The electrochemical membrane reactor (ecMR) is a user block modeled in Aspen Custom Modeler (ACM). Details of the complete set of energy and mass balances are described here.

Model equations describing transport phenomena in the electrochemical membrane reactor (ecMR)

1) Basic laws and equations in electrochemistry

Electrochemistry deals with the processes and factors, that affect the exchange of charge between chemical phases, e.g. between an electron donor (anode) or acceptor (cathode), and an ionic conductor. In an electrochemical reactor this charge transfer is realized by an applied cell voltage or current to drive an otherwise non-spontaneous chemical reaction[1].

The cell voltage U_{Cell} of any operating electrochemical reactor consists of nine contributions, which are depicted in Fig. 1 [2]:

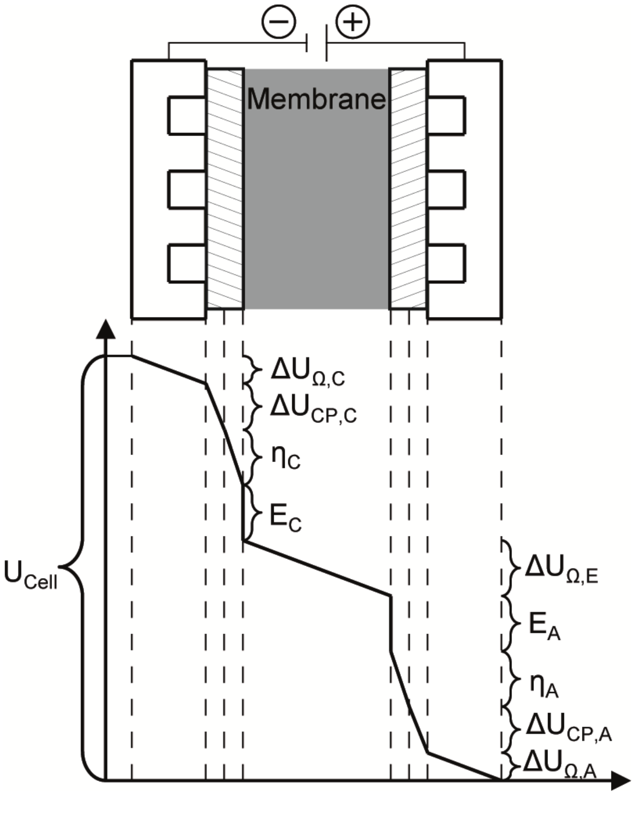

Figure 1. Main elements of the modelled ecMR and model discretization along the flow channel length in single elements (vertical dashed lines). Mass, heat and electron transfer to the surrounding.

1. Equilibrium potential difference of the cell reaction: $U_{EP} = E_A - E_C$
2. Overpotential of the anode required to drive the charge transfer: η_A
3. Overpotential of the cathode required to drive the charge transfer: η_C
4. Ohmic voltage drop due to charge transfer between the anode and the cathode (electrolyte): $\Delta U_{\Omega, E}$
5. Anodic overpotential due to concentration polarization: $\Delta U_{CP, A}$
6. Cathodic overpotential due to concentration polarization: $\Delta U_{CP, C}$
7. Ohmic voltage drop within anode due to ohmic resistance of the anode: $\Delta U_{\Omega, A}$
8. Ohmic voltage drop within cathode due to ohmic resistance of the cathode: $\Delta U_{\Omega, C}$
9. Potential drop due to contact resistance: $\Delta U_{Contact}$

In comparison to the electrochemical potential drops 1.-6. the contributions of the potentials 7.-9. are relatively small and can be neglected[2]. Accordingly, the following equation can be derived[3]:

$$U_{cell} = U_{EP} + \eta_A - \eta_C + \Delta U_{\Omega,E} + \Delta U_{\mathrm{CP},A} + \Delta U_{\mathrm{CP},C} (1)$$

The equilibrium potential of an electrode reaction U_{EP} is determined by the Gibbs free enthalpy of the reaction ΔG [4]:

$$E_{A/C} = \frac{\Delta G}{\nu_e F} (2)$$

where F is the Faraday constant which equals 96485 C/mol and ν_e the number of moles of electrons transferred in the half cell reaction, respectively. In general, the Gibbs free energy depends on temperature and the concentration of the reactants and products:

$$\Delta_R G = \Delta_R G^0 + RTlnQ (3)$$

$$Q = \frac{\prod a_{P,i}^{\nu_i}}{\prod a_{R,i}^{\nu_i}} (4)$$

where $\Delta_R G^0$ denotes the Gibbs free energy at standard conditions, R the ideal gas constant, T the temperature, $a_{P,i}$ and $a_{R,i}$ the activities of the products and reactants and vi the stoichiometric coefficients. Thus the equilibrium potential is also dependent on the concentration and temperature and can be calculated by adding the equilibrium potentials of the two electrodes. This is given by the Nernst's equation[4]:

$$U_{EP} = E_A - E_C (5)$$

$$U_{EP} = \left[E_A^0 + \frac{RT}{\nu_e F} \ln\left(\frac{\prod a_{ox,i}^{\nu_i}}{\prod a_{red,i}^{\nu_i}}\right)\right]_A - \left[E_C^0 + \frac{RT}{\nu_e F} \ln\left(\frac{\prod a_{ox,i}^{\nu_i}}{\prod a_{red,i}^{\nu_i}}\right)\right]_C (6)$$

with E_A and E_C as the equilibrium potential of the anode and the cathode and E_A^0 as well E_C^0 as the standard equilibrium potential of the anode and the cathode, respectively. The activity a of a gas with the partial pressure p is:

$$a = \frac{f}{p^0} p (7)$$

where f is the fugacity coefficient of the gas.

The Butler-Volmer expression correlates the current density, which is comparable with the reaction rate of a conventional chemical reaction, and the overpotential for the charge transfer[4]:

$$j = j_0 \left(exp\left(\frac{\alpha_f \nu_e F \eta}{RT}\right) - exp\left(\frac{-\alpha_b \nu_e F \eta}{RT}\right)\right) (8)$$

where j_0 denotes the exchange current density which is the current density exchanged back and forth under equilibrium potential. The forward and backward charge transfer coefficients α_f and α_b correlate the change of the current densities due to a change in overpotential[4]. In general, it is assumed that α_f and α_b are 0.5 [5]. However, at high overpotential one of the two terms of equation (8) outweighs the other and thus for engineering purposes the Butler-Volmer equation can be shorten to a single term[4]:

$$j = j_0 exp\left(\frac{\alpha_f \nu_e F\eta}{RT}\right) \text{if } \frac{\alpha_f \nu_e F\eta}{RT} \gg 1 (9)$$

or

$$j = j_0 exp\left(\frac{-\alpha_b \nu_e F\eta}{RT}\right) \text{if } \frac{-\alpha_b \nu_e F\eta}{RT} \gg 1 (10)$$

Under these conditions the Tafel equation can be derived:

$$\eta = a + b ln|j| (11)$$

where a equals $\frac{RT}{F\nu_e\alpha} ln j_0$ and b equals $\frac{RT}{F\nu_e\alpha}$ with α either α_f or α_b.

The ohmic potential drop $\Delta U_{\Omega,\ E}$ due to charge transfer between the anode and the cathode is determined by the current density j, the electrode distance d, and the conductivity κ of the electrolyte, i.e. of the membrane[2]:

$$\Delta U_{\Omega,E} = \frac{jd}{\kappa} (12)$$

For an ecMR the electrode distance d is the thickness of the membrane minus the press-in depth of the GDE. The conductivity κ of the membrane is determined as following[6]:

$$\kappa = \frac{F^2}{RT} \sum_i z_i^2 D_i c_i \ (13)$$

where i denotes the components permeating through the membrane, z_i their charges and D_i their diffusion coefficients within the membrane. Within the membrane electro neutrality has to be hold[6]:

$$z_f c_f + \sum_i z_i c_i = 0 (14)$$

where z_f is the charge of the fixed sites within the membrane and c_f its concentration. In the case of the membrane reactor the only mobile ions are protons, thus equation (14) becomes:

$$z_f c_f + z_{H^+} c_{H^+} = 0 (15)$$

Hence, the proton concentration within the membrane is assumed to be constant. Accordingly the conductivity of the membrane can be calculated with equation (16)[6]:

$$\kappa = \frac{F^2}{RT} D_{M,H^+} c_{M,H^+} (16)$$

As mentioned above, an overpotential caused by concentration polarization due to limited mass transfer at the anode and the cathode may arise. The overpotential can be determined by a modified Nernst-Equation:

$$\Delta U_{CP,A/C} = \frac{RT}{\nu_e F} ln \left[\frac{\prod a_{ox}^{\nu_i}}{\prod a_{red}^{\nu_i}}\right]^{x=0} - \frac{RT}{\nu_e F} ln \left[\frac{\prod a_{ox}^{\nu_i}}{\prod a_{red}^{\nu_i}}\right]^{x=\infty} \quad (17)$$

where $a_i^{x=0}$ is the activity of the species i at the electrode surface, $a_i^{x=\infty}$is the activity in the bulk fluid and ν_i is the stoichiometric coefficient of the component i.

2) Mass balance:

The Faraday's law correlates the current and the formed product or converted reactant, respectively:

$$I = \frac{\nu_e F dn_i}{\nu_i dt} (18)$$

with I as the current, dn_i as the amount of component i produced during the time dt and ν_i as the stoichiometric coefficient for the component i in the half cell reaction. With $j = I/A$ it follows:

$$j = \frac{\nu_e F \dot{n}''_{\frac{A}{C},i}}{\nu_i} (19)$$

where $\dot{n}''_{A/C,i}$ denotes the molar flux of component i per geometric surface area A of the electrode. Since the current density can be calculated with equation (19), the mass balance for a differential element of the bulk fluid in the flow channel of the anode and cathode can be derived as shown in Fig. 2.

Figure 2. Mass balance of an incremental flow channel element

Thus the mass balance can be written as equation (20) for the anode and equation (21) for the cathode:

$$\frac{d}{dz}\dot{n}_{A,i} = \omega(\dot{n}''_{P,A,i} - \dot{n}''_{R,A,i})(20)$$

$$\frac{d}{dz}\dot{n}_{C,i} = \omega(\dot{n}''_{P,C,i} - \dot{n}''_{R,C,i})(21)$$

where $\dot{n}_{A,i}$ and $\dot{n}_{C,i}$ are the molar flows of the bulk fluid in the anodic and cathodic flow channel, $\dot{n}''_{R,A/C,i}$ the flux of the reactant consumed per electrode surface area A, $\dot{n}''_{P,A/C,i}$ the product flux per electrode surface area A and ω the width of the flow channel.

3) Mass transfer:

Concentration polarization due to limited mass transfer at the electrodes causes an overpotential. The reactants as well as the products have to pass the boundary layer between the bulk fluid and the Gas Diffusion Electrode (GDE) as well as the GDE itself to reach the active catalyst layer. The concentration at the surface of the GDE can be calculated by balancing the molar flux with the mass transfer coefficient and the driving concentration difference:

$$\dot{n}''_{\frac{R}{P},\frac{A}{C},i} = \beta\left(c_{i,bulk} - c_{i,GDE}\right)(22)$$

The mass transfer coefficient β is obtained from dimensionless correlations of the Schmidt-, Sherwood and Reynolds-Number:

$$Sh = 1.62\left(ReSc\frac{d_{hyd}}{l}\right)^{\frac{1}{3}} (23)$$

$$Re = \frac{v\rho d}{\eta} (24)$$

$$Sc = \frac{\eta}{\rho d} (25)$$

$$Sh = \frac{\beta d}{D} (26)$$

where v is the flow velocity, ρ the density of the fluid, η the fluid viscosity, d the hydraulic diameter of the flow channel and D the diffusion coefficient.

The mass transport of the fluid in the gas diffusion electrode is modeled as multicomponent diffusion in porous media. The Knudsen number determines whether statistical mechanics or continuum mechanics should be used to describe the mass transport. The Knudsen number is given by equation (27):

$$Kn = \frac{\lambda}{d_{por}} (27)$$

For this work the pore size d_{por} is assumed to be 50 µm and the mean free path of the gas molecules λ is about 68 nm[7]. Thus the Knudsen number is about 0.0014. Hence, the Knudsen number is smaller than 0.01 and the mass transport obeys continuum mechanics. Thus, the mass transport can be described by ordinary multicomponent diffusion[8]:

$$\dot{n}_i'' = c_i\dot{n}_{tot}'' - D_{eff}\nabla c_i (28)$$

In case of diluted mixtures, the diffusion process can be considered as two component diffusion[8]:

$$\dot{n}_{tot}'' = \sum_i \dot{n}_i'' \; (29)$$

The effective diffusion coefficient D_{eff} accounts the geometric constraints of the porous media, which reduce the diffusivity. Thus, the open space diffusivity D is modified by a correction factor[9]:

$$D_{eff} = D\varepsilon^{\alpha} (30)$$

$$\alpha = \frac{\log_{10}\left(\frac{\varepsilon}{\tau}\right)}{\log_{10}\varepsilon} (31)$$

Here, the porosity ε of the GDE used for the preparation of the membrane electrode assembly (MEA) is approximately 0.3 and for typical cases the tortuosity τ is three[9].

4) Energy balance:

The energy balance for a differential element of the bulk fluid in the flow channel is shown in Fig. 3.

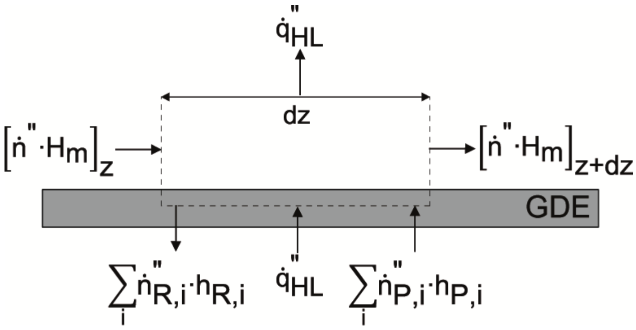

Figure 3. Energy balance of an incremental flow channel element

In the balance, the enthalpy flux due to mass flux, heat loss to the ambient air as well as heat generation due to consumption of electrical energy are considered. Accordingly, the energy balance for the anode and the cathode can be written as equation (32) and equation (33):

$$\frac{d}{dz}\left(\dot{n}_A H_{M,A}\right) = \sum_{i,P} \dot{n}''_{P,i}\, H_{P,i}\omega - \sum_{i,R} \dot{n}''_{R,i}\, H_{R,i}\omega + \dot{q}''_{EE,A}\omega - \dot{q}''_{HL,A}\omega (32)$$

$$\frac{d}{dz}\left(\dot{n}_C H_{M,C}\right) = \sum_{i,P} \dot{n}''_{P,i}\, H_{P,i}\omega - \sum_{i,R} \dot{n}''_{R,i}\, H_{R,i}\omega + \dot{q}''_{EE,C}\omega - \dot{q}''_{HL,C}\omega (33)$$

with $H_{M,A}$ as the specific enthalpy of the molar flow in the flow channel, $H_{i,R}$ as the specific enthalpy of the reactants diffusing from the flow channel into the GDE and $H_{i,P}$ as the specific enthalpy of the products diffusing back from GDE into the flow channel, $\dot{q}''_{HL,A/C}$ as the heat flow transferred per area to the ambient air and $\dot{q}''_{EE,A/C}$ as the heat flow transferred per area due to the conversion of electrical energy.

The Gibbs free energy ΔG of any cell reaction is the minimal amount of electrical energy per mol converted substrate which is required to drive the electrochemical process. However, the total energy to be expended is the reaction enthalpy ΔH which is the sum of ΔG and the entropic term TΔS:

$$\Delta H = \Delta G + T\Delta S (34)$$

Any electrochemical process with $\Delta G > 0$ and negative reaction entropy must transfer heat from the cell to the surroundings if the reaction is performed reversibly, but at constant temperature, as ΔH is smaller than ΔG. Therefore any process involving positive reaction entropy has to be supplied with thermal energy. If the electrochemical process is conducted under adiabatic conditions, the thermoneutral voltage U_{th} - instead of U_0 - must be applied to balance the energy required for the cell reaction with the electrical energy[2]:

$$U_{th} = \frac{\Delta_R H}{z_e F} (35)$$

If a portion U_D of the cell voltage U_{Cell} exceeds the thermoneutral voltage U_{th}, heat is generated[2]:

$$\dot{q}''_{EE} = jU_D = j(U_{Cell} - U_{th}) (36)$$

As mentioned before, a term describing the heat transfer from the membrane reactor to the ambient air has to be considered:

$$\dot{q}''_{HL,A/C} = k(T_{x,\frac{A}{C}} - T_0)(37)$$

with $T_{x,A/C}$ as the temperature in the anodic or cathodic flow channel, T_0 as the ambient temperature and k as the heat transfer coefficient.

5) Heat transfer:

As described before, heat is transferred from the inside of the membrane reactor to the ambient air. The heat transfer from the fluid to the ambient air can be considered as heat transfer processes connected in series. Thus the heat transfer coefficients add inversely:

$$\frac{1}{k} = \frac{1}{k_{we}} + \frac{1}{k_w} + \frac{1}{k_{fw}}(38)$$

with k_{we} as the heat transfer coefficient for the heat transfer between the outside of the reactor wall and the ambient air, k_w as the heat transfer coefficient through the reactor wall and k_{fw} as the heat transfer coefficient for the heat transfer between the fluid at the anode or cathode and the inside of the reactor wall, respectively. The heat transfer coefficient through the reactor wall is given by:

$$k_w = \frac{\lambda}{d_w}(39)$$

where λ is the thermal conductivity of the reactor wall and d_w its thickness. The heat transfer between the outside of the wall and the surrounding air can be considered as heat transfer due to free convection along a vertical surface. The Nusselt-Number is defined as the ratio of convective to conductive heat transfer across the boundary:

$$Nu = \frac{k_{se} l_{se}}{\lambda}(40)$$

For this kind of heat transfer the Nusselt number can be calculated as follows:

$$Nu = \left(0.825 + 0.387\left(Raf(Pr)\right)^{\frac{1}{6}}\right)^2 (41)$$

with Ra as Rayleigh number and the function f(Pr) which takes the influence of the Prandtl number Pr into account:

$$Ra = \frac{g\beta}{\nu\alpha}(T_w - T_0)l(42)$$

$$f(Pr) = \left(1 + \left(\frac{0.492^{\frac{9}{16}}}{Pr}\right)\right)^{-\frac{16}{9}} (43)$$

$$Pr = \frac{\nu}{\alpha}(44)$$

with g as the acceleration due to gravity, β as the thermal expansion coefficient which is given by $\beta = 1/T_0$ for ideal gas, v as the kinematic viscosity of the surrounding air, α as the thermal diffusivity, T_w as the surface temperature of the wall and T_0 as the temperature of the ambient air. Finally, the heat transfer between the fluid in the flow channel and the reactor wall has to be considered. The heat transfer is considered as forced convection in a fully developed laminar pipe flow with uniform surface temperature. In this case the Nusselt number is constant:

$$Nu = 3.66 \quad (45)$$

$$Nu = \frac{k_{wf} d_h}{\lambda_f} \quad (46)$$

with d_h as the hydraulic diameter of the flow channel and λ_f as the thermal conductivity of the fluid within the flow channel.

6) Pressure loss:

The pressure in the reactor influences the concentration of the product and therefore the equilibrium potential of the half-cell reaction. The convective flow along the electrodes causes a pressure loss, which can be calculated by using the law of Hagen-Poiseulle for laminar flows:

$$\frac{dp}{dz} = \frac{32 \rho v^2}{Red} \quad (47)$$

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