Utility of an Empirical Method of Modeling Combined Zero Gap/Attached Electrode Membrane Chlor-Alkali Cells

Clifford W. Walton
*University of Nebraska-Lincoln*

Ralph E. White
*University of South Carolina - Columbia, white@cec.sc.edu*

Follow this and additional works at: https://scholarcommons.sc.edu/eche_facpub

Part of the Chemical Engineering Commons

Publication Info
*Journal of the Electrochemical Society*, 1987, pages 565C-574C.
© The Electrochemical Society, Inc. 1987. All rights reserved. Except as provided under U.S. copyright law, this work may not be reproduced, resold, distributed, or modified without the express permission of The Electrochemical Society (ECS). The archival version of this work was published in the Journal of the Electrochemical Society.
http://www.electrochem.org/
DOI: 10.1149/1.2100894
http://dx.doi.org/10.1149/1.2100894

This Article is brought to you by the Chemical Engineering, Department of at Scholar Commons. It has been accepted for inclusion in Faculty Publications by an authorized administrator of Scholar Commons. For more information, please contact digres@mailbox.sc.edu.
Utility of an Empirical Method of Modeling Combined Zero Gap/Attached Electrode Membrane Chlor-Alkali Cells

Clifford W. Walton*

Department of Chemical Engineering, University of Nebraska-Lincoln, Lincoln, Nebraska 68588-0126

Ralph E. White*

Department of Chemical Engineering, Texas A&M University, College Station, Texas 77843-3122

ABSTRACT

An extensive survey of the Docktor-Ingenieur Dissertationen of Jakob Jörissen and Klaus-R. Menschig, both originally from the Universität Dortmund, is presented in regard to the empirical modeling of membrane chlor-alkali cells and how it can be applied to a combined zero gap/attached porous electrode layer membrane cell. Particular emphasis is placed on Menschig’s work on zero gap (ZG) and attached porous electrode layer (APEL) membrane chlor-alkali cells, the first such research to appear in the open literature. Menschig developed various computer programs to characterize these ZG and APEL membrane chlor-alkali cells. He characterized these cells by using the following parameters: the current density distribution over the membrane, the species concentrations on the membrane surfaces, equivalent diffusion layer thicknesses for the mesh electrodes/current collectors and attached porous electrode layers, and the electrode overpotentials and equilibrium potentials using the surface concentrations for the ZG and APEL cell configurations. He used empirical equations for both ZG and APEL type cells holistically with his own experimental observations for a cell which used Nafton 390, a bilayer perfluorosulfonic acid membrane, to determine values for these parameters. His empirical relations describe the dependence of the flux of OH⁻ from catholyte to anolyte as a function of catholyte caustic concentration (C_{\text{NaOH}}) and the membrane potential drop as a function of catholyte caustic (C_{\text{NaOH}}) and anolyte salt concentrations (C_{\text{NaCl}}). By using the experimental values for total cell potential, current density, and cell outlet concentrations with the empirical equations, Menschig calculated values for the characteristic parameters mentioned above. He used these values and other information (e.g., membrane and porous electrode layer conductivity) to predict the total cell potential for the ZG configuration. With prior knowledge of total cell potential and current efficiency for corresponding APEL and ZG cell configurations, membrane surface concentrations were derived and used in the prediction of total cell potential for a combined zero gap/attached electrode cell.

Background

Electrolysis cells which contain ion selective membranes are constructed in three primary configurations: the gap cell or zero gap cell, and so-called solid polymer electrolyte (SPE) cell. Figure 1 shows a gap cell version of a chlor-alkali membrane cell (as in Ref. (1)), which has a space (i.e., a gap) filled with electrolyte between the membrane surface and each electrode. Figure 2 shows a schematic of just the electrode-membrane construction of a zero gap (ZG) cell, where both electrode surfaces have been placed directly against the membrane. The electrodes of a zero gap cell are made of expanded metal or wire mesh (which may have a catalytic layer applied to its surface) backed by an expanded metal current collector that enables the gas bubbles to escape from the electrode surface. Figure 3 illustrates what is referred to by some authors in the literature as a SPE electrode construction which is actually two porous catalyzed electrode layers which have been attached to the surface of the membrane itself (this will be called an attached porous electrode layer, or APEL, cell). Pressed against each porous electrode layer is a fine grid mesh backed by a resilient mat of fine wire which is pressed in by a perforated plate current collector. This provides a path for even current distribution across the surface of the entire electrode. Both the ZG and APEL type cells have the immediate advantage of reducing the potential drop across the cell over that found in a gap cell since the distance between opposing electrodes is reduced significantly.

Various methods and models have been developed to evaluate ion exchange membrane behavior and to relate this behavior to the design of membrane chlor-alkali cells. One approach has been to use empirical relations derived from experimental data to describe various characteristics of a membrane cell (2, 3), such as the correlation of caustic current efficiency (that percentage of the applied cell current that goes to the actual production of sodium hydroxide at the cathode) or the loss of OH⁻ from the catholyte at the membrane surface (C_{\text{NaOH}}). These relations are then used in conjunction with additional experimental data to predict such things as the outlet concentrations of a cascade arrangement of electrolytic gap cells (2) or the concentrations on the membrane surface (3).

This paper presents the essence of the empirical approach to membrane cell modeling as done by Jörissen (2) and Menschig (3) and how these methods can be used to evaluate the chlor-alkali cells currently being developed. Jörissen’s primary objective was to develop a computer model which could be used as a basis for economic evaluation and process optimization of a chlor-alkali electrolyzer with cascade connection of membrane cells. Menschig’s goals were to determine experimentally any differences between APEL and ZG cells with respect to the cell voltage and current efficiencies, to characterize empirically these cells, and to develop criteria for the selection of a practical electrolyzer for chlor-alkali production. Menschig predicted from his results that a combined porous anode layer (PAL) and zero gap cathode (ZGC) cell (together referred to as a PAL/ZGC cell) had the potential of saving the most energy (3). It is important to note that this proposed configuration was based on earlier, less efficient membranes which allowed excessive loss of OH⁻ from the catholyte to the anolyte.

*Electrochemical Society Active Member.
From his experimentally derived species concentrations on the membrane surface of the ZG and APEL cells, Menschig predicted a current efficiency of only 74.2% based on caustic production for his hypothetical PAL/ZGC cell. Newer bilayer membranes made with perfluoroalkoxy acid functional groups in the layer toward the cathode and perfluorosulfonic acid functional groups toward the anode have greatly reduced the problem of the loss of OH−, yielding caustic current efficiencies up to 94% in gap cells (4, 5). These newer membranes could make it possible to use attached porous cathode and/or anode layers. This led to an interest in the combination of zero gap and attached porous electrode layers, either as anode/cathode or cathode/anode combinations, respectively. These will be referred to as the zero gap anode/attached porous cathode layer (ZGA/PCL) or attached porous anode layer/zero gap cathode (PAL/ZGC) configurations. Since Menschig uses many of the relations for gap membrane cell behavior (as derived by Jörisse), for his evaluation of the ZG and APEL configurations, Jörisse's work is reviewed first, followed by an extensive development and analysis of Menschig's work which includes examples of his calculations. Next, the direct application to present membranes could make it possible to use attached porous cathode and/or anode layers. This led to an interest in the combination of zero gap and attached porous electrode layers, either as anode/cathode or cathode/anode combinations, respectively. These will be referred to as the zero gap anode/attached porous cathode layer (ZGA/PCL) or attached porous anode layer/zero gap cathode (PAL/ZGC) configurations. Since Menschig uses many of the relations for gap membrane cell behavior (as derived by Jörisse), for his evaluation of the ZG and APEL configurations, Jörisse's work is reviewed first, followed by an extensive development and analysis of Menschig's work which includes examples of his calculations. Next, the direct application to present membrane cells is presented and conclusions drawn.

Jörisse's Work

As mentioned previously, Jörisse was interested primarily in developing empirical relations to describe a gap membrane chlor-alkali electrolysis cell in order to construct a material balance program which describes the performance of a cascade of gap cells in various connections, such as concurrent or countercurrent flows of anolyte and catholyte (2). He derived specifically empirical relations from experimental data to describe the chlorine and caustic current efficiencies, by-product formation (the accumulation of which is a problem of the cascade arrangement of cells), water transport through the membrane, and the cell potential.

Development.—In Jörisse's experimental work, he used a Nafion™ 355 membrane, which is a bilayer perfluorosulfonic acid membrane with the following construction: inner diameter 52 mm, 1500 equivalent weight layer (cathode side), 4.0 ml (0.1 mm) 1100 equivalent weight layer, and T-25: Teflon™ scrum with 70% free membrane surface.

All of his experiments were carried out at steady-state conditions, allowing a minimum of 4h to reach that condition and then data were collected over another 4h period. Figure 4 shows a diagram of his experimental apparatus. The inner diameter of the cell was 52 mm, the length of each half-cell was 40 mm (i.e., an electrode to electrode gap of 80 mm), the membrane surface area was 21.2 cm², and the cell volume including the overflow connections was 90 ml for each chamber (2). The anode was a titanium plate coated with mixed ruthenium oxide and the cathode was a plate of Y4A steel. Each half-cell was mixed using a magnetic stirrer. The cell was operated at 3000 A/m² and 80°C. Anode, cathode, and membrane potentials were measured using movable Luggin capillaries. The deliberately large interelectrode distance allowed the separation of the cell potential into its individual components (2).

In his analysis, Jörisse used a factorial experimental design to obtain the information needed to formulate empirical models to describe cell behavior based on the assumption that each half-cell was well mixed. This assumption means that there is no effective boundary layer on the membrane surface and therefore the empirical relations describing the membrane can be based on the bulk concentrations of the chemical species. He used regression analysis to determine which effects were significant, while ignoring interactions among more than two parameters. Statistical methods were used to determine the best models, retaining only the effects of the highest significance. Several of the model equations produced did not have a theoretical basis for the relationship obtained by the statistical evaluation (2), i.e., a standard form, such as a linear or quadratic model, was used rather than a complex relationship derived from theory.

The derived expression for the transport of OH− from the catholyte through the membrane to the anolyte (typically called back-migrating OH−) is [p. 55 of Ref. (2)]

\[ N_{\text{back}} = 5.42 + 4.44c_{\text{NaOH}} - 0.125c_{\text{NaOH}}^2 \]  
\[ (0 < c_{\text{NaOH}} < 18) \]  

where \( N_{\text{back}} \) = OH− flux through the membrane (mol/m²·s) and \( c_{\text{NaOH}} \) = bulk NaOH concentration in the catholyte (mol/L). Note Eq. [1] applies only to Nafion 355 at 3000 A/m² and 80°C. Anolyte by-product models include such things as the formation of active chlorine (as hypochlorite) given as [p. 65, 66 of Ref. (2)]

\[ c_{\text{A,act}} = 0.00705 + 0.000407c_{\text{A,non}} - 0.000449c_{\text{A,Y}} \]  
\[ (0 < c_{\text{A,non}} < 20) \]  

Note Eq. (1) applies only to Nafion 355 at 3000 A/m² and 80°C. Anolyte by-product models include such things as the formation of active chlorine (as hypochlorite) given as [p. 65, 66 of Ref. (2)]

\[ c_{\text{A,act}} = 0.00705 + 0.000407c_{\text{A,non}} - 0.000449c_{\text{A,Y}} \]  
\[ (0 < c_{\text{A,non}} < 20) \]  

where \( N_{\text{back}} \) = OH− flux through the membrane (mol/m²·s) and \( c_{\text{NaOH}} \) = bulk NaOH concentration in the catholyte (mol/L).
or
\[ c_{\text{AUMoC}} = -c_{\text{A催}} h^+ + (0.00705 - 0.000449c_{\text{A催}}) \exp(30.3c_{\text{H催}} h^+) \quad \text{(for } c_{\text{A催}} h^+ < 0) \quad [3] \]

where \( c_{\text{A催}} \) is active chlorine concentration in anolyte (mol/l), \( c_{\text{A催}} h^+ = H^+ \) ion excess in anolyte (mol/l) (OH\(^-\) ion excess is expressed as a negative value of \( c_{\text{A催}} h^+ \)), and \( c_{\text{A催}} \) is total concentration of dissolved material in anolyte (mol/l NaCl + NaClO\(_3\) + HCl + HOCl + Cl\(_2\) (aq)) (calculated from the sum of analyzed values for NaCl + NaClO\(_3\) + HCl + NaOH + Cl\(_2\) (aq)). Additional empirical relations are given for oxygen and chlorate (ClO\(_3\)) formation under acidic or alkaline conditions of the anolyte.

Jörisen also gives relations that fit the water transport through and the potential drop across the membrane. His statistical analysis showed that the water transport was affected significantly by only the Na\(^+\) ion transport across the membrane and the dissolved species concentration in the anolyte, giving the equations [p. 91 of Ref. (2)]

\[ N_{\text{net H2O}} = N_{\text{H2O}} - N_{\text{H2O}} \quad [4] \]

\[ N_{\text{H2O}} = h - N_{\text{H2O}} \quad [5] \]

\[ h = 9.47 - 0.826c_{\text{A催}} h^+ - 0.0222N_{\text{A催}} \quad [6] \]

where \( N_{\text{net H2O}} \) is net water transport (mol H\(_2\)O/m\(^2\)-m\(^3\)) (net quantity of water moving from anode to cathode chamber), \( N_{\text{H2O}} \) is water transport through the membrane (mol H\(_2\)O/m\(^2\)-m\(^3\)) (net water transport + water for back-migrating OH\(^-\) ions), \( h \) is average hydration number for Na\(^+\) ions during migration from anode to cathode chamber (mol H\(_2\)O/mol Na\(^+\)), and \( N_{\text{H2O}} \) is Na\(^+\) ion transport through the membrane (mol Na\(^+\)/m\(^2\)-m\(^3\)). Jörisen hypothesizes that the behavior which produces Eq. [4]-[6] indicates that membrane properties do not influence the net water transport when the maximum water transport has not been attained. That is, when the concentration of Na\(^+\) ion in the anolyte is high, complete hydration shells cannot be formed, reducing the average hydration number, and therefore the water transport across the membrane is below its maximum (2). His equation for the membrane potential drop is [p. 115 of Ref. (2)]

\[ \Delta U_{\text{Mem}} = 0.0668 + 0.02555 \cdot C_{\text{CNOSCH}} \cdot c_{\text{A催}} \quad [7] \]

where \( \Delta U_{\text{Mem}} \) is potential drop in and on the membrane under uniform current density (V). He also developed expressions for the electrode overpotential, equilibrium potential, and IR drop in each electrolyte layer.

Present application—The remainder of Jörisen’s work deals with his model of systems of cascade cells with various flow configurations using the previously mentioned empirical relations. He hypothesizes that, in their qualitative form, his empirical relations are not dependent on the type of membrane or cell construction (2). If this were true, then the forms of his equations could be applied to available data for zero gap (ZG), attached porous electrode layer (APEL, i.e., both electrodes are porous layers which are physically attached to the membrane), and combination (ZGA/PCL or PAL/ZGC) cells using standard statistical methods of regression. The greatest problem with this approach is that Jörisen used bulk concentrations instead of concentrations at the membrane surfaces, which would be expected to be significantly different from their bulk values. The use of this approach is discussed further in conjunction with Menschig’s work (3).

Menschig’s Work

Menschig is apparently the first researcher to report work on ZG and APEL cells in the open literature (3). Menschig’s objective was to determine if there exists any significant differences in cell behavior between the two configurations by performing experiments on a laboratory scale cell and analyzing the results using empirical models, both his and those of Jörisen. To meet his objective, Menschig characterized the cells in terms of current density distributions, cell potential, caustic current efficiency, species concentrations at the surfaces of the membrane, overpotentials for the ZG cell, and electrode equilibrium potentials based on the species concentrations at the membrane surfaces. Ultimately, Menschig wanted to develop selection criteria for a practical, optimized chlor-alkali electrolyzer.

Development

Figure 5 shows the construction of Menschig’s experimental apparatus. The membrane used was Nafion 390, which is similar to the membrane used by Jörisen, having the same layers, but a different construction of the scrim (total thickness was 0.33 mm, determined by micrometer). Two different mesh sizes were used for the ZG and APEL cells. For the APEL cells, the corresponding ZG cell meshes were used as intermediate current distributors by being pressed against the porous electrode layers attached to the membrane. All meshes were made of a platinum-10% iridium alloy. Mesh I had a wire diameter of 0.12 mm and 225 openings/cm\(^2\) (open width between wires: 0.55 mm), while Mesh II had a wire diameter of 0.25 mm and 100 openings/cm\(^2\) (open width between wires: 0.75 mm). The two mesh types used are shown in Fig. 6. Both cell configurations used machined metal backing plates (3 mm thick, 70% open) as current collectors which were connected to the terminal leads. The porous electrode layers for the APEL cells were...
formed by electroplating platinum onto the membrane surface (6) and were assumed to have an effective surface area of 100 cm$^2$/cm$^2$ of membrane surface (3, 6). (Note the actual surface area of the porous electrode layer was not measured.)

The cells were operated at steady state with the following experimental conditions being maintained: cell temperature, 80°C; superficial current density, 6500 A/m$^2$; anolyte NaCl concentration, 17.5 weight percent (w/o) (3.28 mol/l); OH$^-$ excess in the anolyte, 0.375 w/o; catholyte NaOH concentration, 20.0 w/o (5.92 mol/l); anode pressure against the membrane, 0.69 bar. The inlet brine feed was a saturated salt solution with concentrations of Ca$^{2+}$ and Mg$^{2+}$ reduced below 0.5 ppm. In order to maintain the OH$^-$ concentration in the anolyte at a constant value, 20 w/o HCl was added by a separate stream at the rate of 40.57 and 24.41 mol/h-m$^2$ for the APEL and ZG configurations, respectively. Measurements were taken continuously over a 3h period after steady state had been reached.

Three computer programs were used to analyze the experimental data in order to obtain values for the characterizing parameters mentioned above. The first program (6MODZ and its subprograms) is used to calculate the current density distribution over the membrane attached to a porous catalytic electrode layer. The second program (ME-NETZP) can be used to calculate a correction factor (what is called $f_{max}$ in this paper) for determining the potential drop across the membrane.”

Menschig also determined equivalent boundary layer thicknesses to represent the porous electrode layers and the mesh electrodes, producing two boundary layers for the ZG cell (one on each side of the membrane) and four for the APEL cell (see Fig. 7). He assumed that the boundary layer representing the mesh against the porous layer of the APEL cell would be the same thickness as that for the same mesh type in the ZG cell configuration. The details of how he derived these boundary layer thicknesses are given under the description of program ME-MODV below.

**Menschig’s Programs**

**Current density/potential distribution for an APEL cell.**—To determine the degree of the nonuniform potential and current distributions over the membrane surface in ZG and APEL cell configurations, Menschig first formulated a mathematical model to calculate the potential and current distributions over a membrane using an equivalent resistance network to simulate the resistances of the mesh wires, porous electrode layer, and membrane (see Fig. 8). He found many difficulties in trying to solve the three-dimensional problem for the ZG configuration and ultimately used a different two-dimensional approach (3, 6). Therefore, program 6MODZ applies only to the APEL configuration. The original program was written using a form of BASIC used by the Hewlett Packard 2000 computer. The program has now been rewritten in FORTRAN 77 for greater portability. The input data consists of membrane conductivity data at the outlet stream conditions, conductivity data for the catalyzed porous electrode layers, wire conductivity data, wire diameter, open width between wires in mesh, and applied mean current density (i.e., current density based on the superficial membrane surface area). Menschig used a specific resistance for platinum at 80°C of 1.18 × 10$^{-4}$ Ω-cm and an assumed value of 20 Ω/cm$^2$ for his porous platinum layer (3).

![Fig. 7. Model of the diffusion layers on an APEL cell membrane [from Ref. (3)].](image)

![Fig. 8. Equivalent circuit diagram of an APEL cell [from Ref. (3)].](image)
Menschig could not solve the three-dimensional representation of the ZG cell configuration, he developed a two-dimensional model of parallel wires on opposite sides of the membrane (i.e., he ignored the "cross" wires in the mesh on either side of the membrane). He then formulated an equation to describe the potential drop between two facing wires and extended this to include the interaction of adjacent wires on both sides of the membrane. This results in an analytical solution for the potential drop across the membrane for a ZG configuration, which is [p. 73 of Ref. (3)]

\[ \Delta U_{\text{ZG}} = \frac{b i_n}{\kappa} \]  

where \( \Delta U_{\text{ZG}} \) is the potential drop across the ZG membrane for a mesh of configuration \( j \) (V), \( i_n \) = mean current density (A/m²), \( L_j \) = mesh width (center to center distance between two parallel wires) (m), \( \kappa \) = specific membrane conductivity (1/Ω-m). When Menschig assumed a uniform potential distribution across the membrane, he used Ohm's law to obtain his Eq. [G1.15] [p. 50 of Ref. (3)], which is

\[ \Delta U_{\text{MC}} = \frac{b i_n}{\kappa} \]  

Selecting program output:

<table>
<thead>
<tr>
<th>Node</th>
<th>Driving voltage [V]</th>
<th>Current through the membrane [A]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.68*4729E + 00</td>
<td>0.40*4862E - 04</td>
</tr>
<tr>
<td>2</td>
<td>0.68*4729E + 00</td>
<td>0.40*4862E - 04</td>
</tr>
<tr>
<td>3</td>
<td>0.68*4729E + 00</td>
<td>0.40*4862E - 04</td>
</tr>
<tr>
<td>4</td>
<td>0.68*4729E + 00</td>
<td>0.40*4862E - 04</td>
</tr>
<tr>
<td>5</td>
<td>0.68*4729E + 00</td>
<td>0.40*4862E - 04</td>
</tr>
<tr>
<td>6</td>
<td>0.68*4729E + 00</td>
<td>0.40*4862E - 04</td>
</tr>
<tr>
<td>7</td>
<td>0.68*4729E + 00</td>
<td>0.40*4862E - 04</td>
</tr>
<tr>
<td>8</td>
<td>0.68*4729E + 00</td>
<td>0.40*4862E - 04</td>
</tr>
<tr>
<td>9</td>
<td>0.68*4729E + 00</td>
<td>0.40*4862E - 04</td>
</tr>
<tr>
<td>10</td>
<td>0.68*4729E + 00</td>
<td>0.40*4862E - 04</td>
</tr>
<tr>
<td>11</td>
<td>0.68*4729E + 00</td>
<td>0.40*4862E - 04</td>
</tr>
<tr>
<td>12</td>
<td>0.68*4729E + 00</td>
<td>0.40*4862E - 04</td>
</tr>
<tr>
<td>13</td>
<td>0.68*4729E + 00</td>
<td>0.40*4862E - 04</td>
</tr>
<tr>
<td>14</td>
<td>0.68*4729E + 00</td>
<td>0.40*4862E - 04</td>
</tr>
<tr>
<td>15</td>
<td>0.68*4729E + 00</td>
<td>0.40*4862E - 04</td>
</tr>
<tr>
<td>16</td>
<td>0.68*4729E + 00</td>
<td>0.40*4862E - 04</td>
</tr>
<tr>
<td>17</td>
<td>0.68*4729E + 00</td>
<td>0.40*4862E - 04</td>
</tr>
<tr>
<td>18</td>
<td>0.68*4729E + 00</td>
<td>0.40*4862E - 04</td>
</tr>
<tr>
<td>19</td>
<td>0.68*4729E + 00</td>
<td>0.40*4862E - 04</td>
</tr>
<tr>
<td>20</td>
<td>0.68*4729E + 00</td>
<td>0.40*4862E - 04</td>
</tr>
<tr>
<td>21</td>
<td>0.68*4729E + 00</td>
<td>0.40*4862E - 04</td>
</tr>
<tr>
<td>22</td>
<td>0.68*4729E + 00</td>
<td>0.40*4862E - 04</td>
</tr>
<tr>
<td>23</td>
<td>0.68*4729E + 00</td>
<td>0.40*4862E - 04</td>
</tr>
<tr>
<td>24</td>
<td>0.68*4729E + 00</td>
<td>0.40*4862E - 04</td>
</tr>
</tbody>
</table>

Table II. Example of the determination of the correction factor for the membrane potential of a ZG cell

The following is a simulated run of the program ME-NETZP using the data for Mesh I (with wires center to center on opposite sides of the membrane)

Input for Mesh type 1:

| Wire diameter in [mm]| 0.12 |
| Gap between wires in [mm]| 0.55 |

Are nets offset on either side of membrane (Y/N)? Y

How many wires across entire electrode (use min 100)? 100

Result:

The factor \( f_{\text{MC}} \) is 0.490924.

\[ f_{\text{MC}} = \frac{2\pi b}{L_j \cdot \ln \left( \frac{\kappa}{\kappa^*} \right)} \]  

\[ f_{\text{MC}} = 0.67 \cdot \Delta U_{\text{ZG}} \]  

\[ f_{\text{MC}} = 0.6 \cdot \Delta U_{\text{ZG}} \]  

where the ohmic potential drop of an APEL cell is lower than for a ZG cell using the same mesh, current density, and specific membrane conductivity (e.g., for Mesh I, the membrane potential drop for the APEL cell is 87% of the equivalent ZG cell as shown in Eq. [12]). Also, the potential drop of a ZG membrane increases with increasing mesh spacing (recall that Mesh II has a larger spacing than Mesh I).
Characterizing parameters for ZG and APEL cells.—Menschig developed the ME-MODV program to analyze his experimental data to determine species concentrations on the membrane surfaces, membrane potential, effective boundary layer thicknesses, and electrode overpotentials and open-circuit potentials based on these surface concentrations. He used the empirical equations developed by Jörissen to describe the behavior of his membrane, that is, Eq. [1] for the OH⁻ flux through the membrane and Eq. [7] for the membrane potential. Menschig applied a scaling factor to these relations, because Jörissen used a current density of 3000 A/m² while he used 6500 A/m². Akin (7) found that the caustic current efficiency of Nafion 300 was independent of the current density in the range of 2 kA/m² to 6.5 kA/m², so the flux of OH⁻ across the membrane changes (at least approximately) in proportion to the current density (3), giving [p. 45, of Ref. (3)]

\[
\frac{N_{\text{OH}^-}(i_g)}{N_{\text{OH}^-}(i_s)} = \frac{i_s}{i_g}
\]

where \(i_s\) is current density for Eq. [1] (3000 A/m²) and \(i_g\) is new mean current density (A/m²). Menschig also assumed that his membrane had constant electrical resistance over the range of current density used in his and Jörissen's work, so that the membrane potential drop is also scaled as [p. 45 of Ref. (3)]

\[
\Delta U_{\text{MCDO}}(i_g) = \frac{i_g}{i_s} \cdot \Delta U_{\text{MCDO}}(i_s)
\]

Equilibrium potentials were calculated using activity coefficients based on local concentrations with only the Cl⁻ discharge reaction considered at the anode. The anode overpotential was calculated from the regression equation (8) [p. 48 of Ref. (3)]

\[
\eta_a = \frac{i_s + 1000}{45,200} \ln \frac{i}{i_s} - 0.11
\]

(for 80°C, 25 w/o NaCl) and the cathode (hydrogen) overpotential was calculated from the regression equation

\[
\eta_c = \frac{-5.34}{8.16} \ln \frac{i_g}{i_s} + 0.11
\]

where \(i_c\) is the current density based on the actual electrode surface area (A/m²), obtained using the data presented by Vetter (9).

Menschig obtained the diffusion layer thicknesses from Vogt's mass transport model (10) for smooth gas-evolving electrodes. Vogt gives the following equation for the diffusion layer [p. 77 of Ref. (3)]

\[
Sh = f_v \cdot 0.925 \cdot \text{Re}^{0.5} \cdot \text{Sc}^{0.47}
\]

where \(f_v\) had a value of 0.3785 [which is 1/FVOGT, the factor which is given by the program ME-MODV (3, 6)]. Menschig assumed that the correction factor was the same for both the anode and cathode sides (for the same mesh type).

An alternate method for determining the diffusion layer thicknesses representing the electrodes can be obtained using the bulk and surface concentrations in the kinetic expressions given by Vetter (9). Under 100% chlorine and caustic current efficiencies (8), the anode diffusion layer thickness, \(\delta_a\), formed during the electrochemical reaction due to transport to the anode is approximated by [p. 48 of Ref. (3)]

\[
\delta_a = \frac{2zFD_{\text{Cl}^-}}{(\text{c}_{\text{M},\text{Cl}^-} - \text{c}_{\text{M},\text{Cl}^-})} \frac{i}{i}
\]

while the diffusion layer thickness for the cathode, \(\delta_c\), is approximated by

\[
\delta_c = \frac{zFD_{\text{OH}^-}}{(\text{c}_{\text{M},\text{OH}^-} - \text{c}_{\text{M},\text{OH}^-})} \frac{i}{i}
\]

Procedure used by program ME-MODV.—In order to determine the characterizing parameters, such as the species concentrations on the membrane surfaces, equivalent diffusion layer thicknesses for the mesh electrodes/ current collectors and porous electrode layers, and the electrode overpotentials and equilibrium potentials using the surface concentrations, the program ME-MODV requires applied current density, current collectors and porous electrode layers, and the electrode overpotentials and equilibrium potentials using the surface concentrations, the program ME-MODV requires applied current density, current collectors and porous electrode layers, and the membrane, and total experimental cell potential, in addition to the two empirical relations of Jörissen (Eq. [1] and [7] in this paper). The program first solves for the diffusion layer thicknesses according to Eq. [18], then determines the characterizing parameters for the APEL configuration, followed by the determination of those parameters for the ZG configuration.

The calculations for the APEL configuration are begun with the determination of the membrane surface concentration of NaOH on the cathode side, \(c_{\text{M},\text{NaO}^-}\), by solving for \(c_{\text{M},\text{NaO}^-}\) in Eq. [1] in conjunction with Eq. [14]. Note that \(c_{\text{M},\text{NaO}^-}\) is the NaOH concentration on the membrane surface since Eq. [1] was based on the assumption that no diffusion layer existed in the experimental configuration used to obtain the empirical relation. Next, the chlorine current efficiency, OH⁻ flux through membrane from catholyte to anolyte (derived from the above factors), and others current efficiency, bulk outlet concentrations, membrane surface area, actual surface area of electrode mesh per unit surface area of membrane, attached porous electrode layer surface area per unit surface area of membrane, and total experimental cell potential, in addition to the two empirical relations of Jörissen (Eq. [1] and [7] in this paper). The program first solves for the diffusion layer thicknesses according to Eq. [18], then determines the characterizing parameters for the APEL configuration, followed by the determination of those parameters for the ZG configuration.
potential drop for the APEL cell (△U_{APEL}) is determined. Using this value with Eq. [7], modified by Eq. [15], the concentration of NaCl on the membrane surface, C_{AM,NaCl}, is obtained. An iterative procedure is now used to recalculate the equilibrium and overpotentials and C_{AM,NaCl} until a converged answer is obtained.

Next, the program solves for the characterizing parameters for the ZG configuration, solving for C_{AM,NaOH} by again using Eq. [1] in conjunction with Eq. [14]. Then an average of the bulk and membrane surface concentration of NaOH is used to determine the physical properties of the electrolyte surrounding the zero gap electrode. These properties are used to calculate the diffusion layer thickness representing the zero gap cathode by Eq. [21], using a value for \( i \) obtained by correcting the mean current density by the caustic current efficiency. From this value (\( \delta_{ZGC} \)) and the diffusion layer thickness for a flat plate cathode (\( \delta_{FPC} \)) obtained from Eq. [18], the correction factor, \( f_v \), is obtained from

\[
f_v = \frac{\delta_{FPC}}{\delta_{ZGC}}
\]

and used in Eq. [19] to calculate the diffusion layer thickness related to the zero gap anode (\( \delta_{ZGA} \)). (Note the program uses the factor called FVOGT, which is the inverse of \( f_v \).) Next, C_{AM,NaOH} is calculated iteratively using Eq. [20], starting with an initial guess which is averaged with the bulk concentration of NaCl (C_{AM,NaCl}) to determine the physical properties at the zero gap anode. Finally, the zero gap electrode equilibrium and overpotentials are calculated using the concentrations obtained above.

Also, Menschig calculates the membrane potential drop by two methods, one using the correction factor \( f_v \) obtained experimentally with those obtained from Eq. [11] with Eq. [7], [10], and [15] and the other, "experimental" value obtained by solving for \( \Delta U_{ML} \) using the experimental ZG cell potential with the physical properties at the zero gap anode, solving for the characterizing parameters.

### Table III. Example of the characterizing parameters for an APEL and a ZG cell

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH: 20.0 w/o (5.92 mol/l)</td>
<td></td>
</tr>
<tr>
<td>Total current: 18.38A</td>
<td></td>
</tr>
<tr>
<td>Chlorine current efficiency: 0.837</td>
<td></td>
</tr>
<tr>
<td>Relative area of Mesh I: 1.131</td>
<td></td>
</tr>
<tr>
<td>Back migrating OH- for APEL cell: 0.252 mol/h</td>
<td></td>
</tr>
<tr>
<td>Experimental total APEL cell potential: 3.94V</td>
<td></td>
</tr>
<tr>
<td>True surface area of porous electrode per unit membrane area: 100 cm²/cm²</td>
<td></td>
</tr>
<tr>
<td>Back migrating OH- for ZG cell: 0.1769 mol/h</td>
<td></td>
</tr>
<tr>
<td>True surface area of Mesh I per unit membrane area: 1.131 cm²/cm²</td>
<td></td>
</tr>
<tr>
<td>Experimental total ZG cell potential, Mesh I: 4.22V</td>
<td></td>
</tr>
<tr>
<td>Experimental total ZG cell potential, Mesh II: 4.41V</td>
<td></td>
</tr>
</tbody>
</table>

The results are as follows:

**Results for APEL (SPE) cell configuration:**

\[
\Delta U_{APEL} = C_{AM,NaCl} \cdot 1.602475V \quad C_{AM,NaOH} \cdot 2.142384 \text{ mol/l} \\
\epsilon_{1} = 1.534362V \quad \epsilon_{2} = -0.9831623V \quad \eta_{1} = 0V \quad \eta_{2} = 0V
\]

**Results for ZG cell configuration:**

\[
\Delta U_{ZG} = \frac{C_{AM,NaCl} \cdot 1.1792V \cdot 1.695V}{1.871335V} \quad \Delta U_{ZG} = \frac{2.866343 \text{ mol/l}}{6.458219 \text{ mol/l}}
\]

\[
\epsilon_{1} = -0.9325033V \quad \epsilon_{2} = 0.392327V \quad \eta_{1} = -0.2963566V \quad \eta_{2} = 0.367298E - 03V \quad \eta_{2} = -0.2561314V
\]

**Diffusion layer thicknesses:**

\[
\delta_{i} \text{ from Eq. [18]} \quad \delta_{1} \text{ from Eq. [18]} \\
\delta_{i} = 0.0024 \text{ cm} \quad \delta_{1} = 0.00123 \text{ cm} \\
\delta_{i} = 0.00591 \text{ cm} \quad \delta_{1} = 0.00325 \text{ cm} \\
\delta_{i} = 0.005 \text{ cm} \quad \delta_{1} = 0.009 \text{ cm}
\]

**FVOGT:** [unitless]

\[
\delta_{i} = 0.01169 \text{ cm} \quad \delta_{1} = 0.03762 \text{ cm}
\]
with the zero gap correction factor, $f_{MZ}$, he obtained $\Delta U_{MZ}$, the potential drop for a ZG membrane, by using Eq. [10]. Menschig then averaged these two membrane potential drops and called the result the membrane potential drop for the combined cell. Using this value with the equilibrium potentials and overpotentials, again from the corresponding APEL and ZG cell configuration, a potential balance predicted a total cell potential of 3.66V for Mesh 1 (225 openings/cm$^2$) at 6500 A/cm$^2$.

**Application to Combined Cell Configurations**

Menschig's work has limited application to combined zero gap/attached porous electrode layer configurations. His method can be used to predict the total cell potential of a ZG cell configuration, given the necessary empirical correlations. Also, the cell potential of combined cells can be predicted by first having experimental data on the corresponding ZG and APEL cells, based on Menschig's assumption that each half of a combined cell will perform like its corresponding half of a ZG or APEL cell. His methods can be used as described previously to characterize the ZG, APEL, and combined cells (ZGA/PCL and PAL/ZGC) in terms of current density distributions (under his limiting assumptions), species concentrations at the surfaces of the membrane, and overpotentials and electrode equilibrium potentials based on local species concentrations near the membrane surfaces.

Menschig's method requires experimental data for the particular membrane in a gap cell at a set current density and temperature for various combinations of cell outlet concentrations of NaOH and NaCl. Empirical relations describing the flux of OH$^-$ across the membrane from catholyte to anolyte (i.e., the caustic current efficiency) and the membrane potential drop must be derived from this data, producing equations corresponding to Eq. [1] and [7]. Since these relations are used to obtain the concentrations on the membrane surfaces, they must be functions of these surface concentrations. As noted previously, Menschig used Jørissen's equations which were derived under the assumption that each half-cell of Jørissen's gap cell was well mixed and that there was no significant diffusion layer on the membrane surface. Therefore, Jørissen could construct his correlations using his bulk concentrations, assuming that these were approximately the same as those on the surface of the membrane. Since concentrations on the membrane surfaces cannot be measured directly, the experimental gap cell which is used to obtain the necessary data to develop the correlations must be designed and operated so as to minimize any diffusion layers on the membrane surfaces.

These empirical equations combined with the additional information listed in Table IV allow the prediction of the total cell current for a ZG cell at a specified catholyte caustic and anolyte salt outlet concentration (for the same current density). Next, by knowing the total cell potential for the corresponding APEL configuration, the surface concentrations needed to estimate the membrane potential of a combined cell can be obtained. The surface concentrations from the ZG and APEL cells can then be used with the empirically derived equivalent to Eq. [7] to obtain the equivalent membrane potential for an APEL cell at these surface concentrations. This value, $\Delta U_{M_{APEL}}$, is then corrected using $f_{MZ}$ derived from the program ME-NETZP and Eq. [11] to obtain $\Delta U_{MZ}$. These two membrane potentials are averaged and combined with the electrode overpotentials and equilibrium potentials to predict the total cell potential of the combined cell, just as described previously.
Membrane thickness
Membrane conductivity data at the outlet stream conditions
Membrane surface area
Actual surface area of electrode mesh per unit surface area of membrane
Porous electrode surface area per unit surface area of membrane
Catalyst conductivity data for porous electrode
Mesh wire conductivity data
Mesh width diameter
Open width between wires in mesh
Relative position of wires on opposite sides of membrane, either center-to-center (opposite) or offset
Number of parallel wires across the entire electrode face
Applied current density
Catalyst current efficiency
OH⁻ flux through membrane from catholyte to anolyte (derived from the above factors)
Chlorine current efficiency
Bulk outlet concentrations
Total experimental cell potential
Empirical relations
Flux of OH⁻ across the membrane from catholyte to anolyte as a function of \( f_{MO} \) (the equivalent to Eq. [1])
Membrane potential drop as a function of \( C_{MOH} \) and \( C_{MCl} \) (the equivalent to Eq. [7])

Finally, the concentrations on the membrane surfaces, electrode overpotentials, and equilibrium potentials can be summarized for the combined cells.

### Conclusions

1. The empirical method presented by Jörissen and Menschig has a limited application to describing the behavior of combined zero gap/attached electrode membrane cells.

   (i) Extensive experimental data for each type of membrane in a gap cell, at a set current density and temperature, is required in order to derive the empirical relations describing the OH⁻ flux from catholyte to anolyte (Eq. [1]) and the membrane potential drop (Eq. [7]) for a membrane chlor-alkali cell by regression.

   (ii) Given the above relations and various caustic current efficiencies (CCE), the total cell potential of a ZG cell can be predicted as a function of current density (CD) and CCE.

   (iii) The concentrations on the membrane surfaces for APEL and ZG cell configurations can be estimated given the above relations and cell performance data (total cell potential, CCE, ClCE, and CD).

   (iv) Menschig’s method can be used to predict the total cell potential of combined membrane cells (ZG/ABC or PAL/ZG configuration) given experimental data on both the corresponding APEL and ZG cell configurations.

2. A more theoretically based method is required if combined zero gap/attached electrode membrane cell behavior is to be estimated without extensive experimental work.

### Acknowledgments

The authors acknowledge gratefully the financial assistance for this work from the Dow Chemical Company, Texas Applied Science and Technology Laboratories, Inc., Organic Chemicals Research, and the many hours of helpful explanation and discussion with Dr. K. R. Menschig of Dow Chemical GmbH, Stade, Germany.

Manuscript submitted Sept. 22, 1986; revised manuscript received Dec. 23, 1986.

Texas A&M University assisted in meeting the publication costs of this article.

### LIST OF SYMBOLS

- **A**: electrode surface area (m²)
- **b**: membrane thickness (m)
- **\( C_{AML/CT} \)**: active chlorine concentration in anolyte (mol/l)
- **\( C_{AML/H⁺} \)**: H⁺ ion excess in anolyte (mol/l) (OH⁻ ion excess is expressed as a negative value of \( x_2 \))
- **\( C_{ANACL} \)**: local concentration of NaCl in anolyte, bulk value for Jörissen (mol/m³)
- **\( C_{AT} \)**: total concentration of dissolved material in anolyte (mol/l NaCl + NaClO₃ + HCl + HOCI + Cl₂) (calculated from the sum of analyzed values for NaCl + NaClO₃ + HCl + NaOH + Cl₂)
- **\( f_{ZG} \)**: correction factor appearing in Eq. [19] which is used to determine the diffusion layer thickness of a mesh electrode
- **F**: Faraday constant (96,487 A/s/mol)
- **\( f_{MO} \)**: correction factor appearing in the program ME-MODV, equal to 1.24, \( f_{MO} = 0.8785 \) average hydration number for Na⁺ ions during migration from anode to cathode chamber (mol H₂O/mol Na⁺)
- **\( J_{i} \)**: current density (A/m²)
- **\( J_{i,n} \)**: new mean current density (A/m²)
- **\( J_{m} \)**: current density based on the actual electrode surface area (A/m²)
- **\( J_{nc} \)**: mean current density, based on surface area of membrane (A/m²)
- **\( k_{r} \)**: geometric factor calculated by program ME-NETZP
- **\( L_{i} \)**: mesh width (center to center distance between two parallel wires) (m)
- **\( N_{g,OH} \)**: OH⁻ flux through the membrane (mol/m²-h)
- **\( N_{m,OH} \)**: water transport through the membrane (mol H₂O/m²-h) (net water transport + water for back-migrating OH⁻ ions)
- **\( N_{Na⁺} \)**: Na⁺ ion transport through the membrane (mol Na⁺/m²-h)
- **\( N_{NET,H₂O} \)**: net water transport (mol H₂O/m²-h) (net quantity of water moving from anode to cathode chamber)
- **\( Re \)**: Reynolds number = \( \nu D_{ku}/\mu \)
- **\( Sc \)**: Schmidt number = \( \nu/D_{ku} \)
- **\( Sh \)**: Sherwood number = \( \nu D_{ku}/\mu \)
- **\( U_{APEL} \)**: total cell potential for then APEL cell configuration
- **\( U_{ME} \)**: potential drop across membrane with a uniform current density distribution, assumed to be value for APEL configuration
- **\( U_{ZG} \)**: total cell potential of a ZG cell for a mesh of \( \delta \) (V)
- **\( U_{ZG,δ} \)**: total cell potential of a ZG cell for a mesh of configuration \( δ \) (V)
- **\( V_{ZG,δ} \)**: gas evolution rate (m³/s)
- **\( \beta \)**: number of electrons used in the electrode reaction

Greek letters

- **\( \beta \)**: mass transfer coefficient = \( D_{ku}/\delta \) (m/s)
- **\( \delta \)**: diffusion layer thickness (m)
- **\( \delta_d \)**: diffusion layer thickness representing the wire mesh layer on anode side for both ZG and APEL cells (m)
- **\( \delta_{d,δ} \)**: diffusion layer thickness representing the wire mesh layer on cathode side for both ZG and APEL cells (m)
- **\( \delta_{d,α} \)**: diffusion layer thickness representing the porous anode layer of the APEL cell (m)
- **\( \delta_{d,β} \)**: diffusion layer thickness representing the porous cathode layer of the APEL cell (m)
- **\( \delta_{d,γ} \)**: anode diffusion layer thickness (m)
- **\( \delta_{d,δ} \)**: cathode diffusion layer thickness (m)
The natural text is as follows:

\[ \delta_{\text{FPC}} \] diffusion layer thickness for a flat plate cathode (m)
\[ \delta_{\text{ZGC}} \] diffusion layer thickness for the wire mesh cathode of the ZG cell (m)
\[ \varepsilon_A \] anode equilibrium potential (V)
\[ \varepsilon_C \] cathode equilibrium potential (V)
\[ \eta_A \] anode overpotential (V)
\[ \eta_C \] cathode overpotential (V)
\[ \kappa \] specific membrane conductivity (1/\Omega\cdot m)
\[ \nu \] kinematic viscosity (m²/s)

REFERENCES

6. Private communications and conversations with K.-R. Menschig while he was visiting Dow Chemical USA, Freeport, TX (May 1986).