

## Progress Report

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### Aspen Plus Modeling of the Three-Reaction Version of the Copper-Chloride Thermochemical Cycle for Hydrogen Production from Water

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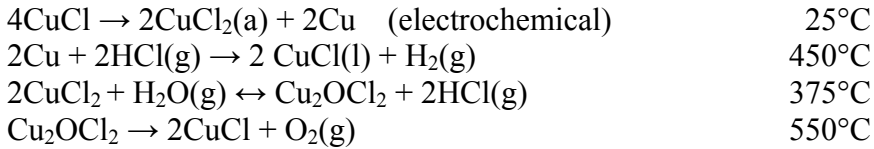
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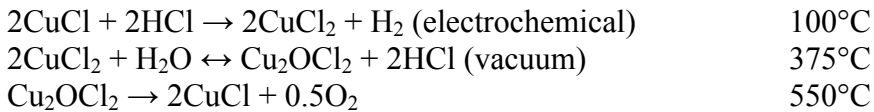
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## Introduction

The Copper-Chloride thermochemical cycle for producing hydrogen from water has the attractive feature of low temperature requirements. A further desirable property is that possibly the cycle can be implemented such that minimal solids transfers are required. Previous modeling efforts for this cycle involved a four-reaction scheme as follows:



The most serious drawback of the four-reaction cycle is the presence of elemental copper. Therefore, a three-reaction scheme has been proposed as follows:



To our knowledge, no prior work has been done on mechanistic modeling of the electrolyzer for the hydrogen production step of the three-reaction scheme. Prior simulations of the four-reaction step used a simple stoichiometric reactor model for the electrolyzer. In the current work, we present an Aspen Plus model for the three-reaction system that includes a realistic model (written as a user-supplied Fortran model) of the electrolyzer.

We developed the Aspen Plus model in three steps. First, a flowsheet was developed in which all reactors are stoichiometric with reactions going to completion. The second phase included the  $\text{CuCl}_2$  hydrolysis step as an equilibrium reactor. The final step involves the inclusion of the Fortran code to describe the operation of the electrolyzer, and this is still a work in progress.

## Phase I Aspen Plus Model

The flowsheet shown in Figure 1 represents an Aspen Plus model for the three-reaction system in which all reactors are stoichiometric and all reactions go to completion. The flowsheet uses an arbitrary rate of 75 kmol/hr of water input, which results in 75 kmol/hr of hydrogen production and 37.5 kmol/hr of oxygen output. The three reactions are carried out in the blocks labeled REACT1, REACT2, and REACT3, respectively. All separations in this preliminary version are implemented as perfect component separators. Later versions will use flash tanks and/or distillation columns where appropriate.

Heat integration is accomplished in an optimal fashion, with high temperature outputs being used to warm inputs to the same section. Heat exchange combinations are indicated by dashed lines connecting two corresponding heat exchangers. Hydrogen is delivered at 100 °C and 23 bar (required pipeline pressure). In this preliminary case, oxygen is delivered at 1.7 bar and 375°C, but this temperature can easily be reduced to a more practical level via further heat integration.

Valves and pumps are placed to produce the desired pressure in each section of the flowsheet. The hydrogen generation section takes place at high pressure (about 23 bar) to satisfy hydrogen pipeline delivery requirements. The HCl regeneration step occurs at a vacuum (about 0.3 bar absolute) while the oxygen generation section is near atmospheric pressure.

## Phase II Aspen Plus Model

The flowsheet of Figure 2 depicts several differences from that of Figure 1. In particular, note the following changes/additions:

1. The REACT2 block is used to convert cupric copper and chloride ions into  $\text{CuCl}_2$  solid according to the reaction  $\text{Cu}^{++} + 2 \text{Cl}^- \rightarrow \text{CuCl}_2(\text{S})$ .
2. The block labeled GIBBS is an equilibrium reactor in which  $\text{CuCl}_2$  is hydrolyzed to  $\text{Cu}_2\text{OCl}_2$  and HCl. By-products are  $\text{O}_2$  and  $\text{Cl}_2$  in small (but significant) amounts.
3. Prior to the GIBBS reactor, a separator called PURGEE- was put in to remove “trace” amounts of  $\text{Cu}^+$  and  $\text{Cl}^-$  ions. Even though the flow rate of these ions is insignificant, the GIBBS reactor model objected to their presence. Therefore, the stream labeled PURGE has zero flow rate and is included only to satisfy the nuances of the reactor model.
4. A reactor labeled FAKERX is included to ensure that all forms of CuCl are in the form of  $\text{CuCl}(\text{SC})$ , a particular crystalline form of CuCl. This, again, is to satisfy the constraints of Aspen Plus.

5. The recycle loop is not closed. This is because the  $\text{Cl}_2$  reaction by-product appears in the COOLRECY recycle stream. We are still contemplating how to deal with the small amount of  $\text{Cl}_2$  produced so that it does not build up when the recycle loop is closed.

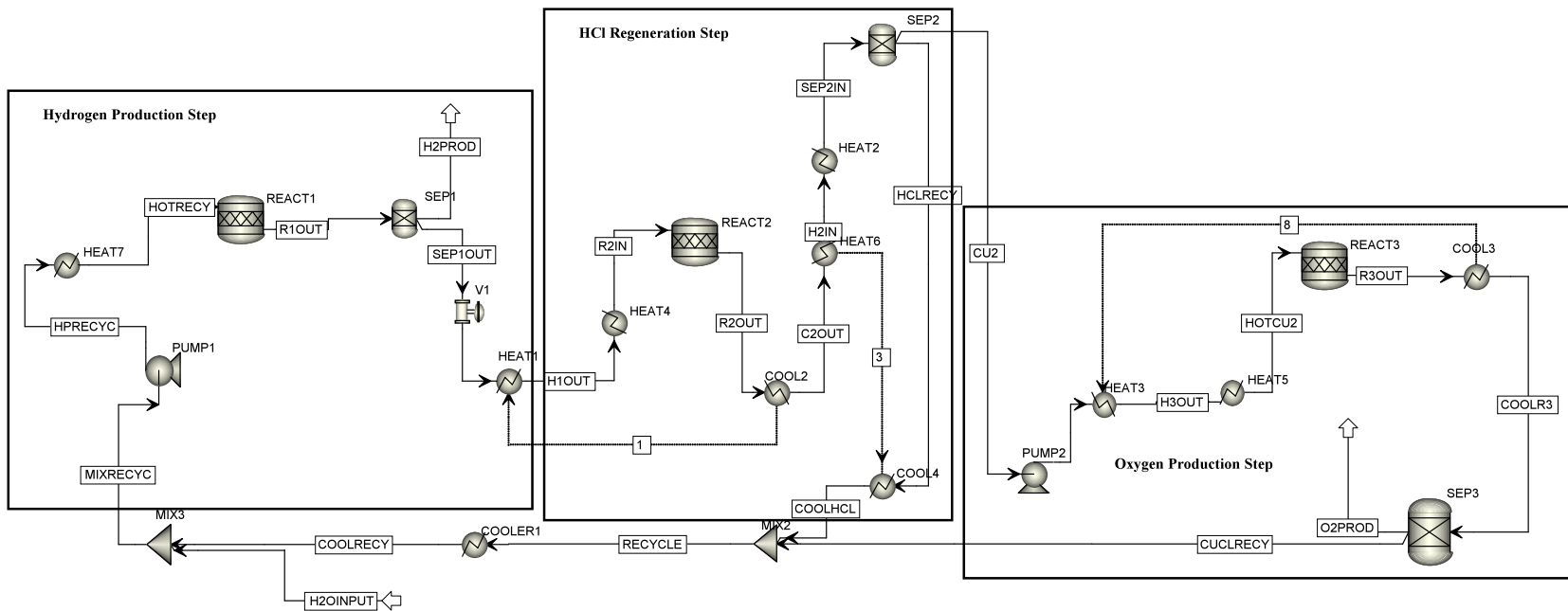


Figure 1: Preliminary Aspen Plus Flowsheet Using Stoichiometric Reactors



### Phase III Aspen Plus Electrolyzer Model

We have developed a model of an electrolyte ion exchange membrane in Aspen Plus that portrays the flow of  $\text{Cl}^-$  ions across the membrane, which as a result governs the flow of electrons in the opposite direction, and thus the  $\text{H}_2$  production.

Aspen cannot conventionally model any type of membrane because it does not have a unit operation block for such a task. Consider an electrolytic membrane like the one in Figure 3:

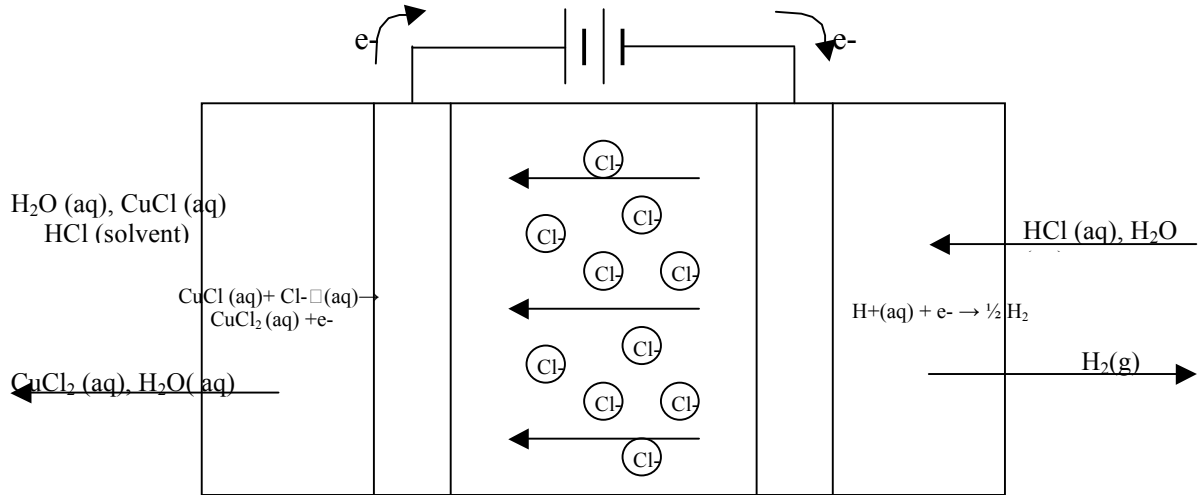


Figure 3: Diagram of the Electrolytic Cell

Aspen Plus allows the user to design a unit operations block that follows equations and specifications that are entered into the system by the user. They are completely independent of any preset Aspen calculations, and thus can be used to model a variety of processes, including ion exchange membranes. The user can specify where the block should be calculated within the system, such as before or after another unit operations block, etc. Aspen does this via “user defined variables” that can serve as input for the calculations specified (import variables), and outputs from the stated equations (export variables). The Aspen model then uses the exported data to proceed in its computational sequence. It should be noted that the electrolyzer replaces REACTI in the flowsheet given previously.

Aspen Plus allows the user to enter in the pertinent equations that govern the new unit operations blocks using two methods, Excel or FORTRAN. The membrane that was modeled in this process was first described using Excel. However, Aspen Plus exhibited several problems and errors when using Excel. As a result Fortran was used to implement the equations for the new block.

After extensive research, Equation (1) (Lakshminarayanaiah, 1969, p. 91) was chosen to represent the flux across the membrane in Figure 3.

$$\begin{array}{c}
 \text{Part I} \\
 \downarrow \\
 J_i = -\bar{D}_i \left[ \frac{d\bar{C}_i}{dx} + \bar{C}_i \frac{d \ln \bar{\gamma}_i}{dx} + z_i \frac{F}{RT} \bar{C}_i \left( \frac{d\bar{E}}{dx} \right) \right] \\
 \uparrow \\
 \text{Part II}
 \end{array} \quad (1)$$

Subscript *i* refers to all species transported across the membrane (only chloride ions in this case). **Part I** of Equation (1) is Fick's Law for non-ideal solutions.  $\bar{D}_i$  represents the diffusivity constant,  $d\bar{C}_i/dx$  represents the flux due to the concentration gradient ( $\text{kmolm}^{-3}\text{hr}^{-1}\text{mm}^{-1}$ ),  $\bar{C}_i$  represents the average concentration of  $\text{Cl}^-$  ions ( $\text{kmolm}^{-3}\text{hr}^{-1}$ ) in the electrolyte,  $d \ln \bar{\gamma}_i/dx$  represents the flux due to the gradient of the natural log of the activity coefficient of the  $\text{Cl}^-$  ions across the membrane ( $\text{mm}^{-1}$ ). **Part II** of the equation accounts for the flux due to the electric potential caused by the flow of electrons from the anode to the cathode.  $z_i$  represents the charge number,  $F$  is Faraday's constant ( $96485.3383 \text{ Cmol}^{-1}$ ),  $R$  is the Gas Constant ( $8.314472 \text{ JK}^{-1}\text{mol}^{-1}$ ),  $T$  represents the absolute temperature (K), and  $d\bar{E}/dx$  is the flux due to the electric field created by the diffusion of charged particles ( $\text{J}\cdot\text{C}^{-1}\cdot\text{mm}^{-1}$ ).

All three gradient terms in the equation were assumed to be constant across the membrane. The first term was calculated by simply dividing the difference in concentration of the  $\text{Cl}^-$  ions on both sides of the membrane by the thickness of the membrane ( $x$ ). The extended Debye-Huckel equation (excluding the linear correction term) (Zuskova, 2006) was used to calculate the second term of Equation 1.

$$\log_{10} \gamma = -\frac{Az_i^2 \sqrt{I}}{1 + Ba\sqrt{I}} \quad (2)$$

In the equation above,  $A$  and  $B$  are constants that are characteristic of the solvent at a given temperature,  $I$  is the Ionic strength ( $\text{kmol}\cdot\text{kg}^{-1}$ ),  $a$  is the effective diameter of the ion whose activity is being calculated, and  $z$  is the charge number. For aqueous solutions at  $25^\circ\text{C}$ ,  $A$  is  $.509(\text{mol}\cdot\text{dm}^{-3})^{-1/2}$ , and  $Ba$  is approximated to be  $1.5(\text{mol}\cdot\text{dm}^{-3})^{-1/2}$  (Zuskova, 2006).

The equation for the  $d\bar{E}/dx$  term was determined using Equation 3 (MacInnes, 1961, p. 464).

$$\frac{dE}{dx} = \frac{(A - B)\delta}{2F[(C_\delta - C_o)x + C_o\delta]} \quad (3)$$

(Note that parameters  $A$  and  $B$  from Equation 3 are not the same as those in Equation 2.)

Equation 4 (MacInnes, 1961, p. 465) was then solved for  $(A-B)\delta$ , and substituted into the numerator of Equation 3.

$$\ln \xi = \frac{(A-B)\delta}{2(C_\delta - C_o)RT} \ln \frac{C_\delta}{C_o} \quad (4)$$

After comparing Equation 5 ((Lakshminarayanaiah, 1969, p. 74) and Equation 6 (Lakshminarayanaiah, 1969, p. 75) below,  $\xi$  was set equal to  $\ln(\lambda_1/\lambda_2)$ , in which  $\lambda_1$  and  $\lambda_2$  are the equivalent conductances of the cathode and anode solutions, respectively.

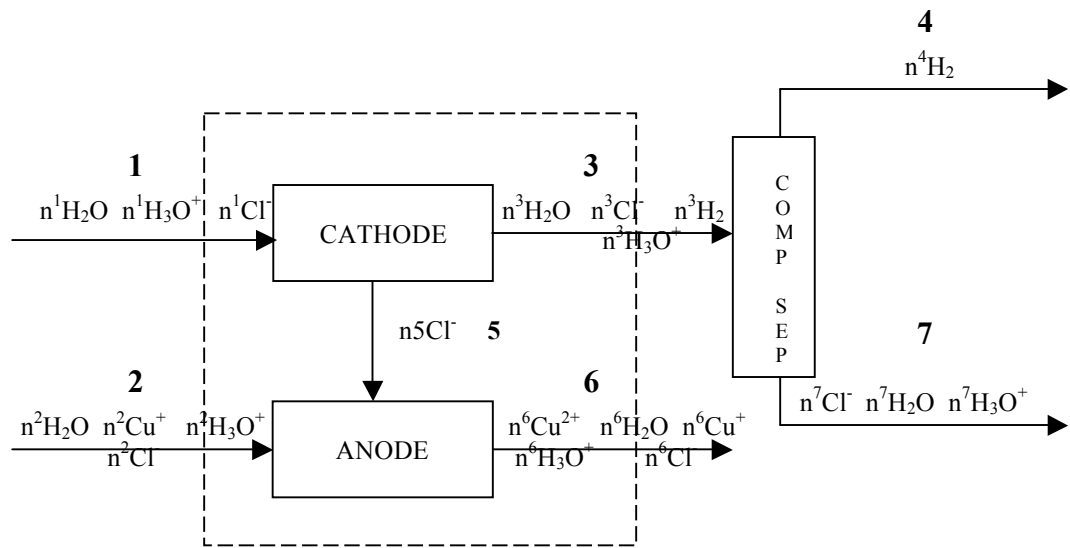
$$E_L = \frac{RT}{F} \ln \frac{\lambda_1}{\lambda_2} \quad (5)$$

$$E_L = \frac{RT}{F} \ln \xi \quad (6)$$

Because  $C_\delta$  and  $C_o$  represent the concentration of  $\text{Cl}^-$  ions on either side of the membrane, they were replaced by  $C_{an}$  and  $C_{cat}$  in order to clarify this point. Following this step, the convention of  $(C_{an} - C_{cat})$  was decided upon due to the flow of electrons from anode to cathode, resulting in the final equation that was used for the  $d\bar{E}/dx$  term,

$$\frac{d\bar{E}}{dx} = \frac{(C_{an} - C_{cat})RT \ln \frac{\lambda_1}{\lambda_2}}{F[(C_{an} - C_{cat})x + (C_{cat} \cdot d)] \ln \frac{C_{an}}{C_{cat}}} \quad (7)$$

Initially, this equation was used in conjunction with three other calculator blocks that served to compute the necessary stoichiometric calculations shown in Figure 4.



$$\begin{aligned}
 n^3 \text{H}_2 &= \frac{1}{2} n^5 \text{Cl}^- \\
 n^3 \text{H}_3\text{O}^+ &= n^1 \text{H}_3\text{O}^+ - 2 * n^3 \text{H}_2 = n^1 \text{H}_3\text{O}^+ - n^5 \text{Cl}^- \\
 n^3 \text{H}_2\text{O} &= n^1 \text{H}_2\text{O} + 2 * n^3 \text{H}_2 = n^1 \text{H}_2\text{O} + n^5 \text{Cl}^- \\
 n^3 \text{Cl}^- &= n^1 \text{Cl}^- - n^5 \text{Cl}^- \\
 n^6 \text{Cu}^{2+} &= n^5 \text{Cl}^- \quad (n^2 \text{Cu}^+ \geq n^5 \text{Cl}) \\
 n^6 \text{Cu}^+ &= n^2 \text{Cu}^+ - n^6 \text{Cu}^{2+} \\
 n^6 \text{Cl}^- &= n^2 \text{Cl}^- + n^5 \text{Cl}^- \\
 n^6 \text{H}_2\text{O} &= n^2 \text{H}_2\text{O} \\
 n^6 \text{H}_3\text{O}^+ &= n^2 \text{H}_3\text{O}^+
 \end{aligned}$$

Figure 4: Schematic of Stoichiometry Calculations for the Electrolyzer.

These blocks were later integrated into a single unit to increase accuracy and efficiency. Currently, C1 performs flux calculations, along with the material balance calculations shown in Figure 4. The latest Aspen Plus model of the electrolyzer can be seen below in Figure 5.

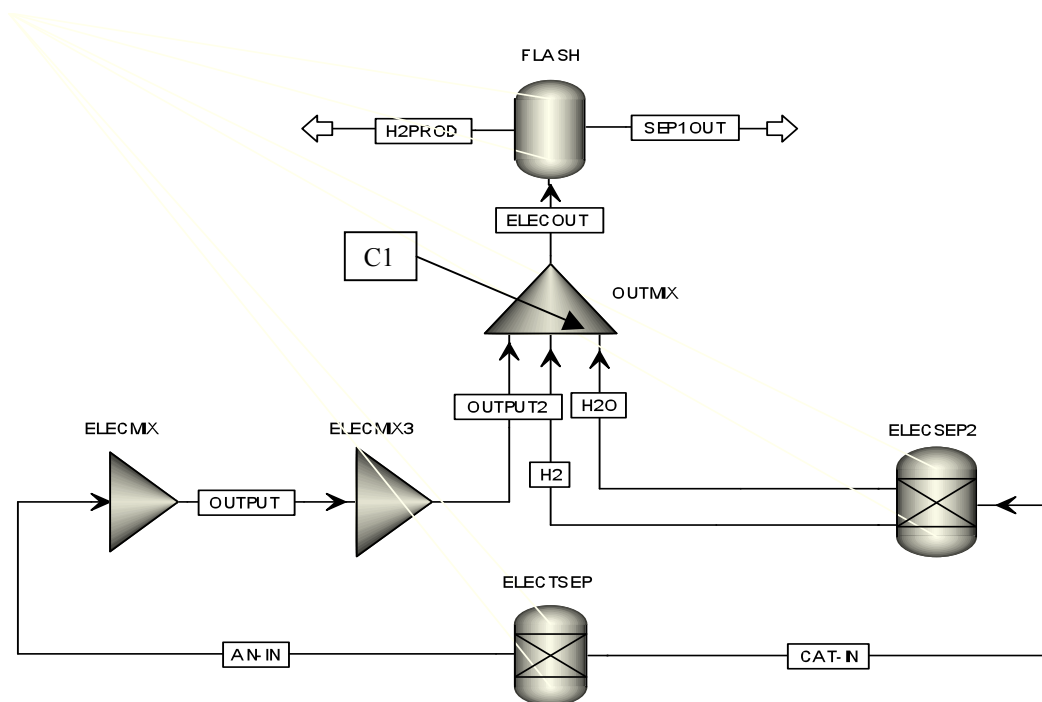


Figure 5: Final Aspen Plus Model of Electrolytic Cell

The calculator block does not appear directly on the Aspen flowsheet, but has been placed in its respective position to provide a clearer idea of what is taking place in the process. In the Aspen file it can be found by accessing “Flowsheet Options”, and then the “Calculator” choice from the menu. This is because the calculator block accepts inputs from anywhere in the entire flowsheet, depending on the way one defines the variables that govern it. However, despite being assigned to perform the calculations at a certain point, the outputs that it produces can also affect any variable within the flowsheet, again depending on the definition of the “Export” variables.

The interval halving method was used in order to determine the  $\text{Cl}^-$  transport rate across the membrane from the flux equation (Equation 1) and the material balance equations provided in Figure 4. The FORTRAN code uses the equations mentioned above, along with real-time input of concentrations, volumes, mass, and system temperature, and calculates a function defined as  $g(n_{\text{Cl}^-}^5) = n_{\text{Cl}^-}^5 - f(x)$ .  $f(x)$  is equal to  $JA$ , in which  $J$  is the total flux, and  $A$  is the area of the membrane. In this method, the maximum value of  $\text{Cl}^-$  that can be transported across the membrane has to be calculated, along with the lowest, and the midpoint value,  $G_{\text{HIGH}}$ ,  $G_{\text{LOW}}$ , and  $G_{\text{MID}}$  respectively. The program then takes these values and continues to half the interval until it obtains a value of  $n_{\text{Cl}^-}^5$  that makes  $g(n_{\text{Cl}^-}^5) = 0$ .

When defining these calculations in FORTRAN, the outputs must not be exported until the final iteration. The output automatically changes the stream flow rates, and as a result the exported values would serve as the imported data for the next iteration which

would lead to an incorrect solution. To correct this problem, variables were defined so that the input to the system would never be disturbed by the calculator block.

Also, the exported data must be defined in a different stream, so that the input never changes (i.e., the molarities needed to perform the calculations are not the molarities of the products, but those of the reactants). For example, data is imported from streams “Cat-in” and “Output”, and exported to the streams “H2O”, “H2”, and “Output2”. This allows for accurate and up to date information from the flowsheet.

Other problems that should be avoided include using variables 6 characters or less (variables longer than this must be compiled, and Aspen Plus 20.0 does not have a compiler), using DLOG for the natural log, and not starting variable names with the letters “i, j, k, l, m, n” (they will be interpreted as integers rather than real numbers, and produce problems within the code).

At this time the C1 block is working properly, however due to the lack of information that describes the membrane such as thickness, area, dielectric constant, equivalent conductance, etc., which is needed to evaluate the  $dE/dx$  term in Eqn. 1, the  $H_2$  produced is not an accurate portrayal of real life performance. These factors have been defined and given arbitrary values within the FORTRAN code, so they need only be changed when accurate characteristics of the membrane are available. For the time being they can be adjusted so that they optimize the system and thus provide researchers with characteristics to strive for in the creation of the membrane.

## References

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