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Low Energy Consumption in Chlor-alkali Cells Using Oxygen Reduction Electrodes

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An air/oxygen gas diffusion electrode for use as a cathode to replace the traditional hydrogen-evolving electrode in chlor-alkali electrolysis was assessed. Attempts to stabilize the cathode have been addressed in order to circumscribe problems associated with "flooding" or "wetting-in" properties. Variation of the hydrophobic concentration in the gas diffusion layer had a significant effect on the electrochemical tests of both the half-cell and electrolysis of the chlor-alkali cells. Life-tests as well as performance characteristics for both types of cells have shown encouraging results at NaOH concentration levels of ca 8M NaOH and temperatures of 70 and ca. 80 ^{o}C, respectively. Though cell voltages of about 2V were achieved and thereby reducing the energy consumption by 30-35% compared to the state-of-the-art membrane cell, the contributions of overvoltages were still high compared to the equilibrium potential of about 1.23V. Efforts to limit the individual parts of overvoltages as well as maintenance of the zero-gap cell at least on the anode side have been carried out. Two different kinds of cation exchange membranes have been used for the electrolysis cell. However, the cation exchange membrane with hydrophilic properties having high initial performances showed tendencies of blister formations.

Keywords: chlor-alkali; electrolysis; oxygen reduction; energy consumption; overpotentials

1. INTRODUCTION

Chlorine as one of the most important bulk chemicals in the world is produced by the electrolysis of brine. Chlorine is not only used in the day-to-day life but also is an essential part in the chemical building block, resulting in a myriad of reactions and products in the major plastic, pharmaceutical, inorganic and fine chemical and specialty industries. It is an energy intensive process, where electrical power consumption between 2100 and 3300 kWh t^{-1} Cl_2 is used depending on the operating parameters and the type of the process. There are three major processes based on mercury, diaphragm and

membrane cells in use for the electrolysis. In the year 2001, the total world production of chlorine was about 43.3 million tons (1), whereas 18 % of this production was met by the mercury cell technology; while the remaining 82% included diaphragm (49%) and membrane cell (28%) technologies and others (5%).

The membrane cell technology as a recent advance since its introduction in 1970 has fewer exhausts to the environment and is relatively more efficient in the use of electric power. Despite the fact that the overall energy intensity, i.e., energy per unit output for the production of the chlorine/caustic soda has been reduced due to the successive introduction of ion exchange membrane cells instead of the "unclean" mercury and diaphragm process, the issue of energy consumption is still a major issue. For example a yearly production of over 4.2 million tons of chlorine in Japan by the membrane process requires a power consumption of 100 TW (2). Thus, there is a great incentive to look into alternative process parameters that have either to be modified or replaced so that less energy and lower capital-intensive alternatives be applied in order to increase productivity and competitiveness for the chlorine industry.

The amount of electric energy needed for driving the electrode reaction depends mainly on the type of the electrolytic cell with their respective thermodynamic decomposition potential difference (ΔE). In the electrolytic process as shown in for the overall reaction 1) for every ton of chlorine produced, about 1.1 tons of caustic is generated and 28 kg hydrogen is evolved as a byproduct.

$$2\ NaCl + 2\ H_2O \rightarrow Cl_2 + H_2 + 2NaOH \qquad 1)$$

During the hydrogen evolution reaction (HER) a high voltage input, i.e., 1.23 V more than the oxygen reduction reaction (ORR) is required and thus, results in an inefficient means of energy consumption for producing the desired and undesired products. Furthermore, investments in equipment and energy input associated with the recovery, further purification, handling and storage of the hydrogen are also needed. Depending on the type of the process, the hydrogen has to pass through a series of systems, such as demisters, coolers, catalytic combustors (for removal of traces of oxygen), heat exchangers, blowers, compressors, etc. Although the value chain of hydrogen in the process does not correspond to the total energy input and investment costs necessary for its recovery, the hydrogen recovered has found applications in chemical processes, such as hydrogenation, catalytic reductions, hydrotreating and hydrocracking reactions, ammonia and methanol syntheses, etc. However, in most cases the hydrogen is used for heating or drying purposes, process steam generations or is simply flared-off.

In an earlier effort, a total voltage cut of 1.0 V was achieved by oxygen reduction electrodes, i.e.; a reduction by ca 34% vis-à-vis a chlor-alkali cell based on the conventional membrane with HER. We have shown that by using non-noble metal electrocatalysts as low-cost alternatives to Pt and Pt alloys and by constructing double-layer gas diffusion electrodes, high performance and stability could be obtained (3). Moreover, due to the thermodynamic relations and changes in entropy for each of the half-cell reactions, the ORR shows more exothermic reaction than the HER, implying that less heat can be supplied to the system (4).

Further studies, however were necessitated in order to look into some of the questions raised during the course of the earlier project. In this study, we report identification and characterization of

the different components of overpotentials, which contribute to the total cell voltage, use of ultrapure brine as well as preparation of gas diffusion electrodes with decreased wettability.

2. EXPERIMENTAL PART

Gas diffusion electrodes were manufactured using the rolling method as described in earlier reports (5,6). In order to reinforce the non-wettability of the electrodes, the initial concentrations of PTFE suspension with 60 wt.% were diluted with Millipore water and painted on the diffusion layer. This procedure was repeated four times on one and the same layer, while drying in oven consequently after each step at 70 ^{o}C. The amount of electrode materials and the catalyst loading was kept constant with slight variations. The active layer is made up of catalysts containing mixtures of perovskite ($La_{0.1}Ca_{0.9}MnO_3$) and pyrolysis product of CoTMPP (5,9) with less proofed carbon.

Half-cell electrochemical tests were carried out in small 4 cm^2-size gas diffusion electrodes with nickel wire mesh as counter electrodes in 8M NaOH and an Hg/HgO as reference electrode. The temperature 70 ^{o}C was regulated by a thermostated water bath and the flow of reactant oxygen to the rear side of the electrode was kept at 40 ml min^{-1} and current-potential readings were obtained for the assessment of the various types of electrodes.

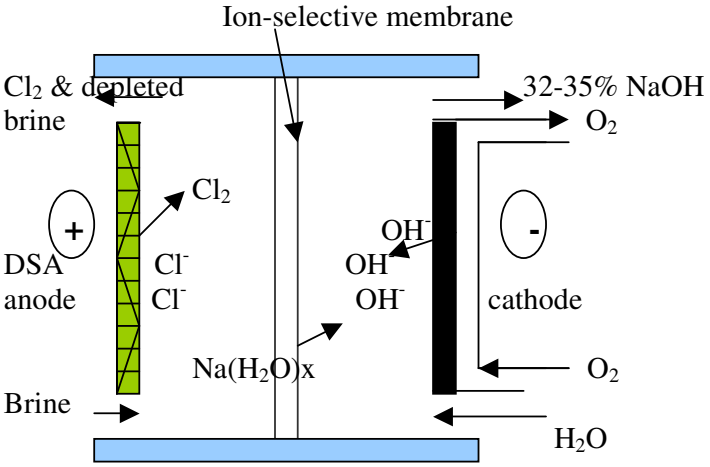

Figure 1. Schematic of an electrolysis cell

An electrochemical reactor shown in Fig. 1 with the schematic cell construction, having a total electrode area of 10 cm^2 was used for the electrolysis of brine. A cation exchange membrane (Nafion 90209®, Du Pont) separates both the anode (DSA, Permascand AB) and the cathode compartments, whereas mass transfer of sodium to the cathode is caused by the movement of the charged ions to the cathode. In order to limit backmigration of the hydroxyl ions leading to the formation of byproducts at the anode, the pH of the salt solution was adjusted to 3 by adding HCl. At the backside of the anode enters brine to be oxidized and released as chlorine, while oxygen is fed to the cathode of the gas diffusion layer, reduced at the active layer facing the electrolyte with ultimate formation of hydroxyl

ions. 300g l^{-1} pure electrolytic brine (Eka Chemicals AB) with a constant flow rate of 120 ml h^{-1} was used in the electrolysis. Though 3.5 to 4.5 mol of water per mol sodium (1) passes through the membrane, additional water with a flow rate of 6ml h^{-1} was supplied from the underneath to the catholyte room so that the concentration of NaOH is kept at 32-35 wt. %. The gap at either side of the ion-exchange membrane was maintained at 3 mm and 4 mm anode and cathode, respectively by placing Teflon tape and EPDM gaskets at the edges of the electrodes. The electrolysis was carried out at 79.7±1.5 ^{o}C, obtained by measuring the electrolyte temperature through a pinhole by a thermocouple and at constant current density of 300 mA cm^{-2}. The product caustic concentration was analyzed using the usual acid-base titration method and hence was used for calculation of the current efficiencies. Moreover, a current interruptor technique (Model 800, Electrosynthesis Corp.) was applied to find out the total overpotential over the entire cathode-anode assembly. A single point probe measurement of the specific resistivity (Rsp) of the electrodes was made by passing a current density of 1 A cm^{-2} and measuring the voltage across the vertical direction of the edge. An average of five measurements at different spots of the electrode gives the Rsp for estimating the overpotential of the cathode.

3. RESULTS AND DISCUSSION

3.1 Electrochemical tests of gas diffusion electrodes

Gas diffusion electrodes were tested in half-cell configuration in order to assess the various types, prepared by painting the diffusion layers with different concentrations of teflon dispersions. The amount of catalysts on the active layer and the teflon concentrations used as extra coating on the diffusion layer are shown in Table 1. The average catalyst loading was found to be about 8.95 with a standard deviation of 0.019, implying that these small variations could hardly result in the change of activity and stability.

Table 1. Catalyst and PTFE concentrations of the active layer.

Electrode No.	Catalyst (mg/cm^2)	Teflon (%)
1	8,95	0
2	8,96	10
3	8,92	15
4	8,96	20

Comparison of the polarization curves among the four different kinds of gas diffusion electrodes are shown in Fig. 2. Slight disparity in the performance are displayed among the electrodes with 10% teflon and without. However, electrode performance decreases with increasing amount of teflon. This is mainly attributed to the surface coverage and further insulation of the current collector by the increased concentration of teflon, especially activities recorded at high current densities. The comparison of the polarization measurements were carried out ca. one day after the electrodes attained a steady state under a cumulative load of current densities.

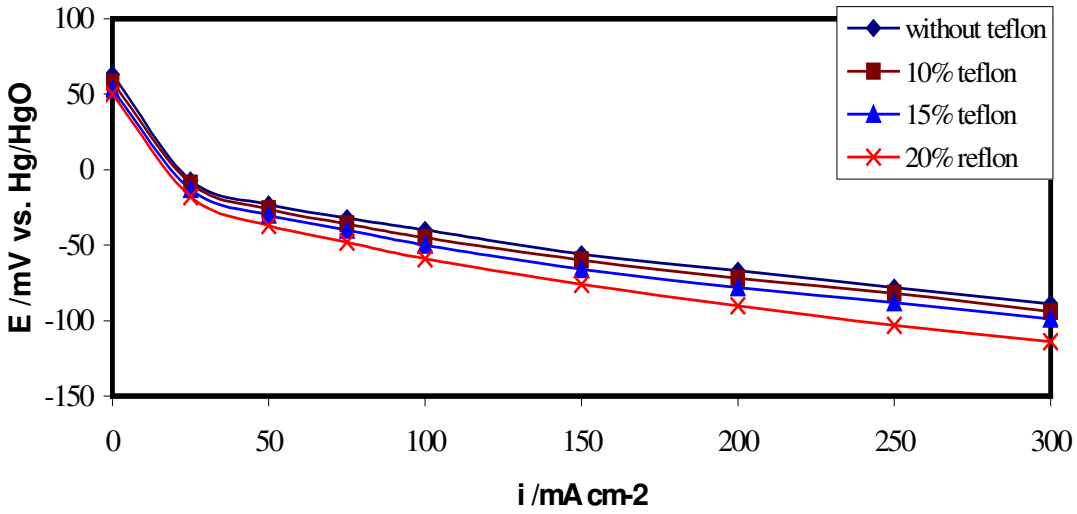

Figure 2. Polarization curves for electrodes with different teflon concentrations

Fig. 3 shows at a constant current density of 300 mA cm^{-2} and 70 ^{o}C long-term measurements on the potential versus time characteristics of the gas diffusion electrodes, having the best performances. Deionized water was supplied in order to keep the NaOH concentration as constant as possible. Initially, the electrode without teflon shows improved activity than the electrode containing 10% teflon painted at the backside of the diffusion layer. However, the durability tests show that the combination carbon+teflon and additional teflon withstands better electrode flooding phenomenon that might be caused by loss of the hydrophobic properties of the porous system of the diffusion layer and eventual intrusion of the electrolyte to the gas room.

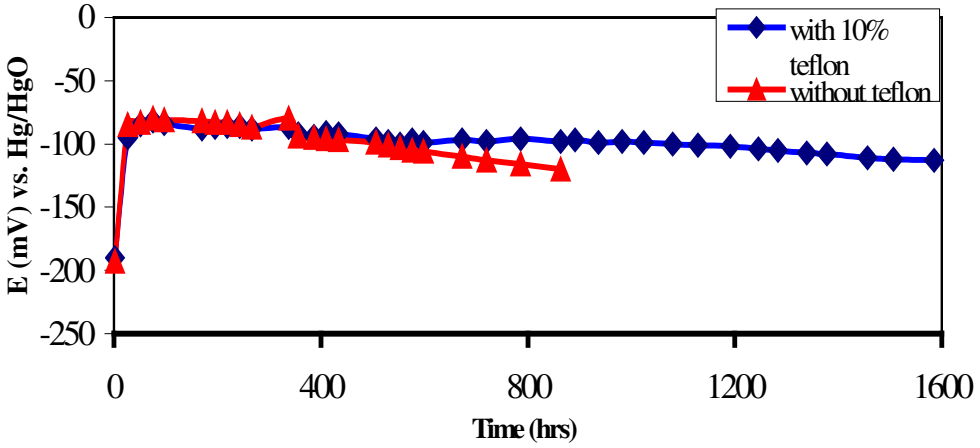

Figure 3. Potential vs. time response of the gas diffusion electrodes

The decay rate for the electrode with 10% teflon lies at 11 µV h^{-1} significantly lower than the electrode without teflon reinforcement, having 41 µV h^{-1}. These decay rates may not essentially be ascribed to the changes of the physicochemical properties of the catalyst or electrode, but to the fact that carbon dioxide from the surrounding air reacts to form carbonates. Though the reactant was pure oxygen supplied from a gas cylinder and attempts to seal the cell from the ambient air were made,

there was air/carbon dioxide coming in through some cavities due to the construction of the cell/holder components. The negative impacts of carbonate build-up on the activity and stability of the electrode are mainly due to increased viscosity leading to the change in the diffusion rate and thereby reducing the limiting current density or amount of current extracted. Moreover, depletion of OH^- ions and replacement by CO_3^{2-} ions slows down the electrode kinetics, whereas the carbonate ions also precipitate in the microporous electrode system altering the non-wetting properties of the electrodes. Therefore, it is important to remove the carbon dioxide to very low concentrations, in order to limit the interaction with the electrode/electrolyte system.

3.2 Electrolysis for the production of chlor-alkaline

A constant current density of 300 mA cm^{-2} was used to carry out the electrolysis. The voltage versus time for two similar cathodes with the distinctive gas diffusion electrodes having 10% teflon at the gas diffusion layer are shown in Fig. 4. At the start of the electrolysis, the cell voltage was found to be high, mainly due to the hydrophobic nature of the active layer, where electrolyte intrusion and establishment of the three-phase interface was not achieved. However, electrolysis shows a cell voltage between 1,98 and 2,1 V, except for cell no.1 which increases steadily after ca 300 hrs and consequently deviates from linearity. The main aspects for this increase was found to be due to the formation of blisters within the ion-exchange membrane, caused possibly due to the start-ups and shutdowns, uneven distribution of the temperature and current profile as well as shielding effects of the gas bubbles as a result of the proximity between membrane and DSA. In contrast due to the high concentrations of caustic concentrations (32-35 wt%) obtained during the length of the limited electrolysis time, current efficiencies of 92-97% were realized for the series of electrolysis conducted in this experiments. This in turn along with the low voltages affect the overall energy consumption to a significant level with energy savings of between 30 and 35% as compared to the conventional membrane process with HER.

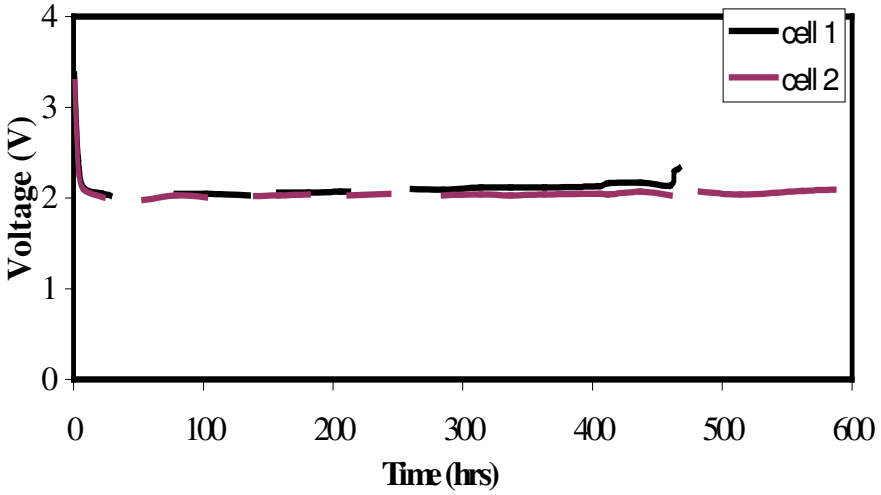

Figure 4. Cell voltage vs. time

Though the thermodynamic decomposition voltage ΔE value of the electrodes is the major component of the total cell voltage for the electrolysis, the overpotentials do considerably contribute to the overall irreversible energy losses by increasing the energy input. The total overvoltage across the anode and cathode compartments estimated using the current interruptor was found to be between 1,01-1,09 V. This value could be used to further determine the constituent parts of the other overpotentials. The specific resistance of the electrode was 0.04 Ω cm^2, which for the current density used for the electrolysis corresponds to 120 mV, while the anode overvoltage is about 100 mV (1 and the ref. within). Another irreversible contribution of 180 mV comes from the ohmic (IR) loss from the electrolytes (salt and NaOH) calculated from the actual temperatures and concentration (8,9). The rest of the overpotential 0.64 V originates from both the ion-exchange membrane and the electrode base contacts (10, 11). Therefore, there is a rationale in further reducing the overpotentials in order to cut the total energy consumption to lower levels.

4. CONCLUSIONS

This study have shown that

- improved and optimized gas diffusion electrodes, demonstrating high activity and good stability for more than 1000 hrs at a constant load of 300 mA cm^{-2},
- 10% additional teflon painted on the gas diffusion layer reinforces protection of electrolyte intrusion with stable performances,
- with the cell configuration used, electrolysis could be carried out for about 600 hrs at a current density of 300 mA cm-2 and a total voltage of ca. 2.0 V,
- the overvoltage and ohmic loss lies at about 1.0 , where high contributions emanate from electrode base contacts and membrane and
- current efficiency lies at around 92-97% in the series of electrolysis with low energy consumption and energy savings between 30-35% compared to membrane process with HER.

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