MASS TRANSFER AND STEADY STATE
CONCENTRATION DISTRIBUTIONS OF
BINARY MOLTEN CARBONATE ELECTROLYTES
AND ADDITIVES IN MCFCs

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Abstract
The ionic mobilities of the cations Li⁺, K⁺ and Na⁺ in alkali carbonate melts is not equal and the small lithium cation is opposite to intuitive assumption but according to the Chemla effect in certain concentration ranges slower than the heavier cations Na⁺ and K⁺ if the lithium carbonate concentration is below the so-called crossing point. For eutectic lithium/potassium carbonate melts this condition holds and considerable accumulation of potassium over lithium carbonate in the cathode is the consequence under operating condition in MCFCs. This effect limits current densities which could be applied in MCFCs as too high accumulation of potassium might lead to crossing the liquidus/solidus line with the consequence of potassium carbonate precipitation. Ionic additives (La₂O₃) dissolved in the carbonate electrolyte experience either uneven concentration distribution in the fuel cell according to their respective internal mobility or, according to their charge and solubility, even complete transfer and deposition into only one of the two electrodes.

Introduction
Since the early investigation of A. Klemm (1), the demixing of the cations of molten binary salt mixtures with a common anion due to the different mobilities of two different cations had been investigated in numerous experiments and the respective results interpreted in terms of structural features of the melts; see for instance (2) and (3). 1-1 electrolytes had been preferentially investigated, but apart from investigations of molten sulfates Okade also reported investigations on lithium carbonate/potassium carbonate mixtures in the temperature range from 980 to 1070 K, (4).

Charge and mass transfer in the electrolyte of molten carbonate fuel cells is accomplished by the movement of the carbonate anions, which are generated at the cathode and decomposed by release of CO₂ at the anode. Against the steadily moving stream of carbonate anions the cations are migrating - but according to their different mobilities with
different velocities. Under steady state conditions the relatively faster cation would accumulate in the catholyte. Steady state conditions are defined by zero velocities of the summed convective, migrative and diffusive mass transfer - see the schematic of Fig. 1.

Fig. 2 reports results in terms of the so-called internal mobilities \( b \) of \( \text{Li}^+ \) and \( \text{K}^+ \) vs. the mole fraction of the potassium salt in binary carbonate mixtures determined at 980 K. At \( x_K \approx 0.32 \) both alkali cations possess equal mobilities and would not separate on prolonged electrolysis, whereas with a higher potassium concentration potassium would be expected to accumulate at the cathode side of an electrolysis cell and with a lower mole fraction than \( x_K = 0.32 \) the same would be expected to occur for lithium.

Since it is felt, that such demixing of the binary electrolyte in MCFCs might have important consequences in defining limits of operation conditions, limiting applicable current densities in particular, the effect had been investigated in experimental fuel cells. The consequences of migrative mass transfer had been investigated also with respect to added lanthanum oxide, (5), as this oxide was believed to influence the nickel oxide solubility in the cathode but could only act there if it would remain there.

**Experimental**

Experimental MCFCs were 20 mm in diameter and of the usual tubular design as described for instance in review (6). Anodes, cathodes and electrolyte matrix had been prepared and assembled according the green foil technology and the cells had been formed from the three foil package in-situ as described by one of the authors and his coworkers elsewhere (7). As an example such cells were typically composed of 0.5 mm thick porous nickel oxide cathodes, 0.8 mm thick anodes of sintered and stabilized carbonyl nickel and 1 mm thick 50% porous and a densely packed LiAlC\(_2\) matrix composed of LiAlO\(_2\) granules of 0.1 to 0.3 \( \mu \)m in diameter. Fuel cell operation was performed with different current densities for more than 100 h, the cell was chilled and carefully disassembled. The separated anode, cathode and matrix specimens were ground and covered with 10 ml of water/ acetic acid, (1/1) and the carbonate melts dissolved within 3 h. The aqueous solutions were analyzed by atomic absorption spectrometry after adequate dilution. For transference measurements of lanthanum oxide to the cathode foil 20 mole % lanthanum oxide (relative to the nickel contents) was added and the distribution of lanthanum across the cell had been monitored by energy dispersive X-ray fluorescence, (EDX), in a SEM (JEOL - TSM 330A) before and after cell operation of 500 h.

**RESULTS**

(a) \( \text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3 \)-electrolyte

Table 1 collects the chemical analyses of a 340 h experiment performed at 650° C with a steady current density of 100 mA cm\(^{-2}\).
Table 1
Potassium and lithium contents of MCFC operated for 340 h at 100 mA cm$^2$

|        | anode | matrix | cathode |
|--------|-------|--------|---------|
| total K/mg | 21,2  | 175    | 25      |
| total Li/mg | 7,0   | 58     | 6,3     |
| thickness/mm | 0,8   | 1,1    | 0,5     |

It is evident that the greatest part of the electrolyte is contained in the matrix (75 to 80%) and that almost equal parts of the remaining electrolyte are contained in both electrodes. The ratio m(K)/m(Li) is almost equal in the matrix and the anode (~3) but it increases to 4 in the cathode.

Table 2 collects the analysis of three experiments - two performed with 100 mA cm$^2$ and the third at somewhat enhanced current density of 150 mA cm$^2$ - by converting the analytical data of the mean concentrations of Li and K in the melts in the three different cell compartments to mole % of lithium carbonate. Fig. 3 presents a schematic plot of the respective Li-mole fractions in the anode, electrolyte matrix and cathode respectively for the same three experiments.

Table 2
Demixing of 62/38 Li$_2$/K$_2$CO$_3$ electrolyte in MCFC

| Operating time /h | c.d./mA cm$^2$ | mole % Li$_2$CO$_3$ | anode | matrix | cathode |
|-------------------|----------------|---------------------|-------|--------|---------|
| 340               | 100            | 64                  | 64    | 58     |
| 147               | 100            | 62                  | 61,5  | 57     |
| 160               | 150            | 57                  | 56    | 42     |

Evidently anode and matrix electrolyte exhibit almost the same chemical composition but the catholyte is seizeably depleted in lithium. This effect becomes much more pronounced at higher current densities. As the current density increases by a factor of 1.5 the concentration difference,

$$\Delta x_{Li_2CO_3} = x_{Li(matrix)} - x_{Li(cathode)}$$

increases by a factor of almost 3, indicating that the current density of a MCFC with Li$_2$CO$_3$/K$_2$CO$_3$ eutectic melt might become a critical operation parameter.

Li$_2$CO$_3$/Na$_2$CO$_3$ electrolyte

Transference experiments had also been performed with Li$_2$CO$_3$/Na$_2$CO$_3$-eutectic (52/48 mole/mole) as this electrolyte is estimated to be a promising alternative to
the lithium/potassium carbonate eutectic. Table 3 lists the analyses of the cell melts in the three different components of a respective lithium-sodium carbonate cell.

| Operating time /h | c.d./mA cm⁻² | anode | matrix | cathode |
|-------------------|--------------|-------|--------|--------|
| 139               | 100          | 56    | 51     | 49     |
| 69                | 150          | 56    | 54     | 53     |
| 116               | 150          | 53    | (57)   | 48     |

Obviously also with lithium/sodium carbonate melts (52/48 mole/mole) the accumulation of the heavier sodium cation is observed in the cathode. Therefore also for this binary mixture of carbonates the Chemla effect is prevalent. But the effect is weaker and the concentration gradient seems to be more evenly distributed across the cell than with lithium/potassium carbonate melts.

**Transference experiments with La₂O₃ as cathode additive**

20 mol % LaNiO₃ dispersed as crystallites of approx. 5 μm diameter had been added to carbonyl-nickel powder (3 to 4 μm). By in-situ reductive sintering which decomposes LaNiO₃ to metallic nickel and La₂O₃ followed by atmospheric oxidation a NiO-cathode doted with La₂O₃ had been formed. A lithiated nickel oxide cathode was formed therefrom by imbibing the electrode with Li₂CO₃/K₂CO₃ electrolyte and was incorporated into an MCFC with Li/K-carbonate electrolyte. After 500 h of operation at 650°C with 100 mA cm⁻² the cell was cooled, disassembled and embedded into a polymer. A cut of the cell, obtained by sawing the polymer block was supplied with a thin gold coating by sputtering and different parts of the cell were examined by EDX for their lanthanum contents. No lanthanum could be detected in the cathode. Fig. 3 depicts the interface between the electrolyte matrix and anode and shows the signal intensity attributed to La at 4.5 eV. Obviously there is no lanthanum present in the electrolyte matrix, but a high lanthanum concentration can be detected in the anode close to the interface and a lower but definitely detectable concentration farther away from the interface.

**Discussion**

(a) Transport balances of binary salt mixtures

As shown schematically in Fig. 1 the faster cation accumulates in the cathode and correspondingly the slower moving cation must be found in enhanced concentration in the anode and matrix. Under steady state conditions migrative, convective and diffusive mass transport of the cation, i, are adding to zero in any virtual plane parallel to the cell surface:

\[
0 = n_{(total)} = n_{conv} + n_{mig} + n_{diff}
\]
With $t_i$ equaling the so-called internal transfer number of cation, $i$, and $x_i$ equaling the mole fraction of the salt $(M_i)_2CO_3$ in the binary mixtures one obtains for the three transport terms

$$
\frac{\partial n_{\text{conv}}}{\partial t} = -\frac{i}{2F} x_i \left[ \frac{i}{F} t_i \right], \quad \frac{\partial n_{\text{mig}}}{\partial t} = -\frac{x_i}{y_i} D_i, \quad \frac{\partial n_{\text{diff}}}{\partial y} = -\frac{\partial x_i}{\partial y} D_i
$$

[2]

and calculates the steady state balance

$$
0 = -\frac{i}{F} (x_i - t_i) - \frac{\partial x_i}{\partial y} D_i
$$

[3]

calculating the volumetric concentration $c_i$ by $c_i = x_i \rho / \bar{M}$ with $\rho$ equal to the density of the melt and $\bar{M}$ equal to the mean molar weight of the melt of one arrives at

$$
\frac{dx_i}{dy} = -\frac{i}{F} (x_i - t_i) \frac{\bar{M}}{\rho} \frac{1}{D_i}
$$

[4]

ti as the internal transfer number is, defined by the internal mobilities, $b_i$ and $b_j$ of the two cations and by the mole fractions, $x_i$ and $x_j$ of the two salts in the binary mixture:

$$
t_i = \frac{x_i b_j}{x_i b_i + x_j b_j} = \frac{x_i b_j}{x_i (b_i - b_j) + b_j}
$$

[5]

A closed solution of diff. equ. [4] is impossible, as the $b_i$, $b_j$ values are not constant as the concentrations of the molten mixture changes. According to equ. [4] the sign of the gradient $dx_i/dy$ depends on the sign of the quantity $(x_i - t_i)$ and its magnitude depends also on the current density, $i$. For $x_K > 0.32$, as is demonstrated in Fig. 5, the quantity $(x - t)$ becomes negative for potassium and hence the gradient $dx_K/dy$ becomes positive, i.e. the concentration of potassium increases in going from the anode to the cathode, whereas the concentration of lithium decreases correspondingly. Since the eutectic has the composition $x_K = 0.38$ we can definitely predict the accumulation of potassium and the depletion of lithium in the cathode as it is observed in Fig. 3. We expect also, that on the anode side of the cell a limiting potassium concentration will be attained that matches the concentration of the crossing point if more and more potassium is dragged into the cathode as would be expected as the current density is increased. Eventually at the anode side the concentration of potassium would become lower than that of the crossing point and lithium starts accumulating in the anode. This prediction is obviously fulfilled at $150 \text{ mA cm}^{-2}$. The mass balance for the experiment with $150 \text{ mA cm}^{-2}$ shows, that the total lithium content of the cell is
too low. This is likely to be attributed to lithium losses for instance by lithiation of nickel oxide and corrosion reactions producing LiFeO₂.

Internal mobilities of the cations in binary lithium carbonate/sodium carbonate mixtures have not yet been published. Therefore in the case of these two cations only some guesses can be made from measurements performed in binary mixtures of lithium and sodium salts with common anions other than carbonate. Okada and Lunden investigated binary mixtures of alkali nitrates [cited in (8)]. In lithium nitrate potassium nitrate mixtures very like in lithium carbonate potassium carbonate melts a crossing point is observed, whereas with mixed lithium sodium nitrate melts a crossing point does not exist and the ratio b_{_{Na^+}} / b_{_{Li^+}} stays almost constant (this value is approximately 1.15 at 380° C) across the whole range of melt composition from x_{Li} close to zero to close to one. As the anions NO₃⁻ and CO₃²⁻ are similar with respect to their geometry, volume and polarizabilities, one would therefore infer, that also for molten Li/Na-carbonate mixtures a crossing point would not exist but the Chemla effect (higher mobility of the heavier cation) would be operative and that the value (x_i - t_i) is positive for the small lithium and negative for the somewhat larger sodium cation. One would therefore anticipate that sodium like potassium accumulates also in the cathode of an MCFC with Li/Na carbonate as electrolyte. This, indeed is actually observed.

(b) Transport of additives

Additives, either dissolved or deposited as little soluble small particles are also influenced by electric field driven transport across the cell as solid state oxides, which are the usual oxides, generate ions if dissolved in the melt. An example is the "acidic" dissolution of nickel oxide in carbonate melts according to equ. [6].

\[
\text{NiO + CO}_2 \rightarrow \text{Ni}^{2+} + \text{CO}_3^{2-}
\]  

[6]

What is valid for the ionic majority species Li⁺ and K⁺ or Na⁺ does hold also for dissolved species of minor concentration. The criterion for their concentration distribution in the cell is still equ. [4] in a modified notation in which mainly the factor \( \tilde{M}/\rho \) is changed in a way which accounts for the stochiometry of the dissolution reaction.

Quantitatively still the expression \( (x_i - t_i) \) is maintained for cations as decisive. If it is positive, the dissolved species tends to be accumulated at the cathode and vice versa. If, however, the enhanced concentration exceeds the solubility, then almost complete transfer from one side of the cell to the other will occur as it was observed with \( \text{La}_2\text{O}_3 \). The same result is affected if the dissolved lanthanum species is anionic and not cationic, e.g. \( \text{[La(CO}_3]_{2n^-}^{3-} \). Anions move anyway towards the anode, for then the respective term in equ. [5] reads \( -(x_m + t_m) \) and \( \text{La}_2\text{O}_3 \) will under these conditions precipitate in the anode, provided initially more \( \text{La}_2\text{O}_3 \) had been deposited than can be dissolved in the whole cell electrolyte.
Conclusions

The well known effect of demixing of binary molten carbonates by electrolysis leads in molten carbonate fuel cells, due to the Chemla effect, to the accumulation of the heavier alkali cation (K⁺ or Na⁺) and depletion of Li⁺ at the cathode. This has several consequences:

(a) the electrode kinetics of oxygen evolution is affected as the solubility of oxygen in the melts depends on the lithium content.

(b) The effective volatility of the melt, which is mainly determined by the mole fraction of the more volatile sodium and potassium carbonates respectively is enhanced to some extent according to their increased concentration (9).

(c) Most serious is the possibility, that at seizureable increased current densities, which are desirable because of the still insufficient power density of MCFCs. The concentration enhancement of potassium cations at the cathode could lead to such enhanced concentrations of lithium in the anode, that there the liquidus/solidus curve is crossed and lithium carbonate begins to precipitate which would certainly destroy the anode. Fig. 6 shows the melting point diagram, which explains that Li₂CO₃ precipitation in the anode is much more likely to occur than K₂CO₃ precipitation in the cathode. In principle this can be avoided only if the whole cell electrolyte is kept at a concentration very close to that of the crossing point of the internal mobilities of two alkali cations.

(d) As in lithium/sodium carbonate melts the Chemla effect is less pronounced than in lithium/potassium carbonate melts, there exists another reason - additionally to the lower volatility of this binary electrolyte - to use Li/Na carbonate melts instead of Li/K carbonate melts as MCFC electrolyte in the future.

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Fig. 1: Schematic of the fluxes of two different cations and carbonate ions in binary molten alkali carbonates in an operating MCFC

Fig. 2: Intrinsic mobilities of lithium and potassium cations vs. mole fraction of $\text{K}_2\text{CO}_3$ in Li/K $\text{CO}_3$-melts at 707 °C (4)
Fig. 3: Experimentally determined concentrations of Li (mole/mole) in an MCFC after 400 h of operation at 100 and 150 mA cm$^{-2}$ at 650°C.

Fig. 4: Distribution of La$^{3+}$ in the matrix and anode of an MCFC after 500 h of operation. The La$^{3+}$ was initially deposited as La$_2$O$_3$ in the cathode.
Fig 5. Melting point composition diagram of Li/K carbonate mixtures at 707 °C according to the data of Fig. 2. (4)

Fig 6. (x-Co/Li) and (x-Co/K) in molten Li/K carbonates at 707 °C according to the data of Fig. 2. (4)