MASS TRANSPORT IN MOLTEN ALKALI CARBONATE MIXTURES

Andreas Bodén, Göran Lindbergh

Department of Chemical Engineering and Technology, Applied Electrochemistry, Royal Institute of Technology (KTH), SE-100 44 Stockholm, Sweden

ABSTRACT

A one-dimensional model based on Stefan-Maxwell theory of mass transfer was used to calculate the composition changes of the electrolyte in MCFC. Stefan-Maxwell diffusivities were calculated from conductivity and transport number data and used in the model. The composition changes calculated agreed with experimental results for lithium-potassium carbonate but less for lithium-sodium. The time dependent change of composition was also calculated but this could not explain the difference. In addition, the influence of the porosity of the fuel cell components, together with the electrolyte filling degree, was calculated and this showed a large influence on the composition change.

INTRODUCTION

The Molten Carbonate Fuel Cell is a well developed fuel cell technology for converting chemical energy to electrical energy. The major limiting factors for longer lifetime are corrosion, nickel shorting and electrolyte losses. All of these processes are dependent on the local composition of the electrolyte. Large efforts are being made to minimise corrosion by trying different materials and adding additives to the electrolyte to decrease nickel solubility. The effects of concentration changes of the electrolyte are considered to be small and negligible.

Kunz (1) investigated movement of electrolyte in a MCFC stack and it was concluded that the movement of electrolyte was a significant problem. Brenscheidt et al (2-4) have done measurements and seen that the electrolyte composition changes in a single cell during different current loads, and have combined these results with a model based on Ficks law to predict changes at different current densities. Their model was based on internal mobility data (5-6) and conductivity data (7). The mobility measurements (5-6) were done using the Klemm method, which measures the separation of two cations in an electrical field. The measurements showed that the mobility of the larger ion is greater than for the smaller, which is not the normal case for diluted electrolytes. The reason for this has been explained in (8-10) where it is also mentioned that segregation of cations will not be a serious problem in MCFC.

The MCFC electrolyte consists of a binary electrolyte with the salts having a common anion. A model for binary molten salts with a common anion based on the Maxwell-Stefan approach for multicomponent mass transport has been developed (11). Input parameters for the model are the Stefan-Maxwell diffusivities, which can be
calculated from conductivity, density and mobility data. Measurement of conductivities (12-14) has been done for a wide range of temperature and compositions for binary systems of potassium, sodium and lithium carbonates. Mobility and density data has also been measured (5-6,15).

The aim of this study was to calculate if segregation of cations occurs, and if so, how large the composition changes of the electrolyte are. A one-dimensional form of the model developed in (11) was used. Stefan-Maxwell diffusivities were calculated using conductivity data (13), density data (15) and internal mobility data (5-6). The model was used to calculate the concentration profiles for different current loading for planar electrodes and for porous electrodes. The time dependent concentration profiles for a typical current load were also calculated. In addition, the influence of different parameters on the melt composition was also investigated for a porous electrode with the same current load.

MODEL

For an isothermal and isobaric system, with no outer forces acting on a unit volume of electrolyte, the driving force is equal to the sum of the friction forces. In a concentrated solution, the motion of species \( i \) relative to other species can be described by the equation for multicomponent transport (16)

\[
c_i \nabla \mu_i = \sum_{j \neq i} c_j c_i RT (v_j - v_i) = \sum_{j \neq i} \frac{RT}{c_j D_j} (c_i N_j - c_j N_i)
\]

For a molten alkali carbonate salt mixture equation [1] gives two independent equations, in this case chosen to be for the two positive alkali ions, and the following equation system can be written as

\[
\begin{bmatrix}
\frac{c_2}{c_2} + \frac{c_3}{c_2} & \frac{c_1}{c_2} D_{12} \\
\frac{c_2}{c_2} & \frac{c_1}{c_2} D_{22} + \frac{c_3}{c_2} D_{23}
\end{bmatrix}
\begin{bmatrix}
\frac{N_i^*}{N_2} \\
\frac{N_i^*}{N_2}
\end{bmatrix}
= \begin{bmatrix}
\frac{c_1 \nabla \mu_1}{RT} \\
\frac{c_2 \nabla \mu_2}{RT}
\end{bmatrix}
\]

**Transport model**

Equation system [2] can be inverted to give the flux of the two positive ions against the velocity of the common anion. To simplify the calculations, the salt is treated as non-dissociated. The electrochemical potential for the salt can be calculated on a mole fraction basis (18). Using that the electrochemical potential for the salt is a weighted sum
of its ions, equation system [2] can be simplified using the superficial current to the following equation system

\[
N_1 = -D \left( 2 + \frac{\partial \ln(y_A)}{\partial \ln(x_A)} \right) \nu c_A + \frac{t_1}{F} i + c_1 v_3
\]
\[
N_2 = -D \left( 2 + \frac{\partial \ln(y_B)}{\partial \ln(x_B)} \right) \nu c_B + \frac{t_2}{F} i + c_2 v_3
\]
\[
N_3 = c_3 v_3
\]

where the fluxes are against a stationary axis.

The flux of carbonate ions is always proportional to the current.

\[
v_3 = \frac{i}{-2c_3 F}
\]

For molten alkali carbonates it has been shown (15) that the density of the electrolyte is not a linear combination of the two different salt densities. The concentration of each species \( i \) can be calculated using the measured density (15), temperature and composition by

\[
c_i = \frac{n_i \rho}{\sum n_i M_i}, \quad n_i = \left| \nu_i \right| x_k \text{ for } i = 1, 2 \text{ and } n_i = \left| \nu_i \right| \text{ for } i = 3
\]

Using [4] and the relationship between the concentrations of the different ions and the two salts as a function of composition [5], [3] can be reduced to one equation. By using a material balance (16) and macro-homogenisation theory for the porosity (17), the time dependent change of salt A can be written as

\[
e \frac{\partial c_A}{\partial t} = -\nabla \cdot \left( -e^\alpha D \left( 1 + \frac{\partial \ln(y_A)}{\partial \ln(c_A)} \right) \nu c_A + \left( t_1 - \frac{c_A}{c_A + c_B} \right) \frac{i}{F} \right) + R_i
\]

where
Conductivity model

For an electrolyte with uniform composition the electrochemical potential for an ion is proportional to the electrical field. Using this fact and inverting [2], an expression for the conductivity can be derived by using the following relationship between the current and the potential gradient

\[ i = F \sum_i z_i (A^{-1} b)_i = -\kappa \nabla \Phi \]  

[8]

where the conductivity is given by

\[ \kappa = \frac{(2c_1 D_{13} D_{23} + c_1 D_{12} D_{13} + 2c_2 D_{13} D_{23} + c_2 D_{12} D_{23}) 2c_F F^2}{c_1 D_{12} + c_2 D_{12} + c_3 (D_{13} + D_{23}) RT} \]  

[9]

Extracting Stefan-Maxwell diffusivities

As it can be seen in [7], the Stefan-Maxwell diffusivities (binary diffusion coefficients) need to be determined in order to get the transport number and the diffusion coefficient required for [6]. The binary diffusion coefficients are assumed to be a function of the composition (a low degree polynomial) and follow Arrhenius relationship with respect to the temperature.

\[ D_{ij,a}(x_A) = D_{ij,a}(x_A) \exp(-E_{ij,a}/RT) \]  

[10]

Calculation of \( D_{ij,a}(x_A) \) and \( E_{ij,a} \) was done with data from (5-7,12,15).

Determination procedure. The relative error (between the measured and calculated values) for both the conductivity and transport number was calculated for the complete data set. The binary diffusion coefficients were obtained by minimising the euclidean norm of these relative errors using the *lsqnonlin* algorithm in MATLAB 6.5.1.
Calculation of concentration changes

In order to decrease the number of unknowns in [6], the calculated diffusion coefficient, transport number and the concentration of salt B were expressed as polynomials of the concentration of salt A. In this model, the effect of activity changes is ignored. Both the steady-state and the time-dependent solutions were calculated using the general equation formulation in FEMLAB 3.0a. The modelling base case is described in Figure 1. Linear current distribution is assumed for the electrodes and there is no flux of electrolyte through the boundaries. Filling levels for cathode and anode were calculated using the method in (19), ignoring the effect of electrolyte wettability of the electrode.

![Diagram of anode, matrix, and cathode](image)

Figure 1. Modelling base case: anode porosity 40% and electrolyte filling level 60%, matrix with 60% porosity and completely filled and cathode porosity 70 % and 30 % filling level.

MODELLING RESULTS AND DISCUSSION

Binary diffusion coefficients

The binary diffusion coefficients have been calculated for Li$_2$CO$_3$/K$_2$CO$_3$ (Li/K) and Li$_2$CO$_3$/Na$_2$CO$_3$ (Li/Na) melts. For Li/K a Li$_2$CO$_3$-mole fraction of 0.4-0.7 and a temperature range between 550-700°C was used to fit the binary diffusion coefficient to the experimental data. A larger parameter window could not be used because the relative errors became too large. For Li/Na a smaller parameter window had to be used. The mole fraction of Li$_2$CO$_3$ varied between 0.4-0.6 and the temperature between 600-675°C. The small parameter window needed to be used because the experimental transport numbers varied without a common trend and the error became too large. To capture the changes in experimental data (i.e. conductivity and transport number), an increase in the number of degrees of freedom in the \( (D_y(x,j)) \) is possible, though it is necessary to maintain the integrity of the fits. This indicated that either some physical changes of the melt were not captured by the model for the whole composition and temperature range, or that more experimental data is needed for the transport number.

Figure 2 shows that the binary diffusion coefficient for the large cation is larger for Li/Na than for Li/K. This is in agreement with the values of the internal mobilities in (5-6), where the mobility for Na$^+$ is larger then for K$^+$ at the same composition and temperature range.
temperature. The same Figure also shows that the binary diffusion coefficient for the two different cations is smaller in Li/Na than in Li/K. The reason for this might be that Na\textsuperscript{+} is smaller than K\textsuperscript{+} and interacts more with Li\textsuperscript{+}. The difference for the binary diffusion coefficient between Li\textsuperscript{+} and CO\textsubscript{3}\textsuperscript{2-} for the two melts cannot be explained, except that it probably comes from input experimental data.

Figure 2. Binary diffusion coefficients at 650°C. For Li\textsubscript{2}CO\textsubscript{3}/K\textsubscript{2}CO\textsubscript{3}: (—) Li\textsuperscript{+}-K\textsuperscript{+}, (——) Li\textsuperscript{+}-CO\textsubscript{3}\textsuperscript{2-} and (•••) K\textsuperscript{+}-CO\textsubscript{3}\textsuperscript{2-}. And for Li\textsubscript{2}CO\textsubscript{3}/Na\textsubscript{2}CO\textsubscript{3}: (-) Li\textsuperscript{+}-Na\textsuperscript{+}, (--) Li\textsuperscript{+}-CO\textsubscript{3}\textsuperscript{2-}, (•) Na\textsuperscript{+}-CO\textsubscript{3}\textsuperscript{2-}.
Figure 3. Mole fraction of $\text{Li}_2\text{CO}_3$ salt for Li/K, curves at the top, and for Li/Na, curves at the bottom. Straight line shows composition at 0 A/m², (•) composition at 4000 A/m².

Planar electrodes with bulk electrolyte

The modelling was simplified by using planar electrodes in order to be able to see how different current densities impacted on the electrolyte composition. The model was tested on a case with two planar electrodes with bulk electrolyte in between. The left boundary ($x=0$) is the anode side in Figure 3. Initial salt composition for the two different melts was 62 mol% $\text{Li}_2\text{CO}_3$ for Li/K and 52 mol% $\text{Li}_2\text{CO}_3$ for the Li/Na.

As can be seen in Figure 3 the composition changes are larger for Li/Na. This is because the value of $D$ is smaller and this affects the composition gradient more even though the $x_i$ values are smaller for Li/Na.

Single cell

The base case model described in a previous section (Calculation of concentration changes) was used in these simulations. In the model, the distribution of electrolyte between the electrodes is not considered to change with the current density. To simplify the calculations the conductivity was not considered to change with the composition, which would make the current distribution more uneven.

Figure 4. Mole fraction of $\text{Li}_2\text{CO}_3$ salt as a function of the current density for Li/K, curves at the top, and for Li/Na, curves at the bottom. Straight line shows composition at 0 A/m², (--) composition at 1000 A/m², (**) composition at 2000 A/m², (•) composition at 4000 A/m².
Figure 4 shows that there will be a large decrease of Li\(^+\) in the cathode for both melts, which agrees with experimental results. The effect is larger for the cathode than for the anode due to the low filling level of the cathode. Comparing the results in Figure 4 with those presented in (2-4), the effect for Li/K is smaller than the experimental, but this is probably because the experimental cell had thinner electrodes. The effect of composition changes according to the model is much larger than what is seen in the experimental results for Li/Na (2-4). In order to be able to compare the two studies better, the filling level and pore size distribution has to be known from the experiment and the right thickness has to be used in the model.

**Time dependent composition changes.** With modelling, the relaxation/evolution of concentration gradients with time can be investigated. This knowledge can be used in two ways. Firstly, it can be used to determine how fast a cooling procedure has to be in order to capture concentration profiles. Secondly, it can be used to determine the characteristic frequency for impedance measurements or other time dependent electrochemical techniques. The same single cell model is used, except that time has to be introduced as a variable.

![Figure 5](image)

**Figure 5.** Mole fraction of Li\(_2\)CO\(_3\) salt at a current density of 1500 A/m\(^2\) as a function of time for Li/K, curves at the top, and for Li/Na, curves at the bottom. Strait line shows composition at 0 s, (-) composition after 500 s, (•) composition after 1500 s, (•) composition at steady state about 3000 s.

The results from Figure 5 show that it takes approximately an hour for the concentration profile to reach steady state. The change of the composition for the cell when the current is interrupted is faster, but not large enough to explain the difference between this model and the experimental results. These results indicate that the cooling time is of importance if accurate measurements are desirable.
Filling level effects. The result of the model depends largely on physical conditions, for example, how the electrolyte distributes between the electrodes, the filling level and the porosities of the different components.

![Figure 6](image_url)

Figure 6. Mole fraction of Li$_2$CO$_3$ salt at a current density of 1500 A/m$^2$ depending on different parameters for Li/K. (-) anode 40% porosity and 60% filling level, matrix 60% porosity and cathode 70% porosity and 30% filling level, (--) anode filling level 30% and cathode filling level 10%, (•••) anode filling level 80% and cathode filling level 60%.

As can be seen in Figure 6, the filling level and porosity greatly influence the distribution of ions between the anode and cathode. This model, together with a model for vaporisation and corrosion, could be a valuable tool for determining the effect of electrolyte composition changes during long-term operation. As Figure 6 demonstrates, a depletion of electrolyte would cause a larger cation separation. It is important to consider the effects of even small changes of composition during long-term operations.

The advantage of the Stefan-Maxwell approach to mass transfer is that it combines the conductivity, diffusion and transport number by the binary diffusion coefficients, rather than viewing the three phenomena as separate entities. In order to be able to make more accurate predictions of the composition changes during current load, more experimental data for the transport number is needed. This data should be obtained for a melt with a composition and temperature close to the operating conditions.

CONCLUSIONS

The segregation of cations in molten alkali melts for MCFC can be modelled using the Stefan-Maxwell approach to mass transfer. The difficulty in the determination
of the Stefan-Maxwell diffusivities was due to problems with the experimental data. The calculated results for the concentration changes in porous electrodes compared well with the experimental results for Li/K. However, the same conclusion cannot be made for Li/Na. The separation is approximately 5% for both Li/K and Li/Na for a typical single cell. It takes approximately one hour to reach steady state, which is important to consider when doing time dependent electrochemical experiments. The porosity of the different components, together with the filling degree, largely influences the composition changes in the cell.

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LIST OF SYMBOLS

\(i\) Index for ion, 1 = Li, 2 = Na or K, 3 = CO\(_3\)\(^{2-}\)
\(k\) Index of salt, A = Li\(_2\)CO\(_3\), B = K\(_2\)CO\(_3\) or Na\(_2\)CO\(_3\)
\(c_i\) Concentration of ion or salt (mole/m\(^3\))
\(\eta_i\) Electrochemical potential of ion or salt
\(R\) Universal gas constant (8.314 J/mole,K)
\(T\) Temperature (K)
\(F\) Faraday number (96485 C/equvi)
\(D_{ij}\) Stefan-Maxwell diffusivity between ion \(i\) and \(j\) (m\(^2\)/s)
\(v_i\) Velocity (m/s)
\(N_{i+}\) Flux of ion \(i\) relative to a common anion (mole/m\(^2\)/s)
\(N_{i-}\) Flux of ion \(i\) relative to a stationary axis (mole/m\(^2\)/s)
\(\gamma_k\) Activity coefficient for salt or ion
\(t_i\) Transport number
\(i\) Superficial current (A/m\(^2\))
\(R_i\) Reaction rate of ion \(i\) (mole/m\(^3\)/s)
\(\kappa\) Conductivity (S/m)
\(\rho\) Density (kg/m\(^3\))
\(n_i\) Number of moles (mole)
\(M_i\) Molar mass (kg/mole)
\(\Phi\) Electric field (V)
\(x_k\) Mole fraction of salt \(k\)
\(v_i^k\) Stoichiometrical number of ion \(i\) in salt \(k\)
\(z_i\) Charge on the ion \(i\)
\(\varepsilon\) Porosity
\(a\) Empirical coefficient dependent on the tortuosity effects

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