane - electrode combinations. Such salts may be carried aboard future space vehicles or habitats or are expected to be available as part of ALSS regenerative technology including bioreactor effluents and brines. In each case, the time dependent production of acid and base was evaluated as a function of current density and salt concentration.

PRODUCTION OF KOH AND HCL FROM KCl

The use of a 2 M KCl to produce a KOH base stream and a HCl acid stream is representative of the

separation of simple salts, although the highest concentration of base was generated with KCl. The pH of acid and base streams as a function of time are shown in Figure 4. The molar concentrations of acid and base are shown in Figure 5. Both acid and base concentrations rose at a constant rate for the first 250 minutes. At longer electro dialysis times, production rates fall due to the rising concentrations of both streams. As the concentration rises, all ions must travel against an increasing concentration gradient, and loss of acid and base by diffusion down this concentration gradient becomes more pronounced. After 300 minutes, 1 M KOH and 2.5 M HCl solutions were produced. The 11.63 mA/cm² current density was reached at ~5.6 V. Gas was generated in the anode compartment at 32 mL/min. The energies needed to produce 2.0 M HCl and 1.0 M KOH were 288.4 kJ/mole and 304.4 kJ/mole, respectively. A final HCl

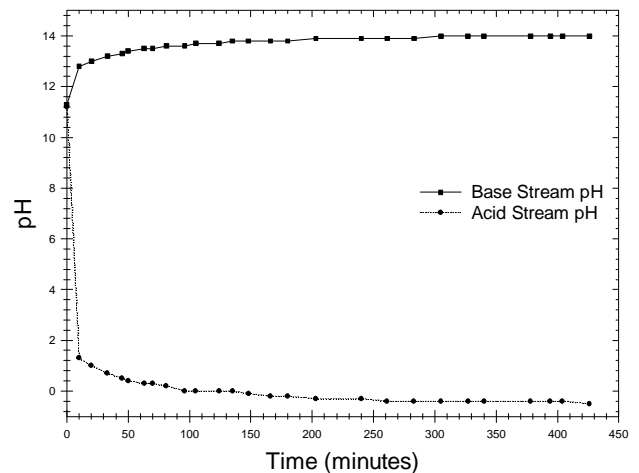


Figure 4: pH as a Function of Time for Electro dialytic Separation of 2 M KCl.

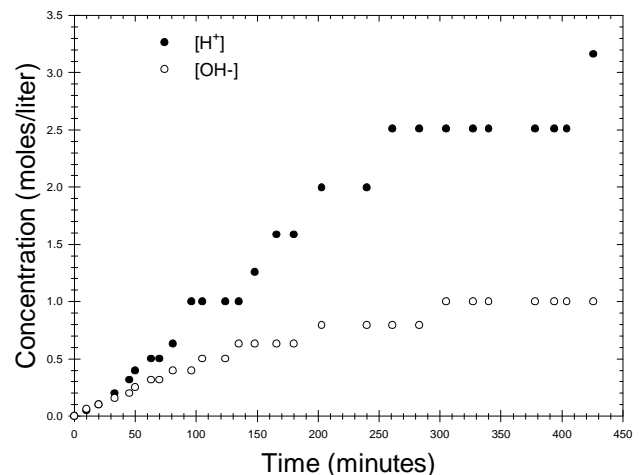


Figure 5: Acid and Base Production from 2 M KCl.

concentration of 3.16 M was reached, illustrating the capability to generate an acid solution in which the concentration is higher than the concentration of the salt

solution. The jump at 400 minutes from 2.5 to 3.16 M HCl is due to the poor resolution of the pH sensor, since this represents a change from -0.4 to -0.5 pH units.

RESULTS FOR NaCl, KNO₃, and Na₂SO₄.

The production of HCl and NaOH from 1 M and 2 M NaCl are shown in Figures 6 and 7, respectively. In both cases, the current density was 11.63 mA/cm² at 5.3 V. A 1 M HCl concentration was produced from 1 M NaCl after 170 minutes of operation. At this point in the electro dialysis run, the specific energy required to create HCl was 240.2 kJ/mole. After an additional 260 minutes, 2 M HCl was generated, requiring 1210 kJ/mole. The gas generation rate was 40 mL/min. The production rate for HCl was greater when 1 M NaCl was replaced by 2 M NaCl. 1 M and 2 M HCl concentrations were reached in 110 and 220 minutes, respectively. A final pH of 2.5 was reached in 311 minutes, requiring 303.7 kJ/mole. The gas generation rate was identical to that of the 1 M NaCl solution.

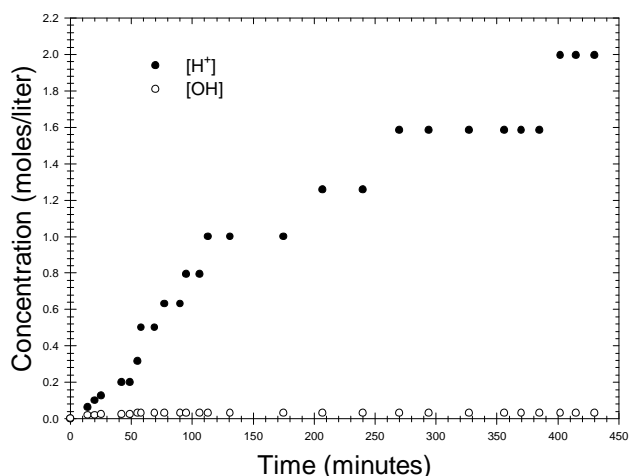


Figure 6: Acid and Base Production from 1 M NaCl.

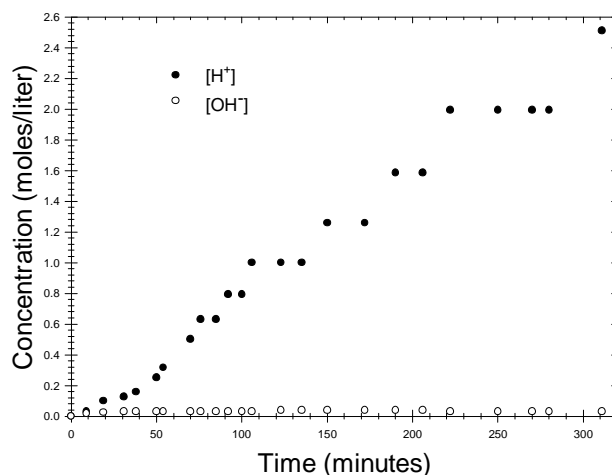


Figure 7: Acid and Base Production from 2 M NaCl.

These data indicate that, as the salt concentration increases, the concentration of acid and the production rate also increases, while the specific energy required to produce the acid decreases. These results reflect the fact that the acid production rate depends on both the sum of electric field driven ionic motion and the diffusion loss of acid into adjacent chambers. Since chloride ions travel from salt to acid streams along a concentration gradient, the magnitude of this gradient determines the ionic flux at a constant electric field strength. Consequently, greater acid production rates and higher achievable acid concentrations occur for higher precursor salt solution concentrations. Since the sign and magnitude of the concentration gradient changes during electro dialysis (i.e., an initially high positive value followed by an ending negative value), the limiting acid concentration is determined by a balance between the maximum differential concentration that can be achieved by the electric field and the loss of acid through the adjacent membranes.

A comparison between the molar ratio of NaOH to HCl production from NaCl to that of KOH to HCl production from KCl indicated that a significantly lower relative concentration of NaOH was produced. The higher fractional generation of base from KCl, (i.e., NaOH/HCl = 2 % versus KOH/HCl = 40 %) indicated that the permeation of KOH through the bipolar and cation membranes surrounding the base stream chamber was less than the permeation of NaOH. This behavior has significant consequences when mixed salt streams are processed, since the permeability and selectivity of all membranes towards all ions and salts will determine overall process efficiency.

The generation of nitric acid was then investigated using a 2 M KNO₃. A voltage of 5.5 V produced a current density of 11.63 mA/cm². The resulting concentrations of HNO₃ and KOH are shown in Figure 8. The relative concentrations of acid and base were similar to those generated by 2 M KCl. The

generation of 1 M HNO_3 acid corresponded to the production of 0.32 M KOH (i.e., 32 %). The acid stream

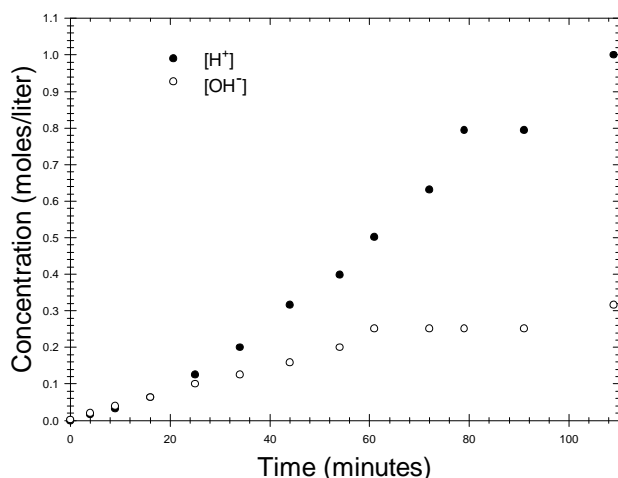


Figure 8: Acid and Base Production from 2 M KNO_3 .

volume changes, however, were significantly greater with a loss of 350 mL of the original 500 mL volume after only 110 minutes. As a result, the specific energy requirements were much larger at 647.5 kJ/mole. Evidently, the balance of electroosmotic and osmotic forces changed due to differences in ionic mobility of NO_3^- and Cl^- . The gas generation rate was 34 mL/min. Nevertheless, the use of KNO_3 demonstrated that an important reagent, HNO_3 can be produced by this technique.

The production of a diprotic acid, H_2SO_4 , from a Na_2SO_4 solution was investigated for a salt stream concentration of 0.5 M Na_2SO_4 . The acid and base streams were initially filled with a 0.1 M Na_2SO_4 solution to decrease the cell resistance, and the electrode rinse remained 0.1 M NaOH . The concentration of hydronium and hydroxide ions as a function of time is shown in Figure 9. The EDWS cell was operated at 5.1 V with a current density of 11.63 mA/cm². The gas generation rate was 36 mL/min. The production of NaOH was very low, and as in the case for NaCl , indicates the reduced permeability of the CR67 and bipolar membranes to NaOH .

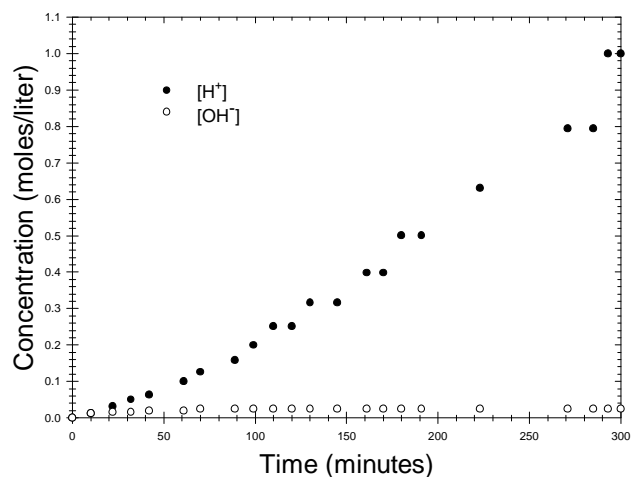


Figure 9: Acid and Base Production from 1M Na_2SO_4 .

The specific energy required to produce a 1 M H_2SO_4 solution was 660.8 kJ/mole. The increase in specific energy compared to that required in the formation of HCl was due to the relatively low permeability of $\text{SO}_4^{=}$ through the anion membrane. Due to the greater charge and larger size of the $\text{SO}_4^{=}$ anions, diffusion rates through the membrane are less than for smaller monovalent anions such as Cl^- . Additionally, the transport of a divalent anion through an anion exchange membrane containing monovalent quaternary amine functional groups requires that each $\text{SO}_4^{=}$ be associated with two quaternary amine groups in diffusing through the membrane. As a result, the overall permeation rate is less than is the case for Cl^- . Since the permeation rate is reduced, the production rate for H_2SO_4 is much less than for HCl . Because the energy requirements to produce a mole of acid represents the balance between productive versus unproductive ionic migrations, decreased permeation rates also favor competitive processes which reduce the formation of H_2SO_4 and increase energy usage.

SEPARATION OF MIXED SALT STREAMS

The selective separation of mixed salt streams is one of the ultimate goals of this technology, since mixed brines will be a major chemical resource in future ALSS technology. The EDWS cell can be reconfigured to purify and/or concentrate acids and bases, regenerate flue gas scrubber solutions, and separate and concentrate mixtures of salts with acids and bases.⁶⁻¹¹ All of these applications have potential to be incorporated into future ALS systems for reduction in the use of expendables. Typical anion and cation exchange membranes exhibit strong selectivity for transport of monovalent over divalent ions, as well as selectivity between similarly charged ionic species. For example, a

strong base anion exchange membrane transports chloride over sulfate by a factor of ~200, while a strong acid cation exchange membrane selectively transports sodium over magnesium by a factor of ~10.⁷ Utilization of this selectivity to separate mixed salt solutions would demonstrate the applicability of this technology to extract useful products from wastes including real solutions such as VCD or RO brines. For this reason, two mixed salt streams were investigated to demonstrate selective separation of ionic constituents by the EDWS cell membranes. The first mixed salt solution contained 0.4 M sodium acetate (NaCH_3CO_2) and 1 M NaCl. This combination was designed to represent the case in which organic and inorganic monovalent anions must be separated. The second mixed salt solution contained 1.25 M NaCl, 0.2 M KCl, 0.008 M K_3PO_4 , and 0.16 M Na_2SO_4 . This solution was designed to represent a brine produced from urine, containing multiple ionic constituents (i.e. metabolic salts) common to urine. Typical organic impurities were omitted for simplicity.

1 M NaCl AND 0.4 M Sodium Acetate

The production of acid and base from a 0.4 M sodium acetate (NaCH_3CO_2) and 1 M NaCl mixed salt solution is shown in Figure 10. A current density of 11.63 mA/cm^2 was produced at 5.5 V. A specific energy of 540.2 kJ/mole was needed to produce an acid stream pH of 2.5 and a higher relative hydroxide concentration (i.e., 15.8 %) than previously obtained with NaCl. Gas was generated at 36 mL/min . More importantly with regard to separation, the 2.5 M acid solution contained 0.083 M acetic acid, indicating a ten-fold concentration preference for chloride over acetate.

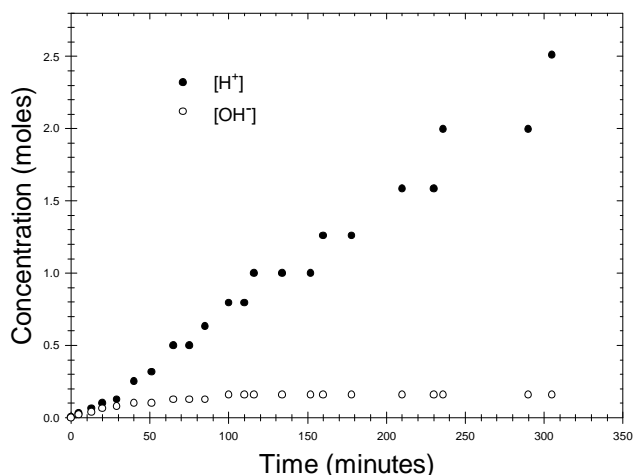


Figure 10: Acid and Base Production from 1 M NaCl plus 0.4 M Sodium Acetate.

SIMULATED COMPOSITE URINE BRINE

The production of acid and base from a 1.25 M NaCl, 0.2 M KCl, 0.008 M K_3PO_4 , and 0.16 M Na_2SO_4 mixed salt solution is shown in Figure 11. A current

density of 11.63 mA/cm^2 at 5.3 V resulted in a specific energy requirement of 614.1 kJ/mole and a gas generation rate of 34 mL/min . The 1.6 M acid solution contained 98.2 mole % Cl^- , 1.75 mole % SO_4^{2-} , and 0.05 mole % PO_4^{3-} . This represents a fifty-fold concentration preference of chloride over sulfate and a ten-fold concentration preference of chloride over phosphate.

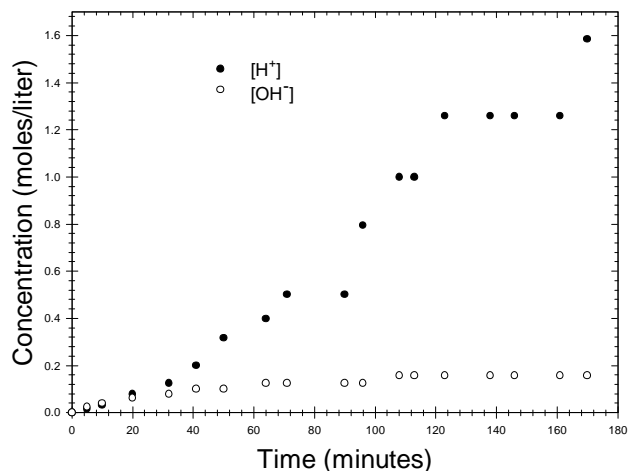


Figure 11: Acid and Base Production from 1.25 M NaCl, 0.2 M KCl, 0.008 M K_3PO_4 , and 0.16 M Na_2SO_4 .

The 0.16 M base solution contained 69.9 mole % Na^+ and 30.1 mole % K^+ . This represents a 2.4:1 concentration preference of potassium over sodium. The molar base production represented 25.9 % of the acid production. These results indicate a moderate selectivity for specific ions in impure brines that can be used to generate more pure acid and base streams. This also indicates, that with more selective membranes, the separation of specific components from composite water may be accomplished using electroalytic water splitting technology.

TWO COMPARTMENT ELECTROOXIDATION CELL

To investigate the electrochemical production of oxidants, a normal electrolysis cell was modified by the insertion of a Nafion[®] membrane between the cathode and anode to inhibit the reduction of newly formed persulfate, while maintaining a conductive pathway between electrodes. Two versions of the two chamber electrooxidation cell were utilized to evaluate platinum foil, carbon, and Ebonex[®] electrodes for the production of various persulfates. The cells differed primarily in size. Ebonex[®] and porous carbon electrodes were tested in the larger cell. Platinum foil electrodes were tested in the smaller cell. A schematic of the two chambered electrooxidation cell is shown in Figure 12. This cell limited the turbulent transfer of the freshly formed persulfate within the electrolysis chamber while maintaining low cell resistance to the passage of hydronium ions.

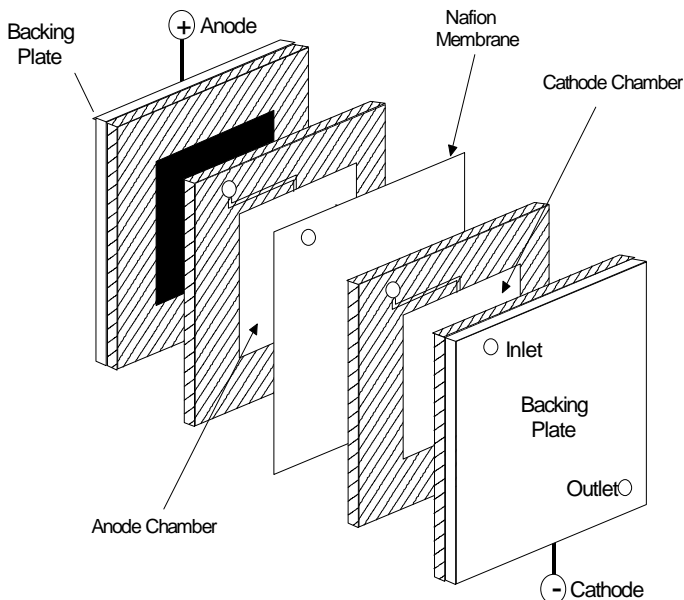


Figure 12: Electrooxidation Cell with Anode and Cathode Chambers.

ELECTROOXIDATION CELL OPERATION

Operation of the electrooxidation cell utilized between 100 and 150 mL of solution that was continuously recirculated through the two chambers from a common reservoir. Solutions of sulfuric acid, ammonium sulfate, and a mixture of sodium sulfate and sulfuric acid were oxidized at voltages between 4 and 5 V. The cell was operated at a constant voltage and current was monitored. Current densities between 2 and 194 mA/cm² were produced. During each electrooxidation run, samples were withdrawn periodically to determine the persulfate concentration. The presence of persulfate in the electrolysis solution was determined by mixing a small aliquot into a buffered KI solution. Under these conditions, iodide is oxidized to iodine, the iodine is then determined by titration with sodium thiosulfate.¹²

ELECTROOXIDATION RESULTS

A 4.5 M H₂SO₄ solution was electrooxidized at 5 V producing a current density of 133 mA/cm². The ammonium persulfate (H₂S₂O₈) concentration and current efficiency as functions of time are shown in Figure 13. A 0.07 M (NH₄)₂S₂O₈ solution was produced with a current efficiency of ~50%. The current efficiency decreased with time, probably due to the increase in persulfate concentration and the consequent increase in persulfate reduction reactions.

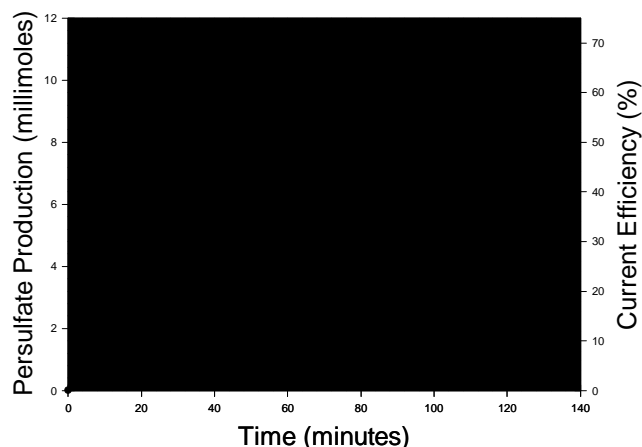


Figure 13: Production of H₂S₂O₈ from 4.5 M H₂SO₄ in the Two Chamber Electrolysis Cell.

A mixture of 2.85 M Na₂SO₄ and 3 M H₂SO₄ was then electrooxidized at 5.06 V with a current density of 170 mA/cm². A 0.56 M Na₂S₂O₈ solution was produced. The current efficiency at the beginning of the electrolysis run was close to 100% and fell to 64% towards the end of the run. These results are shown in Figure 14. These data clearly indicate that, from various sulfate salts, a variety of persulfate salts can be electrochemically generated.

CONCLUSION

The feasibility of producing expendable reagents such as strong acids, bases, and oxidants from simple salts or mixtures of salts using electrical energy has been demonstrated. The core technology, which allows the efficient conversion of salts to their conjugate acids and bases utilizes a bipolar membrane based electro-dialytic water splitting (EDWS) cell. With strong acids prepared by this method, strong oxidizers can then be produced in a membrane based, two chambered electrooxidation cell. The combined technology will mitigate safety issues associated with handling and storage of these dangerous chemicals since only simple salts and electrical power are needed to produce each reagent. The advanced development of these technologies will provide the basis for separation and reuse of chemical resources produced by future ALSS technologies. The use of simple and mixed salts recovered from waste streams provides an opportunity to bring inorganic material balances nearer to closure. This technology will become more significant as missions move further away from low earth orbit and resupply penalties become progressively more restrictive. The onboard production of reagents from simple materials will make an important contribution toward minimizing this limitation.

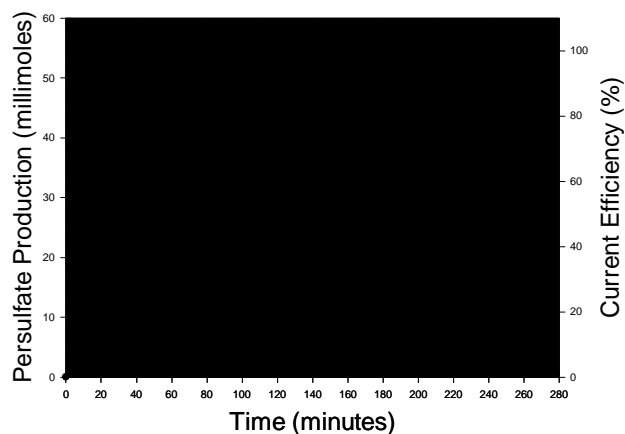


Figure 14: Production of $\text{Na}_2\text{S}_2\text{O}_8$ from 2.85 M $(\text{NH}_4)_2\text{SO}_4$ and 3M H_2SO_4 Solution.

The development of the next generation of advanced life support technology will focus on reductions of size and weight, minimization of power usage, and most importantly, the elimination of expendables. Ideally, such systems will need only energy to provide life support resources within a spacecraft. Currently, strong acids, strong bases, and oxidizers are required for routine ALSS operation and scientific experimentation. Future ALSS technologies will be designed to improve recycling of fixed spacecraft chemical resources. Such resources already include brines, a rich source of salts. In the near future, chemical resources will be expanded to include inedible biomass, which will be further processed to carbon dioxide, water vapor, and ash. UMPQUA has successfully demonstrated the electrochemical production of useful reagents using simple salts and electrical energy. In addition, the initial ground work has been laid to recycle chemical resources such as mixed salt solutions.

ACKNOWLEDGMENT.

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BIBLIOGRAPHY

1. Figueroa, C., and Akse, J. R., Conversion of Inedible Plant Biomass to Pumpable Slurries, Final Report NASA Contract NAS2-97038, July 1997.
2. Akse, J.R., Atwater, J.E., Schussel, L.J., Thompson, J.O., Garmon, F., Verostko, C.E., and Flynn, M., Electrochemical Generation of Hydrogen Peroxide for Aqueous Phase Catalytic Oxidation, SAE Technical Paper Series No. 961521, presented at

- 26th International Conference on Environmental Systems, Monterey, CA, July 8-11, 1996.
3. Akse, J.R., Atwater, J.E., Schussel, L.J., and Thompson, J.O., Electrochemically Generated, Hydrogen Peroxide Boosted Aqueous Phase Catalytic Oxidation, Final Report NASA Contract NAS9-19281, 1995.
4. Akse, J.R., Figueroa, C., Wisely, M.T., Lunsford, T.D., and Gill, H., Electrochemically Generated, Hydrogen Peroxide Boosted Aqueous Phase Catalytic Oxidation, Final Report NASA Contract NAS2-14317, 1998.
5. Huff, T.L., Danford, M.D., Walsh, D.W., and Rodgers, E.B., Results of Microbiological and Corrosion Analysis of Three Urine Pretreatment Regimes with Titanium-6Al-4V, SAE Technical Paper 932046, presented at the 23rd International Conference on Environmental Systems, Colorado Springs, Colorado, July 1993.
6. Mani, K.N., Electrodialysis water splitting technology, *J. Membrane Sci.*, **58**, 117-138, 1991.
7. Audinos, R., Nassr-Allah, A., Alvarez, J.R., Andres, J.L., and Alvarez, R., Electrodialysis in the separation of dilute aqueous solutions of sulfuric and nitric acids, *J. Membrane Sci.*, **76**, 147-156, 1991
8. Bolton, H.R., Use of Bipolar Membranes for Ion Exchange Resin Regenerant Production, *J. Chem Tech. Biotechnol.*, **54**, 341-347, 1992.
9. Chian, Y.C., Chlanda, F.P., and Mani, K.N., Bipolar membranes for purification of acids and bases, *J. Membrane Sci.*, **61**, 239-252, 1991.
11. Strathmann, H., Bauer, B., and Rapp, H.J., Better bipolar membranes, *Chemtech*, 17-24, June, 1993.
12. Williams, J.W., *Handbook of anion determinations*, Butterworths, Boston, 1979.