

Effect of residual gases in the electro dialysis cell on mass transfer

J. Erkmén

Department of Chemical Engineering, Faculty of Engineering and Architecture, Kafkas University, Kars 36300, Turkey

Received August 5, 2016; Revised April 4, 2017

The present work investigated the problems associated with the gases generated during the production of an acid and an alkali from a sodium salt in a three-chamber electro dialysis cell with bipolar membranes remaining in the cell. The study was conducted at three different flow rates, three different potentials and at two different concentrations. All experiments were conducted repeatedly under both conditions where the gas exhaust ports of the cell were either on or off. The system was observed to underperform particularly under conditions where the gas produced during the process could not be removed and thus formed a surface film on the membrane and the electrodes of the cell. The loss of current efficiency was in the range of 15 – 28%. The study highlighted the significance of maintaining the optimal operating conditions in electro dialysis processes for the prevention of loss of energy and workforce.

Keywords: Electro dialysis, Bipolar Membrane, Mass Transfer, Gas

INTRODUCTION

Membrane processes are among the most environmentally friendly production processes. Electro dialysis is a process where ions are removed from an electrolyte solution or where an electrolyte solution becomes more concentrated through the use of electrical potential as the driving force [1]. Electro dialysis was employed in order to obtain potable water from salt- or brackish water, removal of juice acidity, pH control and in the recovery of heavy metals, as well as in the production of caustic soda in chlorine-alkaline production plants [2, 3]. Bipolar membrane electro dialysis was used to generate protons and hydroxyl ions [4]. This process was frequently employed in environmental applications [5-7] such as the recovery of carbon dioxide in the treatment of wastewater containing organic acids [8, 9] from the food industry [10, 11]. Numerous previous studies on bipolar membranes established their economic feasibility for the recovery of inorganic, organic or amino acids [12].

Separation processes are affected by the differences in the charge of the ions in solution. Separation using charged membranes is facilitated by the exclusion of the ions with a similar fixed charge as that of the fixed charge of the ions in the structure of the membrane. Ion-charged membranes were used to separate electrolytic solutions [13-15]. A comparison of the conventional ion exchange method and bipolar electro dialysis in the production of acid and alkali from salt solutions indicated a decrease in energy requirements as low as 1 kWh/kg at a current density of 10-12 mA/cm² [16]. One of the most important aspects in a successful electro dialysis application was attributed to the cleanliness of the membrane and electrode

surfaces [17]. Earlier studies demonstrated the direct proportionality between the efficient use of membranes and electrodes and efficiency of the cell. The performance of the membrane was determined through selectivity and current parameters [18].

The current study investigated problems in mass transfer associated with the adverse effect of the gases generated during the three-chamber membrane separation process coating the surface of the membrane. The aim of the study was to facilitate the employment of bipolar membrane electro dialysis systems in the broadest possible operating capacity possible. The study highlighted the significance of maintaining the optimal operating conditions in electro dialysis processes for the prevention of loss of energy and workforce.

EXPERIMENTAL METHOD

NaF, HF, NaOH, and all other chemicals were obtained from MERCK. The analyses on sodium were performed using flame photometer and the analyses on fluoride were performed using a Mettler Toledo ion meter.

The temperature, concentration, flow rate and the changes in voltage were investigated separately. The changes in current density were investigated for different experimental trials. The experiments were conducted in a lab-scale, three-chamber bipolar membrane commercial electro dialysis cell. The cell was constructed from polyethylene. The cathode was stainless steel whereas the anode was made from Pt /Ir-MMO coated titanium of dimensions 110 mm x 110 mm. The characteristics of the membranes used in the study are displayed in Table 1. Polyethylene spacers were used to separate membranes from one another. The interspacing between the membranes was 0.5 mm whereas the membrane-electrode interface was 1 mm.

* To whom all correspondence should be sent:

E-mail: jerkmen@hotmail.com

Table 1. Characteristics of the homopolar membranes employed in the study

	PC acid 60	PC SK
Transference number	>0.95	>0.95
KCl (0.1 / 0.5 N) ^{a)}	55	
Acid (0.7/3 N) ^{b)}		
Resistance / Ω.cm ²	~ 2	~ 2.5
Water content (wt%)	~ 17	~ 9
Ion exch. capacity	ca 1.14	n/a
Strong basic (meq.g ⁻¹):	ca 0.45	
Weak basic (meq.g ⁻¹):		

^{a)} calculated from potentiometric measurements

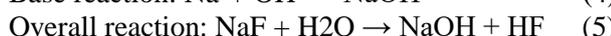
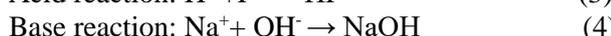
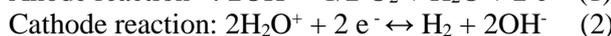
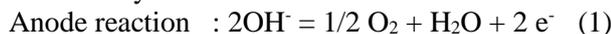
^{b)} observed current efficiencies

The experiments were conducted at concentrations of 0.05 M and 0.025 M, at flow rates of 0.38 L/min, 0.5 L/min and 0.75 L/min, using potential differences of 5V, 7.5V, and 10V. The gas discharge ports of the cell were initially blocked in order to prevent gas exhaust thus the discharge was allowed to facilitate the comparison of the two conditions. The effect of the autochthonous accumulation of gas on the system was investigated under high and low flow rate conditions. The cell efficiency was determined under each condition and the results were compared. All experiments were conducted in repeated trials and the standard deviation was determined to be 0.012 at its maximum.

RESULTS AND DISCUSSION

The desired characteristics of an ideal membrane in electro dialysis are high selectivity or retention and high current density or permeability. H₂ and O₂ gases were always reported to generate during electro dialysis due to the dissociation of water [19]. These gases must be removed from the system to prevent their accumulation. The accumulating gas due to overproduction or failure to remove it will deposit on the surface of the electrode and membrane surfaces. This accumulation is schematically represented in Figures 1 and 2.

The following reactions listed below occur in the electro dialysis cell.



The ion exchanges within the cell are displayed in Figure 3. Mass transfer during electro dialysis occurs either through diffusion or migration:

$$J_i = J_i^{\text{migration}} + J_i^{\text{diffusion}} = D_i \frac{dC_i}{dx} - D_i \frac{z_i C_i F}{RT} \frac{dV}{dx} \quad (6)$$

where J is the ion flux across the membrane (mol/m² s), D_i is the coefficient of ion diffusion, R is the gas constant (8.314 J/ mol K), T is temperature (K), V is the potential (V), and x is the perpendicular distance from the membrane (m). The mean coefficient of dialysis (D_{dif}) is calculated as shown in Equation 7. Here M represented the amount of

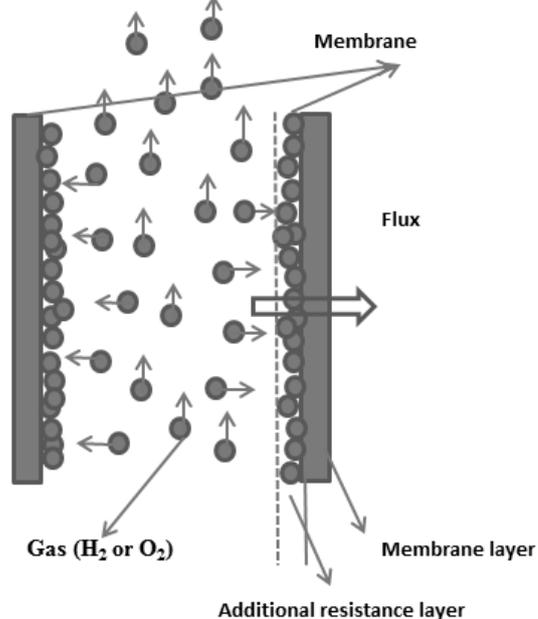


Fig. 1. Gas deposit on membrane surfaces

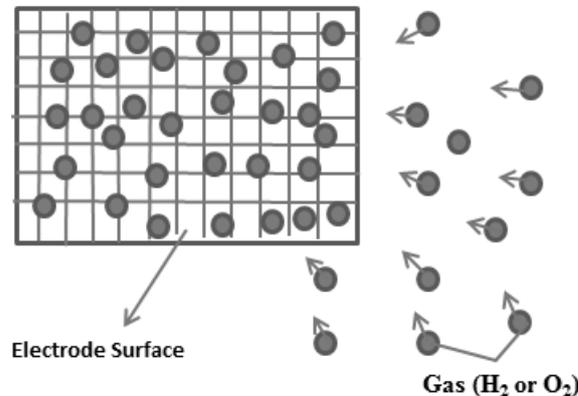


Fig. 2. Gas deposit on electrode surfaces

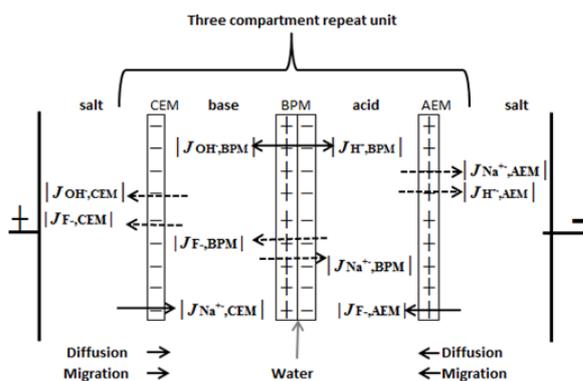


Fig. 3. Ion exchange within the three-chamber cell.

material (mol), A stood for the active surface area of the membrane, t represented time (in hours), and ΔC represented the logarithmic mean concentration between the two compartments [20]. Mass transfer reduced with dx increase, it can be seen from Equation 6.

$$D_{dif} = \frac{M}{A.t.\Delta C} \quad (7)$$

The selective coefficient of dialysis (D_{dif}) was observed to be affected by the membrane surface area for each different membrane as given in Equation 7. Electro dialysis displays the characteristic features of both dialysis and electrolysis thus setting the surface area of the active membrane, which is one of the most important parameters. Although the bipolar membrane electro dialysis process was reported to generate less gas than polar electro dialysis [21], the system performance was reduced by the insufficient removal of the generated gas.

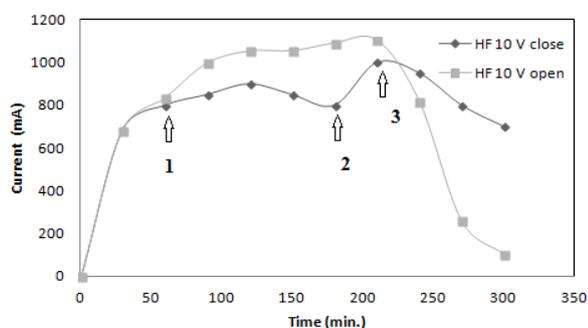


Fig. 4. Plot of current against time for gas exhaust ports of the system remaining on or off (experimental conditions: concentration of 0.05M, flow rate of 0.38L/min, potential of 10 V)

Different amounts of gas accumulation on different membranes was reported to result in concentration polarization [22]. The accumulation reduces the performance of the electrodes and interferes with mass transfer. The additional gas surface film forming on the membrane surfaces causes additional resistance. This film layer also slows down mass transfer by increasing the distance for the molecules to travel since mass transfer across the membrane is directly proportional to the resistance encountered during the transfer and the thickness of the membrane.

The region identified as 1 in Figure 4 represents the drop in current density due to the surface being covered in film layer as the concentration of the gas increased. The region identified as 2 represents the maximum gas compression within the cell. The stoppers were automatically released after this point with incremental increase in pressure as the system was adjusted to release the internal pressure at any

value beyond this point. A major fraction of the gas accumulation within the cell was thus released, leading to a rapid increase in current density.

Figures 5 and 6 represent the effect of the accumulation of gas on mass transfer in the cell. The flow of both the anion and the cation was observed to be reduced during the period when gas discharge was blocked.

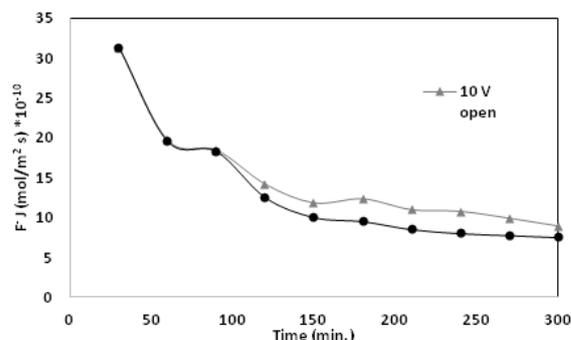


Figure 5. Plot of molar flow of F^- ion for gas exhaust ports of the system remaining on or off (experimental conditions: concentration of 0.05M, flow rate of 0.38L/min, potential of 10 V)

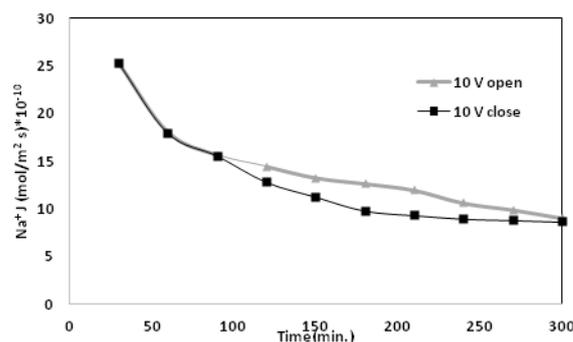


Fig. 6. Plot of molar flow of Na^+ ion for gas exhaust ports of the system remaining on or off (experimental conditions: concentration of 0.05M, flow rate of 0.38L/min, potential of 10 V)

Mixing is a method that is frequently employed to overcome the accumulation of gas on the surface of the membrane. However, the only method to allow mixing in electro dialysis is to adjust the flow rate of materials since the membrane-membrane and membrane-electrode interfaces are small. The idea behind this is to drag the newly formed gas along with the flow to prevent its adherence on the surface of the membrane.

A reduction in or the cessation of mass transfer in electro dialysis can be monitored via the reduction of current density. If the necessary conditions for the discharge of the accumulating gas are not fulfilled, mass transfer will be reduced, as the accumulated gas will coat the membrane surface. Mass transfer will further be reduced since this situation will continue to narrow down the membrane-membrane

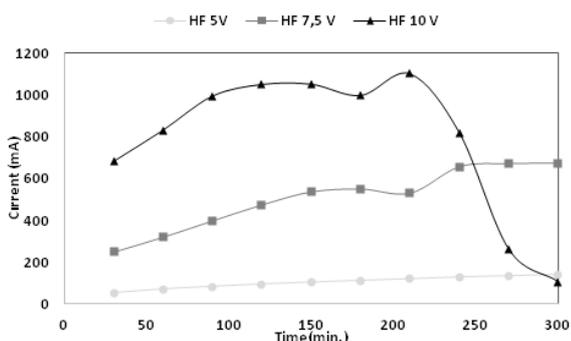


Fig. 7. Plot of current against time for the formation of HF at different potentials (experimental conditions: concentration of 0.05M, flow rate of 0.38L/min)

or membrane-electrode interspace and reducing the total amount of material fed into the system. Additionally in Figure 7, a reduction in the concentration of the ions required for mass transfer below a given limit will sharply reduce the current flow and remain constant at a very low value as observed in the curve for the 10 V potential during the period of 180- 240 minutes virtually ceasing current flow. The 10 V curve in Figure 8 is an example for this phenomenon.

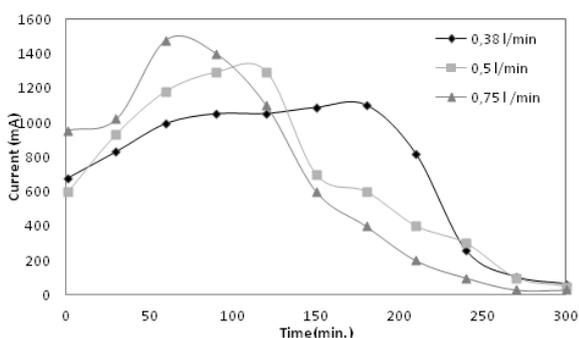


Fig. 8. Plot of current against time for the formation of HF at different flow rates (experimental conditions: concentration of 0.05M, flow rate of 0.38L/min)

Figure 8 displays the direct proportionality between the flow rate and the rate of electro dialysis. An increase in flow rate also increases circulation of the solution, thus dragging the gas away from the environment. Consequently, the accumulation of any matter including that of gas on the surface of the membrane is considerable reduced.

The short membrane-membrane and membrane-electrode interspatial distances do not allow the necessary extent of mixing required for mass transfer operations. The problem of mixing can only be attacked by the determination of an optimum rate of material flow in such systems. A fast circulation of solution simultaneously allows for interspatial mixing in the membrane-membrane and electrode-membrane regions. A concentration gradient forms

on both sides of the membrane under conditions of insufficient mixing, which can be rectified by increasing the flow rate. In commercial electro dialysis systems concentration polarization is controlled by delivering the solution at a high flow rate.

Flow pumps consume approximately 1/4th of the total power of contemporary electro dialysis systems. Concentration polarization occurring under these conditions cannot be fully controlled since the actual energy consumption greatly exceeds the theoretical value. Many adversities in electro dialysis systems are caused by the challenges of controlling concentration polarization. This dysfunction can be summarized as a reduction in the flow across the membrane. Factors affecting this reduction were reported as concentration polarization, adsorption, and the formation of a gel film and the congestion of pores [23].

Ideally, the only resistance observed during the operation of membrane processes is the membrane resistance (R_m). Materials rejected by the membrane were reported to increase in the feed concentration causing concentration polarization resistance (R_{cp}) [23]. An additional film layer forms over the membrane surface as a result of the concentration polarization reducing current flow. This layer of membrane was observed to increase the additional resistance.

The amount of ions carried towards the membrane is directly proportional to the electrical current I (A) or to the current intensity (A/cm^2). Ohm's law states that electrical current is related to the electrical potential as:

$$E=I.R \tag{8}$$

The total resistance of the membrane pack could be represented as R . The value of R was determined by multiplying the number of cell pairs in the membrane pack (N) by the resistance R_{cp} of each cell pair.

$$R_{tot}= R_{cp}.N$$

$$R_{cp} = R_{am}+ R_{pc}+ R_{cm}+ R_{fc} \tag{9}$$

Where R_{cp} is the resistance of a cell pair in unit area, R_{am} is the resistance of the anion exchange membrane, R_{pc} is the resistance of the leakage compartment, R_{cm} is the resistance of the cation exchange membrane, and R_{fc} is the resistance of the feed compartment. The resistance of the cell pair is equivalent to the sum of the four resistances in series. The gas film forming on the surface of the membrane increases R_{cp} , thus increasing energy consumption and resulting in unnecessary energy losses.

The key element in describing the total efficiency in electro dialysis processes is the energy consumed

Table 2. Current efficiency under the investigated experimental conditions

Potential Volt	Initial salt concentration M	Flow rate L/min	Current efficiency Gas output is open	Current efficiency Gas output is close
5	0.5	0.38	0.961791	0.838902
7.5	0.5	0.38	0.969363	0.817584
10	0.5	0.38	0.995128	0.706543
5	0.25	0.38	0.938402	0.757572
7.5	0.25	0.38	0.962072	0.826782
10	0.25	0.38	0.967055	0.802345
5	0.5	0.5	0.981025	0.922792
7.5	0.5	0.5	0.988750	0.915694
10	0.5	0.5	0.991523	0.995981
5	0.25	0.5	0.947786	0.878783
7.5	0.25	0.5	0.981313	0.934263
10	0.25	0.5	0.980593	0.914671

in the separation process. Energy consumption E (kilowatt) is related to the current flowing through the pack I and to the resistance of the pack R in the following relationship;

$$E = I^2 R = V.I \quad (10)$$

Gas accumulation on the surface of the electrode and membrane results in additional resistance, causing an increase in energy consumption and time to achieve the same level of productivity. This means additional energy and time-associated costs for the production process.

Average current density was calculated using the following equation:

$$\text{Average current density} = \frac{\int i . dt}{t . A} \quad (11)$$

where A : membrane area ($9 \times 64 \text{ cm}^2$), t : time (min), $\int i . dt$: amount of current passing during time t (amp.min). $m_{(\text{theoretical})}$ was calculated as given by the Faraday's law:

$$m = \int_a^b \frac{M . i . dt}{n . F} \quad (12)$$

where $M_{(\text{theoretical})}$: theoretical amount of substance released from the electrode (g), M : molecular weight (g), n : valency, i : current intensity (A), t : time (min), F : Faraday constant (96485 As/mol).

Current efficiency was calculated using the relation provided below:

$$\text{Current efficiency} = \frac{m_{(\text{used})}}{m_{(\text{theoretical})}} \quad (13)$$

Here, $m_{(\text{used})}$ represented the amount of material actually used in the experiments that were conducted and $m_{(\text{theoretical})}$ represented the theoretical amount of salt, which should have been consumed, as calculated from the relationship representing Faraday's Law.

The decrease in current efficiency displayed in Table 2 was lower than expected. The bulk flow of the solution removed a large fraction of the gas away from the cell although the gas exhaust ports were off. The fraction, which could not be removed by bulk

flow, remained in the cell, reducing the activity of the membrane. A decrease of minimum 15% and maximum 28% was observed in current efficiency for the experiments conducted by limiting gas exhaust except through bulk flow of materials Table 2. This indicated the undesirable situation of achieving less production by consuming equal amounts of energy. This situation bears the inevitable increase in process time and in workforce requirements.

CONCLUSIONS

This study investigated several situations where selection of incorrect operating conditions caused the accumulation of gas during acid and alkali production employing electro dialysis and suggested alternative modes of operation for the prevention of such problems. Very high current densities were obtained under optimal operating conditions in the present study. The maximum current efficiency achieved was determined as 0.995128. The current efficiency decreased to 0.838902 under similar conditions with the exception of confining the generated gas within the cell. Although a current efficiency value of 0.838902 would appear as very high for the electro dialysis processes, much higher values could be obtained outperforming this trial. Current efficiency was also a measure for conversion of salt into its acid and alkali counterparts, indicating the extent of mass transfer within the system. A decrease in current efficiency also indicated a reduction in mass transfer. A minimum of 15% and a maximum of 28% reduction were observed in current efficiency in the present study. A major disadvantage of the electro dialysis (ED) processes is the excessive consumption of energy. The accumulation of gas created an additional resistance in the system thus increasing energy requirements even further.

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ЕФЕКТ НА ОСТАТЪЧНИТЕ ГАЗОВЕ ВЪРХУ МАСОПРЕНАСЯНЕТО В КЛЕТКА ЗА ЕЛЕКТРОДИАЛИЗА

Дж. Еркмен

Департамент по химично инженерство, Факултет по инженерство и архитектура, Университет Кафкас, Карс 36300, Турция

Получена на 5 август, 2016 г.; коригирана на 4 април, 2017 г.

(Резюме)

В настоящата работа се изследва проблема, свързан с газовете, генерирани при производството на киселини и алкали от натриеви соли в три-камерна електродиализна клетка с би-полярни мембрани. Изследването е проведено при три дебита, три различни потенциала и две различни концентрации. Експериментите са проведени двукратно при включени и изключени изходи на газовете. Наблюдава се влошена работа на клетката, когато газовете не се отделят напълно от нея. Така се формират повърхностни филми върху мембраната и върху електродите. Загубата на добив по ток е между 15 и 28%. Изследването изяснява значението за поддържане на оптимални условия при електродиализата за да се избегнат загубите на енергия.