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Intensification of the chlor-alkali process by using a spinning disc membrane electrolyzer

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Abstract

A zero-gap spinning disc membrane electrochemical reactor (SDMER) is presented for the intensification of the chlor-alkali process at high current densities up to 20 kA/m². Two configurations of the SDMER, namely rotor-stator (RS) and thin-film (TF), are investigated and compared with a conventional parallel plate (PP) cell. The cell voltage as a function of current density is virtually identical for both SDMER configurations, and lower when compared to PP cell. The effect of the rotational speed on the cell voltage shows a decrease of 0.9 V at 6 kA/m² when the rotational speed is increased from 40 to 60 rad/s. The estimated membrane permselectivity, increases with increasing current density to values between 0.95 and 0.98. The intensification of the chlor-alkali process was successful with the SDMER by obtaining an approximately three times higher production compared to the PP cell when increasing the current density from 6 kA/m² to 20 kA/m².
1. Introduction

The chemical industry is continuously striving for the development of substantially smaller, cleaner, and more energy efficient technologies, in other words: process intensification.\textsuperscript{1,2} For energy-intensive industries it is highly desired to decrease the energy consumption of the processes. The chlor-alkali is an example of an energy intensive industry,\textsuperscript{3} with an average energy consumption per tonne of chlorine produced of $\sim$3.4 MWh.\textsuperscript{4} The chlor-alkali process is the electrolysis of aqueous sodium chloride (brine) to yield chlorine, sodium hydroxide and hydrogen. This process is one of the major electrochemical processes rendering an annual chlorine production of 9612 ktonnes in Europe in 2014\textsuperscript{5} that supports the production of about 55\% of the chemicals and pharmaceuticals.\textsuperscript{6} A schematic chlor-alkali cell is depicted in Figure 1 where the following electrochemical reactions occur:

Anode: $\textit{Cl}^- \rightarrow \frac{1}{2} \textit{Cl}_2(g) + e^-$  \hspace{1cm} (1)

Cathode: $\textit{H}_2\textit{O} + e^- \rightarrow \textit{OH}^- + \frac{1}{2} \textit{H}_2(g) + e^-$  \hspace{1cm} (2)

In the past years industrial and academic chlor-alkali research has focused on decreasing the cell voltage ($E_{\text{cell}}$) and increasing the current efficiency ($\eta_{\text{eff}}$) in order to decrease the power consumption ($P_{\text{Cl}_2}$) per tonne of chlorine produced. These quantities are related by:

$$P_{\text{Cl}_2} = \frac{756.1 E_{\text{cell}}}{\eta_{\text{eff}}} \text{ (kW h tonne}^{-1})$$  \hspace{1cm} (3)

The development of novel electrode materials,\textsuperscript{7–10} the design of more efficient and durable membranes\textsuperscript{7,11} and the implementation of zero-gap cells\textsuperscript{12,13} have been the major breakthroughs.
of the chlor-alkali process in the last decades contributing to significant decreases in the power consumption. Typical current densities are now in the range of 5-7 kA/m².\textsuperscript{7,12}

Working at higher current densities inherently decreases the electrode area, and therefore reactor volume, needed to achieve a given production capacity. Thus, ideally the power consumption in (3) can be lowered if the cell voltage is decreased. However operation at higher current densities is associated with several challenges, for instance: 1) increased bubble generation causing larger ohmic drops and increased power consumption (bubble effect), 2) more pronounced concentration gradients in the boundary layer leading to undesired side-reactions and current efficiency losses and 3) an increase in membrane voltage drop and the possibility of loss in permselectivity of the membrane.

In order to achieve the intensification of the chlor-alkali process it is necessary to design an electrochemical reactor that allows operating at high current densities while dealing with the above-mentioned challenges. The spinning disc reactor (SDR) is a type of rotating equipment that is suitable for this purpose. Essentially there are two types of SDR\textsuperscript{14} namely the rotor-stator spinning disc reactor (RS-SDR)\textsuperscript{15,16} and the thin-film spinning disc reactor (TF-SDR)\textsuperscript{17}:

- The RS-SDR consists of a rotating disc in a cylindrical housing, with a typical gap distance between the rotor and the stator in the order of 1-5 mm.\textsuperscript{14} The high velocity gradient between the rotor and the stator and the high shear forces cause high turbulence that intensifies the liquid-solid mass transport and therefore decrease the concentration gradients in the boundary layer. Our previous research regarding the liquid-solid mass transfer to a rotating mesh electrode\textsuperscript{16} indicates that the liquid solid mass transfer coefficient can be one order of magnitude higher than non-rotating configurations. Furthermore, the centrifugal forces generated from the rotation of the disc facilitate the
bubble disengagement resulting in a decrease of the bubble effect. For these reasons, the RS-SDR is a promising process intensification technology for the brine electrolysis.

- The TF-SDR consists of a rotating disc in a cylindrical housing in which the two fluids are mixed due to centrifugal acceleration of the liquid film. At first, the film tangentially accelerates due to formation of shear stresses at the disc-liquid interface. When reaching the local angular velocity the liquid moves outward forming a film with a typical thickness of 50 microns for liquids with similar properties as water.\(^{17}\) The very thin film provides a very high mass, heat and momentum transfer between the gas and liquid and also between the mesh electrode surface and the electrolyte. The supersaturation is kept low by this high mass transfer, which suppresses the formation of gas bubbles.

In this work we present the experimental results of a zero-gap spinning disc membrane electrolyzer suitable for the chlor-alkali process that allows both rotor-stator and thin-film configurations.\(^{18}\) Results of the cell voltage for current densities up to 20 kA/m\(^2\) are presented as a function of rotational speed, electrolyte concentrations and temperatures. Experimental results are compared to a laboratory scale parallel plate cell with a finite gap. Finally, the membrane selectivity is also reported.

2. Experimental

2.1 Spinning disc membrane electrochemical reactor (SDMER)

The proposed spinning disc membrane electrochemical reactor (SDMER) is depicted in Figure 2 and consists of two compartments mounted on a common horizontal rotation axis and placed back to back where the rotor of each compartment is the respective electrode. The cation exchange membrane is placed between the compartments, forming a rotating stack of anode-
membrane-cathode. In this way a zero-gap configuration is obtained. A stator is placed inside each rotating cavity. Each stator consists of a flat disc that is connected at its center to a double concentric cylinder that serves as axis of the reactor. Current is fed to the electrodes through slip rings (type SRH038-2, Gileon B.V.) located at the edges of the rotating axis. The rotating housing is connected to a motor (SEW-Eurodrive) by means of a timing belt. Rotational speeds up to 1000 RPM’s were investigated.

The anode compartment’s body material is stainless steel with an inner thin jacket of titanium (grade 2, 99+% purity, Salomons Metalen). All metal parts in contact with the electrolyte are made of titanium. The anode consists of a titanium (grade 1, 99+% purity, UNIQUE Wire Weaving Co., Inc.) plain weaved mesh of 80 wires/inch woven from 0.13 mm wires and a width opening of 0.2 mm. A triangular area of 10 cm² of the mesh was coated with a Ru/Ir/Ti- mixed metal oxide (MMO) catalyst (coating by MAGNETO Special Anodes B.V.). The cathode compartment’s body material is stainless steel with an inner thin jacket of nickel (99+% purity, Salomon’s Metalen). All metal parts in contact with the catholyte are made of nickel. The cathode is a nickel (purity 99+% , Alfa Aesar) plain weaved gauze of 100 wires/inch woven from 0.1 mm wires and a width opening of 0.15 mm. The cation exchange membrane is Nafion NX-982 (Dupont). Two reactor configurations of the SDMER are possible and are explained below. For clarity, the description below corresponds to one compartment of the reactor, but applies to both compartments as they are symmetrical.

2.1.1 Rotor-stator SDMER

The rotor-stator configuration is depicted in Figure 3-a. The electrolyte enters the reactor through the outermost concentric cylindrical cavity of the stator axis. The flow path of the electrolyte in each compartment is such that it flows past the rotating electrode in a radially
inwards manner. During the electrolysis, a dispersion of bubbles from the gas produced at the electrode is formed in the electrolyte that fills the cavity between the rotating electrode and the stator. This electrolyte mixture exits the reactor through the innermost cylindrical cavity of the stator axis.

2.1.2 Thin film SDMER

The thin-film configuration is depicted in Figure 3-b. The electrolytes enter the reactor through the innermost concentric cylindrical cavity of the stator axis forming a jet of liquid on the rotating electrode. Due to its rotation, a thin film of liquid flowing radially outwards is formed on the rotating electrode. The gas produced at the rotating electrode is collected in the gas pocket formed between the stator and the electrolyte thin film. The liquid and the gas collected at the rim of the rotating electrode exit the reactor by flowing radially inwards past the counter side of the stator and through the outermost concentric cylindrical cavity of the stator axis.

2.2 Experimental setup

The experimental set-up is depicted in Figure 4 and consists of three parts: the electrochemical reactor, the anolyte circuit and the catholyte circuit. Three reactor configurations are used in this study: 1) the rotor-stator SDMER described in 2.1.1, 2) the thin-film SDMER described in 2.1.2 and 3) a parallel plate cell (PP cell). The later was used as comparison of the performance of the SDMER and consisted of an Electrocell® Micro Flow Cell 19 with Ir/Ru-MMO on the Ti anode and a nickel cathode, both of 10 cm² of electrode area, an electrode membrane gap of 4 mm and fitted with the same membrane as described in 2.1. For all cases the electrochemical reactor is connected to a power supply (TDK-Lamba Gen 30-50).
Each electrolyte (anolyte and catholyte) circuit consists of feed, water and waste vessels, a gas cooler and its respective pumps, flow controllers and other sensors. Additionally, the anolyte circuit includes a chlorine removal section and an acid unit. The entire setup is placed in a closed Item® rack which for safety reasons remained closed during operation. An in-house-designed Labview® interface allowed the remote control and operation of the experimental setup via a programmable logic computer (PLC).

All vessels are made of insulated glass and are designed to be leak tight. Both feed vessels are stirred and heated by a tracing cable. Prior to the experiments the anolyte and catholyte feed tanks are filled with aqueous NaCl (VWR Chemicals) and aqueous NaOH (Sigma Aldrich) solutions respectively at the desired experimental condition. Anolyte pH is controlled by addition of 1 M HCl (VWR Chemicals) based on the measurement of the pH; when necessary additional acid solution is fed with the aid of a micropump dosing unit (Burkert). The anolyte and catholyte are circulated to the respective compartments of the electrochemical reactor in separate hydraulic circuits by two gear pumps regulated with their respective mass flow controllers. Unless otherwise noted the electrolyte flowrates were 7 ml/s. Three-way solenoid valves connected to the PLC are used to control the direction of the flow during the experiments and during the rinsing procedure. Pressure sensors and temperature sensors are located at the inlet of the reactor, at the exit of the reactor and after the gas coolers.

The outflows of the electrolysis reactor consist of mixtures of electrolyte-gas and they can be re-circulated to the respective feed tanks for further re-use or the waste tanks for their disposal. The produced gases (Cl₂ and H₂) are separated from the top of their respective tanks. Before the gases are further processed or vented they are cooled in their respective gas coolers. The Cl₂ gas is absorbed by contact with NaOH solution using washing bottles to form NaOCl+NaCl. For safety reasons and to minimize corrosion issues, at the end of each experimental procedure
the reactor and all lines are flushed with nitrogen and water. Due to this rinsing procedure, a small, but unknown amount of water remains present in the lines, which for practical reasons is not removed in between experiments. Therefore some variations in the concentrations occurred between experiments. To make sure that the concentrations of the electrolytes during the experimental procedure are known, sampling valves are located at the outlets of the reactor. Samples of the anolyte and catholyte were taken during the experimental procedure and analyzed offline as explained in section 2.3.

2.3 Analytical techniques

The experimental procedures for the quantification of the concentrations of the electrolytes and the active chlorine content in the brine is explained below. For all cases, each titration was repeated three times and the average concentration is determined. The chloride (Cl\(^-\)) concentration was determined via the back titration of silver nitrate with potassium thiocyanate. The end point of the titration is determined by using Fe(NO\(_3\))\(_3\) as indicator in an acidic environment. The active chlorine content in the brine was determined by its reaction with iodide in acid solution forming an equivalent quantity of iodine. The liberated iodine was titrated with thiosulphate and the end point was determined with the aid of starch as indicator. The caustic concentration was determined by titration with HCl.
3. Results and discussion

3.1 Rotor-stator spinning disc membrane electrolyzer

3.1.1 Effect of the rotational speed

Results presented in this section correspond to the rotor-stator configuration as described above in section 2.1.1. The effect of the rotational speed in the cell voltage is shown in Figure 5 for two cases: 1) Figure 5-a shows measurements at a constant rotational speed while the current density is increased stepwise from 2 to 20 kA/m² and 2) Figure 5-b shows measurements at constant current density while the rotational speed was increased stepwise from 400 to 1000 RPM. For both cases, measurements of the cell voltage during each current density step are taken every 1 second for a period of 180 seconds. The standard deviation of the cell voltage \( \sigma_{\text{Ecell}} \) is defined as:

\[
\sigma_{\text{Ecell}} = \sqrt{\frac{\sum(x - \overline{x})^2}{N-1}}
\]

where \( x \) is the measured cell voltage data at every second, \( \overline{x} \) is the averaged cell voltage, and \( N \) is the number of measurements. The standard deviation of the average cell voltage (\( \sigma_{\text{Ecell}} \)) is presented in Figure 5 as error bars.

A decrease in the cell voltage is observed when increasing the rotational speed, particularly at current densities higher than 6 kA/m². The effect is less pronounced at lower current densities, for instance at 2 kA/m² the cell voltage decreased 0.2 V when increasing the rotational speed from 40 to 60 rad/s (Figure 5-b). At the current density typically used in the chlor-alkali industry (i.e. 6 kA/m²) the cell voltage decreased 0.9 V when increasing the rotational speed from 40 to 60 rad/s (Figure 5-b). These results can be compared to the work presented by Cheng et al. 20 who reported the intensification of the chlor-alkali process in a centrifugal field. The authors
reported a decrease of 0.6 V in the cell voltage at 6 kA/m² in their rotary cell at 190 g of relative acceleration.

At low current densities, both bubble generation and concentration gradients have a relatively small impact on the cell voltage. It is at higher current densities when these become of importance. The higher standard deviation shown in Figure 5 at low rotational speeds, particularly for current densities higher than 6 kA/m², can be attributed to the bubble effect. When the gas formed is not efficiently removed from the reactor, bubbles remain attached to the electrode decreasing its available area and increasing the cell voltage. In practice this was identified by unstable readings of the cell voltage, leading to larger standard deviations.

Results shown in Figure 5 indicate that at high gas production rates, i.e. high current densities, there is a minimum rotational speed that is required to allow a stable operation of the reactor. In other words, a minimum rotational speed is required to efficiently release the gas produced at the electrode, leading to a small variation in the measured cell voltage as reflected in the standard deviation. This is explained in Figure 6-a where the standard deviation of the cell voltage data presented in Figure 5-b is plotted as a function of the rotational speed. From Figure 6-a it can be observed that the standard deviation of the measured cell voltage decreases as a function of the rotational speeds for all current densities investigated. An arbitrary threshold of $\sigma_{Ecell} < 0.1$ V is defined as the limit for the stable operation. Measurements with $\sigma_{Ecell} > 0.1$ are considered as unstable operation. The data presented in Figure 5-b are analyzed accordingly and the results are shown in Figure 6-b where the flow map of the stable operation of the reactor is presented.
3.1.2 Comparison with the parallel plate cell and literature data

The cell voltage obtained from the rotor-stator spinning disc membrane electrochemical reactor (RS-SDMER) is compared in Figure 7 with the results of a conventional parallel plate cell (PP cell) described in section 2.2. As expected, the cell voltage increases as a function of current density in all cases, however the slope at which this increase occurs is different for each case. Results obtained in this work are comparable to those reported by Chandran et al.\textsuperscript{21} for a similar PP cell but with a higher electroactive area (34.3 cm\textsuperscript{2}). It is worth mentioning that the material of the electrodes and the cation-exchange membrane used by Chandran et al.\textsuperscript{21} are different from the ones used in this work (see details in Figure 7). However, results for both PP cells are virtually the same. The RS-SDMER shows a comparably lower cell voltage especially at current densities above 2 kA/m\textsuperscript{2}. This difference increases at higher current densities and it is mainly attributed to a decrease in the bubble effect due to the rotational speed (ω=84 rad/s) and the zero-gap configuration of the RS-SDMER. The error bars in Figure 7 correspond to the standard deviation of the experiments as explained in the previous section. It can be observed that for the case of the PP cell studied here at current densities higher than 6 kA/m\textsuperscript{2} the standard deviation is larger than that of the RS-SDMER. This result indicates that using the RS-SDMER allows a more stable operation at higher current densities.

O’Brien et al.\textsuperscript{7} reported a cell potential of 3.5 V for the electrolysis at 3.5 kA/m\textsuperscript{2} for similar operating conditions and electrodes as used here. This is in line with our measured value of 3.4 V at 3.5 kA/m\textsuperscript{2} (see line RS-SDMER – 80\textdegree C in Figure 7). Newer industrial cell designs with activated cathodes and improved membranes achieve lower cell voltages. For instance, an industrial manufacturer reports a cell voltage of 3.1 V for electrolysis at 7 kA/m\textsuperscript{2} \textsuperscript{22}, which is 0.15 V lower than the voltage measured for the RS-SDMER. It is expected that with these new materials a significant improvement in cell potential can be obtained.
3.1.3 Temperature and concentration effect

In addition to the effect of the rotational speed on the cell voltage, the effects of temperature and concentration have also been investigated. Results of the temperature effect are shown in Figure 8 for various current densities at 80 rad/s. It can be observed that lower cell voltages are obtained at the highest temperature of 80°C as expected from the Nernst equation \(^{23}\). At 20 kA/m\(^2\) the cell voltage decreased from 6.5 V at 42°C to 5.5 V at 81°C. This can be explained by the increase in the conductivity of the membrane and the decrease of the thermodynamic potential at higher temperatures. The effect of the NaCl concentration is shown in Figure 9 where it is observed that increasing NaCl leads to lower cell voltages. Figure 9-a shows the cell voltage as a function of the NaCl concentration at 80 rad/s for three current densities. At the highest current density (20 kA/m\(^2\)) the cell voltage decreased from 7.2 V at 1.6 M NaCl to 6.3 V at 3.5 M NaCl. The NaCl has an effect on various components of the cell voltage. Primarily on the thermodynamic potential, which increases with decreasing NaCl concentration. Also the chlorine current efficiency is linked to the NaCl concentration \(^{24}\) which in turn has an effect on the overpotential.

Results in Figure 9-b show the effect of the rotational speed at various NaCl concentrations at 20 kA/m\(^2\). At lower concentrations the mass transfer effects play a more significant role, and therefore it is expected that the rotational speed has a higher impact than at high concentrations. However only a slightly more pronounced effect of the rotational speed is observed at the lowest concentration, hence no strong mass transfer dependency. For instance, at the lowest concentration studied here of 1.6 M NaCl, the cell voltage decreased 0.3 V from 0.73 rad/s to 105 rad/s, whereas a decrease of 0.2 v from 0.73 rad/s to 105 rad/s was observed at 3.5 M NaCl. The effect of the NaOH concentration is shown in Figure 10 for experiments at 84 rad/s and at three current densities. A slight increase in the cell voltage at the highest NaOH concentration
of 10.4 M for all current densities can be observed. The cell voltage is virtually the same for
3.1 and 4.5 M NaOH for all current densities, and an average increase of 0.35 v is observed
from 4.5 M to 10.4 M. The increase in the cell voltage at highest concentration of sodium
hydroxide is similar to the trend of sodium hydroxide and cation-exchange membrane
conductivity as reported in the literature 7.

3.1.4 Membrane permselectivity

The membrane permselectivity is an important factor in the efficiency of the chlor-alkali
process. This is why the membrane permselectivity has also been investigated in the RS-
SDMER. The membrane permselectivity $(S_{Na^+})$ is defined as:

$$S_{Na^+} = \frac{n_{Na^+} \times F}{i \times A \times t}$$

Where $n_{Na^+}$ is the number of moles of sodium, $F$ is the Faraday constant, $i$ is the current
density, $A$ is the surface area and $t$ is the time.

The total amount of moles of sodium transferred is calculated from:

$$i \times A \times t = n_{Na^+} + n_{OH^-}$$

In which $n_{OH^-}$ is determined from the acid addition to the anolyte and the oxygen production.
The amount of acid needed to keep the pH stable was used to calculate the consumed number
of proton moles. The measurements were corrected with the pH change and from the the oxygen
production. The change in the pH during operation is caused by the side reaction of oxygen
evolution. The current efficiency due to oxygen evolution is assumed 95% which is typically
reported in literature 24 for this type of anodes. Figure 11-a-b show the trend of the estimated
proton moles from oxygen production and the number of proton moles based on the added acid
to keep the pH stable for two different anolyte concentrations as a function of current density respectively.

The change in the sodium selectivity of the membrane is shown in Figure 12 as a function of current density. A general increasing trend is observed as the current density increases which is in line with the estimated increasing trend of number of proton moles produced due to oxygen production as presented in Figure 11-a. Generally a steep increase of sodium transport number from 0.90 at 2 kA/m² to 0.95 at 8 kA/m² is observed. The permselectivity increases up to 0.95 and 0.98 at higher current densities. Sodium permselectivity values between 0.9 and 1 are in line with the values of membrane permselectivity reported in literature 7,25. On the other hand, a decrease in membrane permselectivity at high current densities was observed in the system of sodium hydroxide electrolyte as both anolyte and catholyte 26 for which we do not have a concrete explanation.

Figure 12-a presents the sodium selectivity as a function of current density for three different concentrations of anolyte. It is observed that at the lowest concentration of anolyte, the sodium selectivity is the highest measured. This result is contradictory to the expectations and we attribute this to the overestimation of the chlorine current efficiency at this low NaCl concentration. Hine et al. 24 showed that significantly lower chlorine current efficiencies are achieved at low NaCl concentration. This particular aspect was not considered in the selectivity measurements reported here.

Figure 12-b shows the effect of NaOH concentration on the permselectivity of the membrane. It can be observed that the highest concentration of NaOH (10.4M) has the lowest selectivity, ranging from 0.92 at 6 kA/m² to 0.97 at 20 kA/m². This is attributed to the higher chance of back transport of hydroxide ions in more concentrated NaOH environment compared to lower NaOH concentrations.
3.2 Thin-film spinning disc membrane electrolyzer

Besides the rotor-stator configuration of the SDMER the thin film configuration has been investigated as well. The cell voltage results are presented in Figure 13 and compared to the rotor-stator configuration for two rotation speeds. The cell voltage in the rotor-stator configuration is comparable with the results of the thin film configuration. It has been shown by other people that the thin film spinning disc reactor has a high mass transfer rate. Additionally, efficient removal of the produced gas from a gauze surface with increase in rotation speed has been demonstrated. Due to the high mass transfer and the efficient gas removal in the thin-film SDMER, this configuration has similar performance regarding the cell voltage compared to the RS-SDMER. Therefore, these results suggest that both configurations achieve the desired lower cell voltage compared to a conventional parallel plate cell.

4. Conclusions

The spinning disc membrane electrochemical reactor is a suitable technology for the intensification of the chlor-alkali process allowing stable operation at high current densities. Two configurations (rotor-stator (RS) and thin film (TF)) are reported and compared with a conventional parallel plate cell. Similar voltage vs current density curves are obtained for both RS and TF configurations. A decrease of 0.9 V in the cell voltage is observed at 6 kA/m² when increasing the rotational speed from 40 to 60 rad/s in the RS-SDMER. Results show that the effect of the rotational speed is more pronounced at high current densities, where the gas production is higher. Lower cell voltages are reported for both RS and TF-SDMER compared to the parallel plate cell. Therefore the SDMER is likely to allow an increase of the production capacity while maintaining a low cell voltage. The measured values of cell voltage for the RS
and TF-SDMER are slightly higher than those typically reported in industry. Further optimization of the SDMER, including the use of activated cathodes and improved membranes, is likely to offer even lower cell voltage at high current densities in the future.

Additionally, the effect of operating conditions such as temperature and concentration is reported for the RS-SDMER. Results show that increasing the temperature from 40 °C to 80 °C at 20 kA/m² causes the cell voltage to decrease from 6.5 V to 5.5 V. At low sodium chloride concentrations, at which the mass transfer is important, it is shown that increasing the rotation speed decreases the cell voltage. Increasing the sodium chloride concentration and decreasing the sodium hydroxide concentration decreases the cell voltage. The membrane permselectivity in the RS-SDMER is estimated from the measurements of the acid addition and it is shown that it increases with increasing current density to values between 0.95 and 0.98 at current densities of 20 kA/m².
Acknowledgements

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Nomenclature

Symbols

\( A \)  
Area, \((m^2)\)

\( C^* \)  
Concentration of the electroactive species at the bulk, \((mol/m^3)\)

\( D \)  
Diffusion coefficient, \((m^2/s)\)

\( E_{cell} \)  
Cell potential, \((V)\)

\( F \)  
Faraday constant, \((s \, A/mol)\)

\( i \)  
Current density, \((A/m^2)\)

\( n_{Na^+} \)  
Number of \(Na^+\) ions transferred through the membrane (-)

\( n_m \)  
Mesh size, \((\text{mesh units/in}^2)\)

\( S^{Na^+} \)  
Membrane selectivity towards \(Na^+\) transport, \((Sc=v/D)\)

Greek letters
ω  Rotational speed, (rad/s)

σ_{Ecell}  Standard deviation of the cell voltage, (V)

η_{eff}  Current efficiency, (-)

Abbreviations

CE  Counter electrode

WE  Working electrode

RS  Rotor-stator

SDMER  Spinning disc membrane electrochemical reactor

TF  Thin-film

References


& Sons; 2000.


5. Figures

Figure 1. A typical membrane cell for chlor-alkali process.

Figure 2. Spinning disc membrane electrochemical reactor for chlor-alkali process.
Figure 3. Comparison of the flow paths in the Rotor-Stator (a) and Thin-Film configurations (b).
Figure 4. Schematic drawing of the experimental set-up. In the center the electrochemical reactor is shown; the anolyte circuit is on the left and the catholyte circuit is on the right. The electrolyte from the electrolyte vessels enters the electrochemical reactor through a pump. The temperature and pressure are monitored before and after the reactor. The outlet leaves the reactor back to the electrolyte vessels during operation and it goes to the waste vessel during the rinsing procedure with water. The outlet chlorine and oxygen gas pass through the cooler and enters the bleach bottles to absorb the chlorine. The oxygen and hydrogen leave through the ventilation.
Figure 5. Effect of rotational speed (ω) on the cell voltage (E_{Cell}) of a rotor-stator spinning disc membrane electrolyzer for chlor-alkali. a) Cell voltage as a function of the current density (i) for various rotational speeds. Measurements taken at constant rotational speed and stepwise increase of current density. Operating conditions: T=24±3°C, Anolyte: 3.5±0.1 M NaCl pH=2.5±0.2, Catholyte 4.0±0.1 M NaOH. b) Cell voltage as a function of the rotational speed for various current densities. Measurements taken at constant current density and stepwise increase of the rotational speed. Operating conditions: T=40±2°C, Anolyte: 2.4±0.1 M NaCl pH=2.5±0.2, Catholyte 3.4±0.1 M NaOH.

Figure 6. Stable operation of the rotor-stator spinning disc membrane electrochemical reactor (RS-SDMER) as a function of the rotational speed and current density. a) Standard deviation (σ_{E_{Cell}}) of the cell voltage data presented in Figure 5-b as a function of the rotational speed for various current densities. Operating conditions: T=40±2°C, Anolyte: 2.4±0.1 M NaCl pH=2.5±0.2, Catholyte 3.4±0.1 M NaOH. The dashed area marks the limits of stable operation according to the definition of σ_{E_{Cell}} <0.1 V. b) Flow map of the stable operation of the RS-SDMER. The line denotes the minimum rotational speed needed to achieve stable operation (σ_{E_{Cell}} <0.1 V) as a function of the applied current density according to a).
Figure 7. Comparison of the experimental cell voltage as a function of current density for the rotor-stator spinning disc membrane electrochemical reactor (RS-SDMER), the parallel plate cell (PP cell) studied here, and a PP cell reported in the literature. Operating conditions: ◦ = PP cell (reported by Chandran et al.), T=90° C, saturated NaCl, 10 M NaOH, RuO$_2$-TiO$_2$ anode, steel cathode, membrane: Nafion 901, 34.3 m$^2$ electroactive area. ○ = PP cell (this work), T=53±2° C, Anolyte: 5.0±0.1 M NaCl pH=2.5±0.2, Catholyte 10.0±0.1 M NaOH, 10 m$^2$ electroactive area. □ = RS-SDMER (this work), T=42±2° C, Anolyte: 3.0±0.1 M NaCl pH=2.5±0.2, Catholyte 10.4±0.1 M NaOH, $\omega=84$ rad/s. ▲ = RS-SDMER (this work), T=80±2° C, Anolyte: 5.0±0.1 M NaCl pH=2.5±0.2, Catholyte 10.4±0.1 M NaOH, $\omega=84$ rad/s.

Figure 8. Effect of temperature on the cell voltage of the rotor-stator spinning disc electrochemical reactor for chlor-alkali. Cell voltage ($E_{\text{cell}}$) as a function of the temperature ($T$) for various current densities. Operating conditions: T=40±2° C, Anolyte: 4.0±0.5 M NaCl pH=2.5±0.2, Catholyte 10.4±0.5 M NaOH, $\omega=84$ rad/s.
Figure 9. Effect of NaCl concentration on the cell voltage of the rotor-stator spinning disc electrochemical reactor for chlor-alkali. a) Cell voltage ($E_{\text{Cell}}$) as a function of the anolyte (NaCl) concentration ($C_{\text{NaCl}}$) for various current densities at 84 rad/s. Operating conditions: $T=24\pm3^\circ\text{C}$, Anolyte: 1.6, 2.4 and 3.5 M NaCl pH=2.5±0.2, Catholyte 4.0±0.1 M NaOH, $\omega=84$ rad/s. b) Cell voltage ($E_{\text{Cell}}$) as a function of the rotational speed ($\omega$) for various anolyte concentrations at 20 kA/m$^2$. Operating conditions: $T=24\pm3^\circ\text{C}$, Anolyte: 1.6, 2.4 and 3.5 M NaCl pH=2.5±0.2, Catholyte 4.0±0.1 M NaOH.

Figure 10. Effect of NaOH concentration on the cell voltage of the rotor-stator spinning disc electrochemical reactor for chlor-alkali. a) Cell voltage ($E_{\text{Cell}}$) as a function of the catholyte (NaOH) concentration ($C_{\text{NaOH}}$) for various current densities at 84 rad/s. Operating conditions: $T=41\pm3^\circ\text{C}$, Anolyte: 3.5±0.2 M NaCl pH=2.5±0.2, Catholyte 3.1, 4.5 and 10.4 M NaOH, $\omega=84$ rad/s.
Figure 11. Number of $H^+$ moles in the anolyte solution from the (a) oxygen production (b) the amount of acid needed to keep the pH stable as a function of current density. Operating conditions: $T=24\pm3^\circ C$, Anolyte: 1.6 and 3.5 M NaCl $pH=2.5\pm0.2$, Catholyte 4.0$\pm0.1$ M NaOH, $\omega=84$ rad/s.

Figure 12. Membrane selectivity towards Na$^+$ ion ($S_{Na^+}$) as a function of the current density for the chlor-alkali electrolysis in a rotor-stator spinning disc electrochemical reactor. a) Effect of anolyte concentration (NaCl) on membrane selectivity. Operating conditions: $T=24\pm3^\circ C$, Anolyte: 1.6, 2.4 and 3.5 M NaCl $pH=2.5\pm0.2$, Catholyte 4.0$\pm0.1$ M NaOH, $\omega=84$ rad/s. b) Effect of catholyte concentration (NaOH) on membrane selectivity. Operating conditions: $T=41\pm3^\circ C$, Anolyte: 3.5$\pm0.2$ M NaCl $pH=2.5\pm0.2$, Catholyte 3.1, 4.5 and 10.4 M NaOH, $\omega=105$ rad/s.
Figure 13. Comparison of thin film (TF) and rotor-stator (RS) configurations of the spinning disc membrane electrochemical reactor (SDMER). Cell voltage as a function of the current density (i) for two rotational speeds (84 and 105 rad/s) for two reactor configurations (TF-SDMER and RS-SDMER). Measurements taken at constant rotational speed and stepwise increase of current density. Operating conditions: $T=25\pm5^\circ C$, Anolyte: $4.5\pm0.2$ M NaCl $pH=2.5\pm0.2$, Catholyte $6.3\pm0.2$ M NaOH, $\omega=85$ and 105 rad/s.