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Candidate membranes for the electrochemical salt-splitting of Sodium Sulfate

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Abstract This work examines the properties of selected cation and anion exchange membranes for use in the electrochemical separation of sodium sulfate into sodium hydroxide and sulfuric acid. The effect of membrane type, electrolyte composition and ion exchange membrane thickness on the current efficiency was investigated. A decrease in current efficiency was observed due to ion migration under the influence of the electric field, and, to a lesser extent, diffusional losses. Increasing the membrane thickness improves the current efficiency at the cost of higher power due to the higher cell potential.

Keywords Electrodialysis · Electrolysis · Ion exchange membranes · Salt-splitting · Sodium sulfate

1 Introduction

Black liquor, a byproduct of pulp mills, is combusted for the energy contained in its organic components. However, black liquor also contains inorganic components, such as sodium sulfate (Na_2SO_4), which is recovered from the boiler flue gas by an electrostatic precipitator [1]. In addition to black liquor combustion, preparation of bleaching chemicals, such as chlorine dioxide, may also produce Na_2SO_4 as a byproduct. The common method of Na_2SO_4 disposal is by sewering. Environmental concerns

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regarding the sewering of this waste have led to prohibitions against this practice in some British Columbian and Southern U.S. rivers [2]. The current work examines anion and cation membranes for use in an electrochemical cell that would allow recycle of the sodium sulfate waste.

An electrochemical cell can be used to separate the dissolved ions that make up the salt (Na^+ and SO_4^{2-}) and produce sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) by the phenomena of water electrolysis and electrochemical ion migration as well as the counter-ion to co-ion selective property of ion exchange membranes. A three compartment reactor can be considered for the efficient production of sulphuric acid and sodium hydroxide, as shown in Fig. 1. A center compartment, with no electrodes, is used to provide the feed of fresh sodium sulphate solution. The central feed chamber is separated from the cathode (negative electrode) by a cation exchange membrane (CEM) and separated from the anode (positive electrode) by an anion exchange membrane (AEM). Under the influence of an electric field, cations (H^+, Na^+) migrate toward the cathode (the negative electrode) and anions (OH^-, HSO_4^-, SO_4^{2-}) migrate toward the anode (the positive electrode). In the cathode chamber water is reduced; OH^- and H_2 are produced. Na^+ migrates across the CEM into the cathode chamber to neutralize the charge and NaOH is formed. The diffusive flux of ions through a membrane is described by the Nernst–Planck Equation, given by Eq. 1.
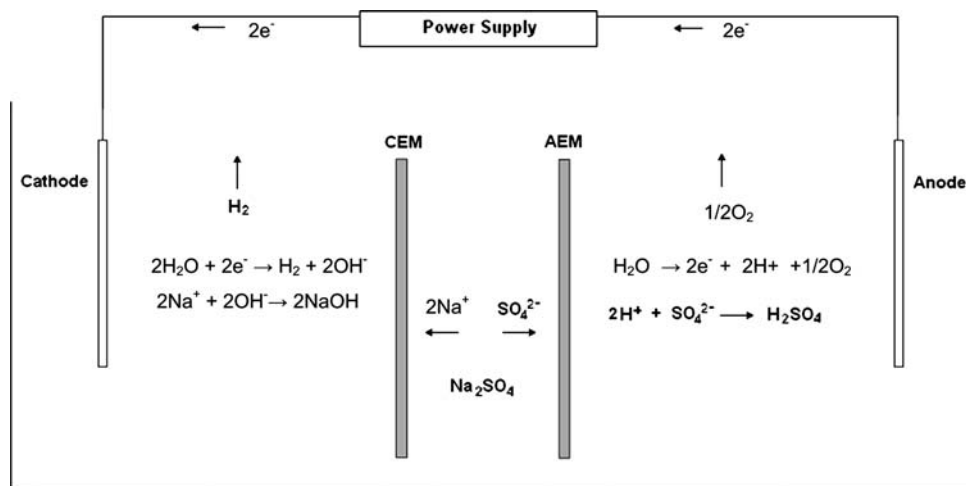
$$J_i = -D_i \frac{\partial C_i}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi}{\partial x} \qquad (1)$$

where J_i is the flux of species i, D_i is the diffusion coefficient, C_i is the concentration, x is distance, z_i is the charge, F is Faraday's constant, R is the ideal gas constant, T is the temperature, and ϕ is the potential. The role of the

Fig. 1 Schematic of sodium sulfate salt-splitting in a three compartment electrochemical cell

CEM is to prevent OH⁻ from migrating to the anode and SO_4^{2-} from diffusing into the cathode compartment. In the anode chamber water is oxidized; H⁺ and O_2 are formed.

The fundamentals of Na_2SO_4 salt-splitting have previously been discussed [3–13]. The role of the AEM is to prevent H⁺ from migrating to the cathode and neutralizing the OH⁻ product. It also prevents Na⁺ from diffusing to the anode compartment. As SO_4^{2-} enters the anode chamber, sulfuric acid is formed.

This work examines the properties of specific, commercially available anion and cation exchange membranes. The crucial element of this work is the performance of the ion exchange membranes, especially their ability to inhibit the diffusion of the oppositely charged ions. Counter-ion rejection, especially at high concentrations, is difficult. The overall cell performance and system economics hinge on the selectivity of the cation and anion exchange membranes. This work will examine the performance of two types of CEMs, styrene divinylbenzene and substituted perfluorinated based polymers. A variety of AEMs, based on styrene divinylbenzene polymers, were also evaluated.

2 Experimental details

Membrane evaluation was performed at room temperature using a modified QuickCell QC200, dual cell setup from Astris Energi Inc. (Mississauga, Ontario). A center compartment constructed of translucent polycarbonate was added between the two factory compartments. The bulk of the factory compartments were sealed so that smaller volumes of electrolyte could be used. The electrodes were 5 cm^2 platinized titanium disks. Before the membranes were placed in the cell for electrolysis, they were conditioned according to the manufacturers' specifications. The electrolyte solutions were injected into the proper compartments and left overnight so that membranes could absorb an equilibrium amount of electrolyte solution. Prior to performing the experiment, each membrane was conditioned by running the cell for 20–30 min of electrolysis (approximately 10–20% electrolysis of the center electrolyte). The contents of the cell were removed and each compartment of the cell was rinsed with the proper electrolyte. The percent electrolysis refers to the number of Na⁺ cations in the center compartment that will ideally be transported to the cathode compartment by the application of an electric current.

The cell was connected to a Hewlett Packard 6629A DC Power Supply. The constant current was set to 245 mA. Current was passed for 20 min which corresponded to 10% electrolysis of the center electrolyte. After electrolysis the electrolyte solutions were removed from the cell with a syringe. Electrolyte samples before and after electrolysis were analyzed by acid–base titration, using potassium hydrogen phthalate and sodium hydroxide to analyze alkaline and acid samples, respectively. The samples were titrated using phenolphthalein indicator and an Orion model 410A pH meter in tandem to determine the endpoint.

To appraise membrane performance, the current efficiency of each experiment was measured. Current efficiency is the ratio of the moles net product made (OH⁻ or H⁺) as measured via titration divided by the mole equivalent of coulombs passed.

3 Results

3.1 CEM and AEM testing

Tables 1 and 2 show the CEMs and AEMs tested, respectively, and some of their properties as listed by the manufacturer. The membranes were selected to test a variety of properties such as the polymer backbone of the membrane, the ion exchange capacity (sometimes referred

Table 1 CEMs tested and their properties as listed by the manufacturer

Membrane	Electropure Excellion I-100	GE Ionics CR67-HMR	Sybron Ionac MC-3470	Dupont Nafion 324	Dupont Nafion 982
Polymer matrix	Styrene Divinylbenzene	Styrene Divinylbenzene	Styrene Divinylbenzene	PTFE	PTFE
Exchange capacity (meq g^{-1})	1.8–2.0	2.1	1.4	0.91–1.0	0.91–1.0
Water permeability (mL h^{-1} ft^{-2})	<1	80	25	X	X
Electrical resistance (Ohm cm^{-2})	12.5–7.5 0.5 M NaCl	10 0.01 M NaCl	25–10 0.1–1.0 M NaCl	4.5 0.6 M KCl	2.6 24% NaCl 15 NaOH
Thickness (cm)	0.033	0.06	0.381	0.03	0.23

Table 2 AEMs tested and their properties as listed by the manufacturer

Membrane	Electropure Excellion I-200	Sybron Ionac MA-3475	Sybron Ionac MA-7500	GE Ionics AR204-SZRA
Polymer matrix	Styrene Divinylbenzene	Styrene Divinylbenzene	Styrene Divinylbenzene	Styrene Divinylbenzene
Exchange capacity (meq g^{-1})	0.08–0.09	0.9	1.1	2.4
Water permeability (mL h^{-1} ft^{-2})	<1	25	50	60
Electrical resistance (Ohm cm^{-2})	5–10 0.5 M NaCl	50–25 0.1–1.0 M NaCl	30–10 0.1–1.0 M NaCl	7 0.1 M NaCl
Thickness (cm)	0.033	0.041	0.046	0.05

to as the acid capacity), and electrical resistance. Membrane performance was compared in a three-compartment, two-membrane cell under identical electrolyte conditions. The two Dupont CEMs are dual layer membranes [14, 15]. The Nafion 324 membrane is reinforced and contains two sulfonate films that differ in equivalent weight. The Nafion 982 membrane, intended for use in the chlor-alkali process, is reinforced and contains both sulfonate and carboxylate layers. This membrane is oriented in the cell with the carboxylate layer towards the hydroxide containing cathode compartment.

CEMs were initially compared in the least rigorous conditions. All three compartments of the cell were filled with 1 M Na_2SO_4 and 10% electrolysis was performed. The use of Na_2SO_4 in all three compartments is described as "neutral" conditions. Four different CEMs were tested using the Electropure Excellion I-200 AEM. The results of this testing are shown in Table 3. The measure of membrane performance is current efficiency which is defined as the ratio of moles of product produced to the equivalent number of moles of electrons passed. The current efficiency for both the anode and cathode are reported.

All the cation exchange membranes tested at neutral conditions demonstrated high current efficiencies, but more realistic conditions require a strong base for the catholyte and a strong acid for the anolyte. These conditions are referred to as "polarized." Each of the five cation exchange membranes under investigation were paired with the Electropure Excellion I-200 AEM and tested at polarized conditions. The resulting current efficiencies are shown in Table 4. Similarly, each of the four AEMs under investigation was paired with the Dupont Nafion 324 CEM under the polarized conditions. The resulting current efficiencies are shown in Table 5.

3.2 Product concentration testing

Based on current efficiency measurements in the screening tests described, the best performing CEM and AEM were selected (DuPont Nafion 324 and Sybron Ionac MA-7500) for additional testing. The object of this series of experiments was to determine the strength of NaOH that could be practically produced in a three-compartment cell. In experiments with 1 M H_2SO_4 as the anolyte, 1 M NaOH as the catholyte, and 1 M Na_2SO_4 in the center compartment, the anodic current efficiencies are shown in Tables 4 and 5. They tended to be much lower than the cathodic current efficiencies across the range of anion and cation exchange membranes. This was attributed to the excessive transport of H$^+$ across the AEM. Therefore, the anolyte was changed to a ½ M NaHSO$_4$ + ½ M Na_2SO_4 solution that buffers near pH 2. Thus, the proton diffusion across the AEM was

Table 3 Anode and cathode current efficiencies with various cation exchange membranes following 10% electrolysis

CEM	CEM current efficiency (%)	AEM current efficiency (%)
Electropure Excellion I-100	85	85
GE Ionics CR67-HMR	87	88
Sybron Ionac MC-3470	92	91
Dupont Nafion 324	97	95

Starting conditions were 1 M Na_2SO_4 in all three compartments. Electropure Excellion I-200 anion exchange membrane

Table 4 Anode and cathode current efficiencies with various cation exchange membranes following 10% electrolysis

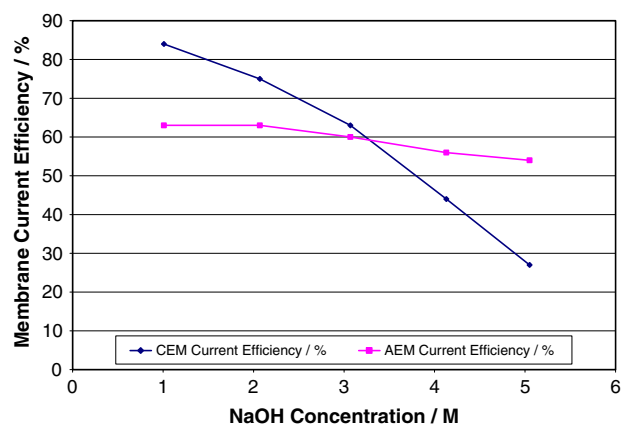| CEM	CEM current efficiency (%)	AEM current efficiency (%)
Electropure Excellion I-100	46	16
GE Ionics CR67-HMR	60	17
Sybron Ionac MC-3470	66	20
Dupont Nafion 324	84	18
Dupont Nafion 982	85	21

Starting conditions were 1 M NaOH catholyte, 1 M H_2SO_4 anolyte, and 1 M Na_2SO_4 in the center compartment. Electropure Excellion I-200 anion exchange membrane

Table 5 Anode and cathode current efficiencies with various anion exchange membranes following 10% electrolysis

AEM	CEM current efficiency (%)	AEM current efficiency (%)
Electropure Excellion I-200	84	18
Sybron Ionac MC-3475	84	35
Sybron Ionac MC-7500	85	36
GE Ionics AR204-SZRA	85	19

Starting conditions were 1 M NaOH catholyte, 1 M H_2SO_4 anolyte, and 1 M Na_2SO_4 in the center compartment. Dupont Nafion 324 cation exchange membrane

eliminated because the concentration of protons on each side of the membrane was essentially the same. A secondary goal of using the buffered anolyte was to fix the anodic current efficiency so that the cathode side of the cell was isolated and studied independently. Using a 1 M Na_2SO_4 center electrolyte, and a 0.5 M $NaHSO_4$ + 0.5 M Na_2SO_4 buffered anolyte solution, the concentration of NaOH catholyte was varied from 1 to 5 M. Figure 2 shows the current efficiencies as a function of NaOH concentration. The goal of this series of measurements was to determine the effect of increased product concentration on current efficiency. As the NaOH concentration increases in the cathode compartment, it becomes more difficult to maintain the net flux of sodium ions because of the

Fig. 2 Current efficiency vs. NaOH concentration after a 10% electrolysis using a DuPont Nafion 324 CEM and a Sybron Ionac MA-7500 AEM. The anolyte is a ½ M $NaHSO_4$ + ½ M Na_2SO_4 buffered solution and the center electrolyte is a 1 M Na_2SO_4 solution

concentration gradient. The current efficiency for the CEM was observed to be 50% at a concentration of about 3 M.

3.3 Testing sources of product loss

In an effort to further understand the sources of inefficiency in the cell, experiments were conducted with a 1 M NaOH electrolyte in all three compartments separated with the DuPont Nafion 324 CEM and Sybron Ionac MA-7500 AEM. This minimizes purely diffusional losses leaving electric field driven migration as the primary mechanism for product loss. Implicit in this notion is the assumption that H^+ and OH^- are generated at 100% efficiency at the electrodes. The result is compared to the other two experiments using the DuPont Nafion 324 CEM and Sybron Ionac MA-7500 AEM (1 M Na_2SO_4 anolyte solution and 0.5 M $NaHSO_4$ + 0.5 M Na_2SO_4 buffered anolyte solution). A charge of 294 Coulombs was passed at a current density of 50 mA cm^{-2}, for each of the three anolyte compositions. The CEM current efficiency was approximately 83% for each composition. This indicates that purely diffusion driven losses through the CEM are insignificant.

To further explore cell efficiencies with strong base conditions in the cathode compartment, the effect of increasing the CEM thickness was examined. Two layers of DuPont Nafion 324 CEM were pressed together to simulate a thicker CEM used with a single layer of Sybron Ionac MA-7500 as the AEM. The catholyte, center electrolyte, and anolyte solutions were 5 M NaOH, 1 M Na_2SO_4, and ½ M $NaHSO_4$ + ½ M Na_2SO_4, respectively. The change from a single layer to a double layer of of Nafion 324 resulted in a current efficiency improvment from 27 to 48%.

Table 6 Results of diffusion only experiments

Membranes	Catholyte compartment		Center compartment		Anode compartment	
	t = 0 min	t = 20 min	t = 0 min	t = 20 min	t = 0 min	t = 20 min
DuPont Nafion 324 CEM/Electropure Excellion I-200 AEM	0.988 M	0.988 M	pH = 7.07	pH = 2.18	1.937 M	1.920 M
DuPont Nafion 324 CEM/Sybron Ionac MA-7500 AEM	5.060 M	5.006 M	pH = 6.92	pH = 2.55	pH = 1.94	pH = 1.97

To isolate diffusional effects from migrational effects, the cell was set up as if for an electrolysis experiment (single layer of CEM). However, no current was applied. After 20 min (the same time as a 10% electrolysis at 245 mA), the electrolyte from each compartment was analyzed. The first diffusion-only test used DuPont Nafion 324 CEM, Electropure Excellion AEM, 1 M NaOH catholyte, 1 M Na_2SO_4 center electrolyte, and 1 M H_2SO4 anolyte. The second diffusion-only experiment used DuPont Nafion 324 CEM, Sybron Ionac MA-7500 AEM, 5 M NaOH catholyte, 1 M Na_2SO_4 center electrolyte, and 0.5 M Na_2SO_4 + 0.5 M $NaHSO_4$ anolyte. The electrolyte concentration of each compartment at the beginning and end of the experiments is shown in Table 6. The results show that diffusion of protons through the AEM from the acidic anolyte was greater than the flow of hydroxide through the CEM from the catholyte.

4 Discussion

4.1 Influence of electrolyte composition

Table 3 shows the polytetrafluoroethylene based CEMs (DuPont Nafion 324 and Nafion 982) exhibit only slightly better current efficiency than the styrene divinylbenzene based CEMs when electrolyte of neutral pH is used in all three compartments. However, the polytetrafluoroethylene based CEMs display much better current efficiency than the styrene divinylbenzene based CEMs at polarized electrolyte conditions. When electrolyte of neutral pH is used in all compartments, the product concentrations after 10% electrolysis are relatively low. The final OH^- product concentration ranged from 0.321 M (Electropure Excellion I-100 CEM) to 0.384 M (DuPont Nafion 324 CEM). The titratable H^+ product ranged from 0.324 to 0.378 M (Electropure Excellion I-200 AEM). Not surprisingly, with small hydroxide concentration gradients across the CEM, diffusional losses of hydroxide product were modest for all membranes.

When the polarized pH electrolytic conditions (acidic anode, neutral center, and alkaline cathode) are used, the H^+ and OH^- concentrations are greater so that the back migration and diffusion of these ions are greater. The styrene divinylbenzene membranes exhibit significantly lower current efficiencies than the PTFE-based membranes. The more hydrophilic nature of the styrene divinylbenzene membranes may account for this difference in performance because higher levels of hydration and swelling are possible. This poorer selectivity for hydroxide is reflected in the center compartment pH measurements. At lower CEM current efficiencies, the pH of the center compartment is higher as more hydroxide passes through the CEM.

4.2 Causes of lower coulombic efficiency

There are three possible sources of CEM current efficiency loss:

1. Destruction of OH^- by migration of H^+ across the cell: Protons generated at the anode migrate toward the cathode. The function of the AEM is to prevent the transport of cationic species (e.g. protons). However, the high diffusivity associated with the proton permits significant transport of protons through the AEM. The protons diffuse or migrate into the center compartment and then to the cathode compartment where an unwanted neutralization reaction occurs. If this were the main cause of CEM inefficiency, the pH of the center compartment would remain the same (slightly acidic) even as the NaOH catholyte concentration is increased. Also elimination of H^+ by using an alkaline electrolyte in all three compartments will increase the CEM current efficiency.

2. Diffusion of OH^- from the cathode to the center compartment: This source of inefficiency is the transport of hydroxide through the CEM driven solely by concentration difference. An ideal CEM would prevent this transport of anions across the membrane, but practical membranes have some non-zero diffusivity of anions through the membrane.

3. Migration of OH^- from the cathode toward the anode: In this case, the driving force for hydroxide transport across the CEM is the electric field across the CEM. Under the influence of the electric field, OH^- generated at the cathode migrates toward the anode. The greater the electric field is, the greater the effects of migration will be. If case 2 or 3 is the cause of CEM inefficiency, the pH of the center compartment will

increase along with an increase in the NaOH catholyte concentration. If case 2 is the dominant cause of efficiency loss, then using an alkaline electrolyte in all three compartments will result in higher CEM efficiency because the driving force for diffusion of OH⁻ across the CEM will be reduced.

Experiments with varying anolyte compositions were carried out in order to examine the nature of product loss at the cathode. The first two experiments used a 1 M NaOH catholyte and 1 M Na_2SO_4 center electrolyte. The first used a strongly acidic anolyte (1 M H_2SO_4). The second used a buffered anolyte (0.5 M Na_2SO_4 + 0.5 M $NaHSO_4$). The third experiment used an alkaline electrolyte (1 M NaOH) in all three compartments. This comparison is made to determine the chief source of OH⁻ product loss at cathode. In all three cases, the CEM current efficiency was slightly above 80%.

By changing the anolyte and center electrolyte compositions, the possibility of proton migration from the anode into the cathode compartment is minimized. In the case of 1 M NaOH in all three comparments, the concentration of free protons is very low. A decrease in free proton concentration in the center compartment does not result in an increase of CEM efficiency for a 1 M NaOH product. Therefore, neutralization of OH⁻ product with protons is concluded to be minimal.

For a 1 M NaOH product, diffusion of OH⁻ from the cathode to the center does not seem to be the major source of inefficiency. When a 1 M NaOH electrolyte is used in all compartments, the OH⁻ concentration gradient across the CEM is greatly diminished. In this case, the CEM efficiency does not increase. This eliminates concentration driven diffusion as the dominant source of OH⁻ loss in the case of a 1 M NaOH product. Electric field driven migration of OH⁻ through the CEM toward the anode is the only remaining possibility. The DuPont Nafion 324 is less than 100% selective when using both 1 M Na_2SO_4 and 1 M NaOH catholyte solutions because the electric field causes OH⁻ anions to migrate across the CEM. In the case of the 1 M NaOH catholyte, it appears that diffusion of OH⁻ anions is not a significant factor in the CEMs' current inefficiency.

However, the role of diffusion increases significantly from 1 to 5 M NaOH product concentration. The CEM current efficiency is migration limited in the case of 1 M NaOH product, while the CEM current efficiency is impacted much more by diffusion in the case of 5 M NaOH product.

Table 6 shows the electrolyte concentration of each compartment for two diffusion only experiments. When a 1 M OH⁻ concentration differential is used no measurable change in catholyte concentration is observed suggesting

very little concentration driven hydroxide transport. However, when a 5 M OH⁻ concentration differential is examined, the OH⁻ concentration in the catholyte dropped from 5.06 to 5.01 M. This loss accounts for about 20% of the total loss in the electrolysis experiment with a similar concentration difference. This suggests that hydroxide migration driven by the electric field is a major source of product loss at low (1 M) catholyte concentrations.

As the OH⁻ concentration differential is increased from 1 to 5 M, the driving force for diffusion is increased, resulting in more hydroxide loss. More importantly, the apparent diffusivity of hydroxide through the membrane appears to be changing with catholyte hydroxide concentration.

5 Summary and conclusions

Of the membranes examined, the DuPont Nafion 324 (based on a perfluorinated polymer backbone which does not absorb electrolyte as styrene divinylbenzene based membranes) appears to be the best suited CEM for a three-compartment cell. The styrene divinylbenzene CEMs all have unacceptably low current efficiencies at elevated catholyte hydroxide concentrations. The DuPont Nafion 324 is tolerant of the SO_4^{2-} anion, because it contains only SO_3^- fixed ionic sites; whereas the DuPont Nafion 982 CEM contains both SO_3^- and COO^- fixed ionic sites. The COO^- layer is extremely sensitive to SO_4^{2-} anions. The Sybron Ionac MA-7500 is the most counter-ion to co-ion selective AEMs tested in this work.

Using the DuPont Nafion 324 CEM and Sybron Ionac Ma-7500 AEM, the CEM current efficiency was tested using concentrations of NaOH catholyte from 1 to 5 M. During these experiments the anolyte is buffered in order to regulate the AEM current efficiency. However, it is observed that the CEM current efficiency decreases with increasing NaOH catholyte concentration. This change in net hydroxide production efficiency is more than can be accounted for assuming constant CEM properties. The apparent diffusivity of hydroxide in the CEM increases with increasing hydroxide concentration in the catholyte. A 1 M NaOH product is made at 85% current efficiency. The production of 5 M NaOH is achieved at 27% current efficiency with a single layer of CEM and 48% current efficiency using a double layer of CEM suggesting concentration driven hydroxide transport is a crucial factor at high hydroxide concentrations. A direct result of the increased hydroxide transport at high cathode product concentrations is that the center compartment becomes alkaline. This results in additional anode product loss as the hydroxide freely moves across the AEM and lowers the AEM current efficiency. The CEM counter-ion to co-ion selectivity declines with increasing NaOH catholyte

concentration indicating a change in CEM properties as the catholyte concentration changes. The diffusivity of hydroxide, and therefore the overall effects of diffusion on current efficiency, increases along with the increase in the concentration of hydroxide in the catholyte.

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