Using electrochemical impedance spectroscopy and a relaxation method with galvanostatic perturbation, the kinetics and mechanism of the reaction occurring on the magnesium electrode immersed in molten binary mixtures of magnesium and potassium chlorides, were studied in a wide range of compositions and at various temperatures. The process was found to consist of decomposition of a magnesium chloride complex, followed by two electrochemical steps: the first slow and diffusion dependent and the second, fast and diffusion independent. Due to changes in the structure of melts and activity of the reacting species with changing concentration of alkali cation, the evaluated current density of the first and slow electrochemical step varied from 2.6 A·cm⁻² for pure MgCl₂ to 4.6 A·cm⁻² for the melt containing 25 mol % of KCl and to 0.75 A·cm⁻² for the melt containing 80 mol % of KCl at 755°C. Parameters for the chemical step of decomposition of the magnesium chloride complex have been also evaluated from impedance spectra and compared with data from equilibrium measurements with reasonable success.

INTRODUCTION

This paper comprises the results of investigation of the electrode reaction at a liquid magnesium electrode in binary molten mixtures of magnesium and potassium chlorides. Two previous papers in this series of studies of the magnesium electrode reaction concerned studies in pure magnesium chloride (1) and in the binary mixture of magnesium and sodium chlorides (2). All these processes show high reversibility with high exchange current densities. Most of the electrochemical methods cannot provide correct values of kinetic parameters of such fast electrode reactions and the corresponding low values of the charge transfer resistance. Values of charge transfer resistances determined by electrochemical impedance spectroscopy are of low accuracy due to their very small magnitude (of the order of 10² Ω). It is therefore necessary to combine two
methods: electrochemical impedance spectroscopy and the potential relaxation method, both described and applied previously (1-5).

Raman spectroscopic studies have shown that in pure and concentrated melts of MgCl₂, polynuclear complexes of the type (MgCl₂)ₙ are formed (6-8). Such a rigid three-dimensional structure tends to break up when adding alkali chlorides. This tendency is stronger the higher the polarizing power of the alkali cation, i.e. the smaller the ionic radius. When adding more alkali chloride, tetrahedral complex anions like MgCl₄²⁻ are formed. The stability and dissociation of those complexes also depend on the ionic radius of the alkali cation, the complex being more stable with increasing ionic radius of the cation. These findings are confirmed by thermodynamic measurements like determination of EMF (9) and phase diagram studies (10). The higher stability of the complexes in the potassium than in the sodium system is shown by the phase diagram of the MgCl₂-KCl system in Fig. 1. In both systems the solid compounds M₂MgCl₄ and MMgCl₃ are found. In the potassium system these compounds melt congruently whereas in the sodium system they melt incongruently. The dissociation constant of the tetrahedral compound in the NaCl system is about 10⁻² and about 10⁻³ in the KCl system.

In the treatment of the NaCl-MgCl₂ system a three (four) step model was proposed for the total cathodic process, not taking into account any nucleation phenomena (2):

The first step is the chemical dissociation of a complex:
- In concentrated melts:
  \[(\text{MgCl}_2)_n \leftrightarrow (\text{MgCl})_{n-1} + \text{Mg}^{2+} + 2\text{Cl}^-\]  \[1a\]
- In more diluted melts:
  \[\text{MgCl}_4^{2-} \leftrightarrow \text{Mg}^{3+} + 4\text{Cl}^-\]  \[1b\]
  (Mg (II) dissociated)

The further process comprise two subsequent charge transfer steps:

\[\text{Mg (II) (dissociated)} + e \leftrightarrow \text{Mg (I)}\]  \[2\]
\[\text{Mg (I)} + e \leftrightarrow \text{Mg (0)}\]  \[3\]

A model including a preceding chemical reaction with diffusion of the Mg (II) species was used for simulating the impedance.
EXPERIMENTAL

Reagents. Anhydrous magnesium chloride was obtained from magnesium chloride hexahydrate (Merck p.a.) by heating it in dried argon and thereafter in HCl atmosphere with increasing temperature up to 600°C. The dehydrated salt was next distilled under high vacuum. Potassium chloride (Merck p.a.) was heated under a high vacuum at 550°C. Magnesium rods of 99.99% purity were used without further treatment.

Apparatus and procedure. Measurements were performed in an alumina crucible placed in a quartz tube, closed with a brass lid and kept in purified argon atmosphere. The working, counter and reference electrodes consisted of Mg metal floating inside alumina tubes. Molybdenum wires in alumina tubes provided the electric contact with the liquid magnesium. The quartz tube was placed inside an electric furnace with a temperature stability of ±1°C. The measuring cell was the same as presented earlier (2).

Impedance spectra were recorded with a computer-controlled phase-gain analyser Solartron 1260 between two electrodes of the same area of 0.12 cm². The investigated compositions are shown as vertical lines in Fig. 1.

Relaxation measurements were performed using an EG&G PAR Model 173 galvanostat and an EG&G PAR Model 175 pulse generator as a galvanostatic impulse source and a Le Croy LS140 200 MHz digitising oscilloscope as a potential recorder. After passing a short constant current pulse lasting for 0.1 ms, between the working and the auxiliary electrode, the overpotential decay of the working electrode vs. the reference electrode was recorded as a file of 2000 points.

RESULTS

A typical impedance spectrum presented in a complex plane plot is shown in Fig. 2a and presented in the Bode plane in Fig. 2b.

It has been shown that for electrode reactions with high values of the exchange current a significant part of the imaginary impedance Z" is positive. It is therefore necessary to introduce an inductance to the equivalent electric circuit when simulating such a system (Fig. 3). Except from the outer inductance, attributed to leads, apparatus and furnace, one should introduce a distinct inductance for every charge transfer step of an electrode process (2,3).

Relaxation measurements. Two types of relaxation curves were recorded: in the millisecond and in the microsecond time range. Both types are similar to the ones presented earlier (1,2). On the basis of the relevant parts of the equivalent circuit, presented in Fig. 3, the equations describing the relaxation curves have been obtained. For the first, slow and diffusion related charge transfer step (step 2) the slow part of the overpotential decay can be described by the following equation:
\[ \eta(t) = A \cdot \exp(\alpha^2 t) \cdot \text{erfc}(\alpha t^{1/2}) + B \cdot \exp(\beta^2 t) \cdot \text{erfc}(\beta t^{1/2}) + C \cdot \exp(-\gamma t) \]  

where for \( t = 0 \), \( \eta(0) = A + B + C \). The coefficients \( \alpha, \beta, \gamma \) allow for the calculation of the charge transfer resistance for the low frequency charge transfer step:

\[ R_2 = L_2 \cdot (\alpha \cdot \beta + \gamma) \]  

and of the diffusion impedance

\[ Z_w = L_2 \cdot (\alpha + \beta) \cdot \gamma \]  

For the second, fast charge transfer step (step (3)) the short time dependence of the overpotential is given by the following equation:

\[ \eta(t) = \frac{\eta(0)}{s_1 - s_2} (s_1 \cdot \exp(-s_1 \cdot t)) - s_2 \cdot \exp(-s_2 \cdot t) \]  

where \( s_1 \) and \( s_2 \) the two angular frequencies, which can be obtained from the fit of the experimental relaxations curve according to equation [7]. Using the high-frequency inductance determined from impedance spectra, one obtains the charge transfer resistance for this step:

\[ R_{ct} = L_1 \cdot (s_1 + s_2) \]  

The exchange current density of every of the above steps can then be evaluated from the equation:

\[ j_0 = \frac{R \cdot T}{A \cdot F \cdot R_{ct}} \]  

where \( A \) is a surface area of both electrodes (0.24 cm\(^2\)), the other symbols having their usual meaning.

The temperature dependence of the inductance of the low frequency step, step (2) is presented in Fig. 4 and the temperature dependence of the exchange cd of this first charge transfer step in Fig. 5.

The exchange cd for the low frequency (slow) charge transfer step (step (2)) is shown in Fig. 6 as a function of composition in the KCl-MgCl\(_2\) system at temperatures varying from 665°C to 785°C. When adding KCl to the MgCl\(_2\) the exchange cd increases to a maximum at about 60 mol % MgCl\(_2\). As shown in Fig. 7 this maximum is lower and
moved to a higher concentration of alkali chloride in the potassium chloride than in the sodium chloride system.

The activation energy $E_a$ of the slow charge transfer step as a function of composition, is shown for the binary systems with NaCl and KCl in Fig. 8. The energy is considerably higher in the potassium system than in the sodium system. For both systems the value of $E_a$ decreases with additions of alkali chloride. The exchange cd of the high frequency charge transfer step is very high, both in the NaCl and the KCl systems (25 - 35 A cm$^2$) and nearly composition independent. This means that the Mg (I) (Mg$^+$) species are very unstable and are immediately reduced to Mg (0). The increase in exchange cd and the decrease in activation energy by addition of alkali chloride to the pure MgCl$_2$ is probably due to the breaking down of the polynuclear three dimensional [MgCl$_2$]$_n$ structure. Due to the higher polarizing power the NaCl is more efficient than KCl in this process.

When adding alkali chloride to MgCl$_2$, the amount of free Mg (II)-ions will increase from the beginning and then decrease by increasing additions, as indicated also by the development of the exchange current. This means that the complex seem not to take directly part in the charge transfer process, at least at low cds, and that the dissociation of the complex is rate determining, at least at high cds.

**THE CHEMICAL DISSOCIATION STEP**

**PARAMETERS OF THE CHEMICAL STEP (REACTION 1)**

It is seen in Fig. 7 that the exchange cd in molten mixtures of MgCl$_2$ in KCl is lower than that for solutions of MgCl$_2$ in NaCl. It results from the fact that the complex ion MgCl$_4^{2-}$ in the presence of the bigger potassium cation is more stable than in the melts with NaCl. The rate constants $k_1$ and $k_2$ of the chemical dissociation step and the equilibrium constant $K$ corresponding to step 1 can be determined from the recorded impedance spectra.

The presence of a chemical step preceding an electrode process, is described according to the general electrochemical notation by the equations:

$$ Y \xleftarrow{k_1}{k_2} O \quad [10] $$

$$ O + ne = R \quad [11] $$

These steps are equivalent to eq [1] and [2] in our process. This results, in addition to the Randles impedance, in an expression describing the impedance of preceding reaction (11,12). One thus obtains:
where:

\[ Z_{pr} = Z' - iZ'' \]  \[ \text{[12]} \]

\[ Z' = R_{ct} + \sigma_R \omega^{-1/2} + \frac{K}{1+K} \sigma_O \omega^{-1/2} + \frac{1}{1+K} \sigma_O \left[ \frac{(\omega^2 + k^2)^{1/2} + k}{\omega^2 + k^2} \right]^{1/2} \]  \[ \text{[13]} \]

\[ Z'' = \sigma_R \omega^{-1/2} + \frac{K}{1+K} \sigma_O \omega^{-1/2} + \frac{1}{1+K} \sigma_O \left[ \frac{(\omega^2 + k^2)^{1/2} - k}{\omega^2 + k^2} \right]^{1/2} \]  \[ \text{[14]} \]

In the above expressions \( \sigma \) is equivalent to the Warburg coefficient:

\[ \sigma = \sigma_O + \sigma_R = \frac{RT}{n^2 F^2 A \sqrt{2}} \left( \frac{1}{D_R^{1/2} \cdot c_R^*} + \frac{1}{D_O^{1/2} \cdot c_O^*} \right) \]  \[ \text{[15]} \]

\( k \) is the sum of the rate constants of the preceding reaction in both directions:

\[ k = k_1 + k_{-1} \]  \[ \text{[16]} \]

and \( K \) is the ratio of the rate constants:

\[ K = \frac{k_1}{k_{-1}} \]  \[ \text{[17]} \]

which is then equal to is an apparent equilibrium constant of the preceding reaction.

The apparent equilibrium constant \( K \) can, in dilute solutions, be expressed as:

\[ K = \frac{[\text{Mg}^{2+}]}{[\text{MgCl}_4^{2-}]} \]  \[ \text{[18]} \]

Having the value of \( K \) determined from impedance measurements, one can calculate the concentration of non-complexed magnesium cations \( \text{Mg}^{2+} \) from equation [18] and knowing the concentration of free chloride anions - also the Temkin equilibrium constant \( K_{eq} \) of the complex dissociation can be calculated:

Electrochemical Society Proceedings Volume 98-11
The molar fractions can be calculated from molar concentrations and known densities of salts. Results of calculations for a melt containing 80 mol.% of KCl are collected in Table 1.

Table 1. The Mg\(^{2+}\) ion diffusion coefficient, the K-value and the Temkin equilibrium constant \(K_{eq}\) of magnesium chloride complex dissociation in a melt containing 80 mol % of KCl and 20 mol % of MgCl\(_2\) at various temperatures.

| t (°C) | D (cm\(^2\)·s\(^{-1}\)) | K | \(K_{eq}·10^3\) |
|-------|-----------------|---|-----------------|
| 675   | 6.73·10\(^{-5}\) | 0.098 | 6.90          |
| 700   | 6.89·10\(^{-5}\) | 0.106 | 7.63          |
| 725   | 7.04·10\(^{-5}\) | 0.113 | 8.38          |
| 750   | 7.18·10\(^{-5}\) | 0.120 | 9.17          |
| 775   | 7.32·10\(^{-5}\) | 0.126 | 9.98          |

The obtained apparent equilibrium constant \(K\) is of the same value as obtained by Brooker and Huang using Raman spectroscopy (13). The Temkin equilibrium constant \(K_{eq}\) is also comparable with the values obtained using true equilibrium methods (9,14,15).

CONCLUSION

It has been shown earlier that the magnesium electrode reaction in binary MgCl\(_2\)-NaCl melts is composed of three steps, a preceding dissociation of a Mg (II) complex, and two charge transfer steps. The first one is comparably slow, diffusion related and composition dependent whereas the second one is fast and nearly composition independent. The same mechanism is confirmed also in the MgCl\(_2\)-KCl melt.
The maximum in the exchange cd with additions of NaCl in the NaCl melt is observed to be lower and moved to higher alkali chloride content in the KCl containing melt. This maximum is assumed to be due to the decomposition of the polynuclear (MgCl₂)_n structure in the pure MgCl₂ melt with the formation of a dissociated and more random structure in the dilute melt. In the diluted melt the prevailing complex is the tetrahedral MgCl₂^2-. The results show that the Na-cation, with its higher polarizing power, is more efficient in breaking down the three dimensional structure in the concentrated melt. The decrease in exchange cd by further additions of alkali chloride follows the normal decrease in the activity of MgCl₂.

The combined method of impedance spectroscopy and potential relaxation is very efficient when studying fast electrode reactions in such complex electrolytes.

REFERENCES

1. A. Kisza, J. Kazmierczak, B. Børresen, G.M. Haarberg and R. Tunold
   J.Appl.Electrochem. 25, 940 (1995)
2. A. Kisza, J. Kazmierczak, B. Børresen, G.M. Haarberg and R. Tunold
   J.Electrochem. Soc. 144(5), 1646 (1997)
3. A. Kisza, Polish J. Chem., 67, 885 (1993); ibid 68, 613 (1994)
4. A. Kisza, J. Kazmierczak, B. Børresen, G.M. Haarberg, R. Tunold
   J. Electrochem. Soc., 142(4), 1035 (1995)
5. J. Thonstad, A. Kisza, J. Kazmierczak; J. Appl. Electrochem., 26, 102 (1996),
6. V.A. Maroni, E.J. Hathaway and E.J. Cairns, J. Phys. Chem. 75, 155 (1971)
7. R.J. Capwell, Chem. Phys. Lett. 12, 443 (1972)
8. C.H. Huang and M.H. Brooker, Chem. Phys. Lett. 43, 180 (1976)
9. H. Ikeuchi and C. Krohn, Acta Chem. Scand. 23, 2230 (1969)
10. H. Flood and S. Urnes, Z. Electrochem. 59, 834 (1955)
11. J.A. Bard and R.L. Faulkner, Electrochemical Methods, Fundamentals and
    Applications, John Wiley, New York, (1980)
12. A. Kisza, Bull. Pol. Acad. Sci., Chem., 43, 337 (1995)
13. M.H. Brooker and C.H. Huang, Can. J. Chem. 58, 168 (1980)
14. D.E. Neil, H.M. Clark and R.H. Wiswall, J. Chem. Eng. Data 10, 21 (1965)
15. P.B. Engseth, Ph.D. Thesis, Department of Electrochemistry, NTH, Trondheim, Norway (1973)
Fig. 1. The phase diagram of the magnesium chloride – potassium chloride system. Vertical lines indicate concentrations of studied samples.
K. Grjotheim, J.L. Holm and M. Røtnes, Acta Chem. Scand., 26(9), 3802 (1972)
Fig. 2. The impedance spectrum of the electrode reaction at a liquid magnesium electrode in a salt melt containing 20 mol % of MgCl₂ and 80 mol % of KCl at 740°C a) in the complex plane, b) in the Bode plane.
Fig. 3. The schemes of equivalent circuits representing a) low frequency step, b) high frequency step, c) total electrode process on a liquid magnesium electrode in a molten mixture of magnesium and potassium chlorides. L_{out} - outer inductance, R_{el} - electrolyte resistance, C_{1}, C_{2} - capacitances, L_{1}, L_{2} - inductances, R_{1}, R_{2} - resistances of subsequent electron transfers, W - Warburg diffusion impedance. (The subscript numbers do not correspond to the superscripts in the text).
Fig. 4. Temperature dependence of the electron transfer inductance for the low frequency charge transfer step (step (2)) of the electrode reaction on liquid magnesium in molten mixture containing 50 mol % of MgCl₂ and KCl.

Fig. 5. Temperature dependence of the exchange cd for step (2) of the electrode reaction on liquid magnesium in molten mixture containing 50 mol % of MgCl₂ and KCl.
Fig. 6. The dependence of the exchange current density of the slow step on the composition of molten mixtures of MgCl$_2$ and KCl at various temperatures.

Fig. 7. The comparison of the concentration dependencies of the exchange cds for molten MgCl$_2$ and its mixtures with NaCl and KCl at 755°C.
Fig. 8. The concentration dependence of the activation energy of the slow step of the electrode process on the liquid magnesium electrode in pure molten MgCl₂ and its binary melts with KCl and NaCl.