CATHODIC DISCHARGE OF Mg(II)-SPECIES AND NUCLEATION OF Mg METAL FROM MOLTEN MAGNESIUM CHLORIDE

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ABSTRACT

The cathodic discharge of Mg(II)-species and nucleation of Mg metal from molten magnesium chloride on glassy carbon, molybdenum and iron have been studied using electrochemical techniques. At potentials more positive than the deposition potential the reaction is mainly controlled by diffusion of dissolved magnesium away from the electrode interface. The standard rate constant for the charge transfer process was determined to be 10^{-4} to 10^{-3} cm/s on the different electrode materials in the temperature range investigated (725°C-780°C). Determination of the electrode capacitance on an iron electrode using galvanostatic pulses gave values in the range 10-50 μF/cm². The nucleation overvoltage was determined by linear potential sweep to be 16 ± 4 mV. A model for the total cathode process is discussed.

INTRODUCTION

The deposition of magnesium from molten chlorides on different electrode substrates, such as glassy carbon and iron, has mainly been studied in solutions with small amounts of MgCl₂. The reaction is found to be controlled by diffusion of Mg(II)-species toward the electrode surface [1,2]. In recent studies electrochemical techniques have been applied to study the cathode reaction in pure molten magnesium chloride [3]. Measurements by AC impedance spectroscopy combined with a galvanostatic relaxation technique have shown that the discharge of Mg(II) species on a reversible Mg electrode is a two step process, and that the discharge from divalent to monovalent Mg species probably is the rate determining step [4].
In the pure MgCl₂ system a remarkable unstability of the nuclei formed on glassy carbon electrodes was observed. The unstability was detected using both cyclic voltammetry and potential step chronoamperometry. This unstability, which was observed even at rather low potentials (high negative overpotentials) is proposed to be due to a sudden homogeneous nucleation in the electrolyte, reducing the supersaturation of dissolved reduced magnesium species (metal). This homogeneous nucleation probably creates so-called "metal fog" observed during deposition of metals from molten salts.

On the basis of the previously mentioned observations a model of the total cathode process during discharge of Mg(II) species and deposition of magnesium metal is proposed. A schematic drawing of the model is given in Fig.1.

As part of the investigation of the total process we have studied the charge transfer reaction of Mg(II)-species and the diffusion process in pure molten MgCl₂ on glassy carbon, iron and molybdenum.

EXPERIMENTAL

Magnesium Chloride-Hexahydrate (p.a. Merck) was predried under HCl atmosphere up to 450°C and subsequently distilled under vacuum.

The working electrodes were rods of iron (Johnson Matthey, specpure), glassy carbon (Tokai, GC30S) and molybdenum (99.97%). The active electrode area was determined by visual inspection of the wetted area after each experiment. The reference electrode was liquid Mg cathodically deposited on a molybdenum wire placed in an MgO tube. The presence of oxide material in the melt is a source of oxide contamination. Samples taken from the melt during experiments were analyzed by iodometric titration to contain approximately 1500 ppm magnesium oxide, which corresponds to saturation of the chloride melt.

The system was studied by linear sweep voltammetry, chronoamperometry and galvanostatic pulses.

RESULTS AND DISCUSSION

A typical voltammogram obtained on iron in this system is shown in Fig.2. One should notice the considerable cathodic current at potentials more positive than the Mg reference potential. This cathodic current is probably due to formation of dissolved Mg species.

Previously reported measurements on glassy carbon, using a platinum reference
electrode, has shown an unstable behaviour of the formed Mg nuclei [3]. In the reported measurements, where the melt was saturated with oxide, this unstability was not observed on any of the electrode materials. The overvoltage associated with the deposition of Mg on the three substrates was determined by linear sweep voltammetry at 0.1 mV/s. The nucleation overpotential was found to be 16±4 mV on all the electrode materials. It is surprising that the nucleation overvoltage on glassy carbon is not considerably higher than on iron and molybdenum. This can probably be explained by the presence of the oxide tube in the melt that saturates the melt with oxide. As a result the dissolved oxide may stabilize the nuclei formed on the electrode which favours growth of the nuclei instead of dissolution.

The standard rate constants for the discharge of Mg(II)-species on glassy carbon, iron and molybdenum were determined by extrapolation of current transients at different potentials. The logarithm of the rate constants as a function of potential should be linear. From the slope of this line the product of the cathodic charge transfer coefficient and number of electrons in the rate determining step, \( z \cdot \alpha \), can be calculated. The activation energy of the electrode process, \( \Delta E^\# \), can then be calculated from the temperature dependency of the standard rate constants. The values for the standard rate constant, charge transfer coefficient and activation energy for the three electrode materials are given in Table 1. Unpublished work using an AC impedance technique has shown that the rate determining step is a one electron transfer, probably from Mg(II) to Mg(I) [4]. The number of electrons in the rate determining step, \( z \), is therefore taken to be one.

Table 1 Kinetic parameters obtained on glassy carbon (GC), molybdenum (Mo) and iron (Fe) in pure molten MgCl₂ [standard deviation for \( \Delta E^\# \) is given]

| Temp (°C) | GC  | Mo  | Fe  |
|-----------|-----|-----|-----|
|           | \( k^o \cdot 10^4 \) (cm/s) | \( \alpha \) | \( \Delta E^\# \) (kJ/mol) | \( k^o \cdot 10^4 \) (cm/s) | \( \alpha \) | \( \Delta E^\# \) (kJ/mol) | \( k^o \cdot 10^4 \) (cm/s) | \( \alpha \) | \( \Delta E^\# \) (kJ/mol) |
| 725       | 4   | 0.2 | 85±4 | 7   | 0.7 | 13   | 0.6 |
| 735       | -   | -   | -    | 8   | 0.5 | 13   | 0.5 |
| 750       | 5   | 0.3 | 140  | 14  | 0.2 | 18   | 0.2 |
| 780       | 7   | 0.2 | 17   | 17  | 0.6 | 21   | 0.1 |

As can be read from Table 1 the value of the standard rate constant for the discharge process on the different electrode substrates vary between \( 10^4 \) and \( 10^3 \) cm/s in the temperature range studied. If the electrodes were only a source of electrons one should
expect the rate of the discharge process to be independent of the substrate. The standard rate constant is about three times higher on iron than on glassy carbon. The differences found on the three substrates might be due to unequal number of active sites on the materials or an influence of oxide layers on the metal electrodes. One may also notice that the values for the charge transfer coefficient vary considerably. However, the standard rate constants and the activation energy determined on glassy carbon and iron has nearly the same value as found by AC impedance measurements on a molten Mg electrode[4]. On Mo the value of the activation energy is nearly two times the values obtained on GC and Fe. This value shows also a high degree of uncertainty which might be due to special difficulties in determining the active electrode area on this material.

Fig.3 shows typical current transients obtained on iron. From the figure a hump is easily observed, which could be caused by a monolayer formation. The charge associated with this peak is approximately 0.4 mC/cm². The charge required to form a dense monolayer of Mg atoms can be calculated to be ~ 0.8 mC/cm².

The electrode capacitance for the iron electrode has been calculated from potential transients obtained by galvanostatic pulses after 2-3 μs. It was found that the capacitance increases with time, which could be explained by the formation of a monolayer. The electrode capacitance (recorded after 2-3 μs) was found to vary between 10 μF/cm² and 50 μF/cm².

From current transients it has been found that at potentials positive to the nucleation potential the process seems to be mainly diffusion controlled. A plot of current density versus $t^{1/2}$ gives a straight line in an intermediate region, but the intercept for $t^{1/2} = 0$ is not equal to zero. This deviation is probably caused by convection, playing a role at longer times (t>1s.). Plots of i versus $t^{1/2}$ obtained on molybdenum and glassy carbon are given in Fig.4. From the slope of the straight lines the product of the concentration gradient and the square root of the diffusion coefficient can be determined. The interfacial concentration of the diffusing species may then be calculated assuming that the diffusion coefficient is known and that the bulk concentration is taken to be zero. The process occurring at this potential (0 mV vs Mg) probably is independent of the electrode material. Assuming that the process is reversible the interfacial concentration of dissolved metal, at the standard reversible potential, should be equal to the solubility of dissolved metal found by Wypartowicz et al [6], which is $2.5 \cdot 10^5$ mol/cm³. This indicates that our values are somewhat high. An alternative method for determining the concentration of the diffusing species was also applied. The electrode was polarized to a given potential (-20 mV) for a certain time (2s.). After the polarization period the potential was swept anodically with varying sweep rates. As can be observed from Fig.5 the $i_p$ versus $\nu^{1/2}$ is close to linear for both glassy carbon and molybdenum. From
the slope of these lines the concentration at the interface can be calculated to be $3 \cdot 10^{-5}$ mol/cm$^3$ and $7 \cdot 10^{-5}$ mol/cm$^3$ on glassy carbon and molybdenum respectively. The reason for the higher value found on Mo is not clear, but could be caused by nucleation on Mo which would tend to increase the peak current. The theoretical value at this potential assuming a reversible process is $4 \cdot 10^{-5}$ mol/cm$^3$.

Finally, a qualitative discussion of the proposed model is appropriate. The initial step is a two step charge transfer reaction. The rates of the following parallel paths are determined by the applied potential and the electrode materials. At potentials positive to the nucleation potential, the magnesium formed at the electrode dissolves in the melt independently of the electrode material. The dissolved metal diffuses away from the electrode to the melt. At more negative potentials, the concentration of dissolved metal is high enough for Mg nuclei to form. This critical nucleation potential is determined by the interfacial properties. The different wetting properties of Mg on the electrode materials are of decisive importance when it comes to the stability of the nuclei formed on the electrode. If Mg wets the electrode poorly, the concentration of dissolved metal at the electrode interface has to be high to facilitate the nucleation. The small nuclei would, if the concentration of dissolved metal decreases (ie homogeneous nucleation in the melt), tend to dissolve. However, if the nuclei are covered by a protective oxide layer, the dissolution would be hindered and the nuclei are stabilized.

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Fig. 1 A model of the total process for cathodic discharge of Mg(II) species

\[ \text{Mg}^{2+} + 2e \rightarrow \text{Mg}_{\text{interface}} \]

\[ \text{Mg}_{\text{interface}} \rightarrow \text{Mg in MgCl}_2(\ell) \]

\[ \text{Nucleation (heterogeneous)} \]

\[ \text{Diffusion} \]

Anodic dissolution → Growth → Homogeneous nucleation → Diffusion

Fig. 2 Cyclic voltammogram obtained on iron in pure MgCl$_2$ at 735°C. Sweep rate: 100 mV s$^{-1}$. Electrode area: 0.32 cm$^2$. 

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Fig. 3  Cathodic current transients obtained on iron in pure MgCl₂ at 780 °C. Applied potential: 1) +50 mV, 2) +40 mV and 3) +20 mV versus the Mg reference electrode. Electrode area: 0.22 cm².

Fig. 4  Cathodic current density as a function of $t^{1/2}$ obtained on glassy carbon (crosses) and molybdenum (filled squares) in pure MgCl₂ at 725°C. The applied potentials was 0 mV versus the Mg reference electrode.
Fig. 5  Peak current density versus the square root of scan rate obtained on glassy carbon (filled squares) and molybdenum (asterisks). Temperature: 725 °C. Applied potential was -20 mV vs Mg reference with a residence time of 2s.