STUDY OF THE ANODE PROCESS ON CARBON ELECTRODES IN THE PURE MAGNESIUM CHLORIDE MELT WITH DISSOLVED MAGNESIUM OXIDE AT 1023K.

M. Mohamedi,* B. Borresen, G. M. Haarberg and R. Tunold

Department of Electrochemistry, The Norwegian University of Science and Technology, N-7034 Trondheim, Norway

ABSTRACT

The anodic behaviour of carbon electrodes in molten MgCl₂ containing magnesium oxide at 1023K was investigated by cyclic voltammetry and square wave voltammetry. The experimental square wave voltammograms are compared directly with the exact numerical solution for the boundary problem via COOL algorithm, a numerical method yielding estimates of transfer coefficient and rate constant for the process. The anodic reaction was found to occur in one irreversible two-electron charge transfer process under diffusion control. The agreement between experimental and calculated voltammograms is excellent over a wide range of experimental conditions. Diffusion coefficient of the oxygen containing species, charge transfer coefficient and standard rate constant were found to be 6.65x10⁻⁶ cm²s⁻¹, 0.46 and about 10⁻⁴ cm s⁻¹ respectively.

INTRODUCTION

The presence of small amounts of oxygen containing species during electrolysis in chloride melts may have a detrimental influence on the preferred electrode reaction. Successful harvesting of the metal during magnesium electrolysis is dependent on the size of the magnesium droplets detaching from the cathode. Dissolved oxides may be electroactive and potentially harmful to the process (1). Furthermore dissolved oxide species will during operation react at the anode and cause evolution of CO₂/CO, a process which wears the anode and contaminate the anode gas. The consumption of carbon material is unfavorable both due to environmental consideration and also because it causes an increase of the electrode distance in the cell, which increases the ohmic drop in the cell and decreases the energy efficiency.

The current work was therefore undertaken to investigate the anode process on carbon electrodes in the pure magnesium chloride melt (MgCl₂) with dissolved magnesium oxide (MgO) at 1023K by means of cyclic voltammetry (CV) and square wave voltammetry (SWV). It was also of interest to compare the electrochemical behaviour of

* Present address: Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, Aoba-ku, Sendai, 980-8579, Japan.
the MgO/MgCl₂ and CaO/CaCl₂ systems (2).

Square wave voltammetry has previously been successfully applied for studies of molten salt solutions (3-8). The increased sensitivity of SWV over traditional CV is, among other reasons, due to its ability to eliminate charging and background currents. The theoretical of SWV of systems complicated by electrode kinetics or by preceding, following, or catalytic homogenous chemical reaction, has been addressed by O'Dea et al. (9).

EXPERIMENTAL

Salt preparation
Magnesium chloride hexahydrate (Merck, p.a.) was dried under HCl atmosphere by increasing the temperature to 450°C and subsequently distilled twice under vacuum. The purified salt contained less than 20 ppm oxygen determined by iodometric titration. Magnesium oxide (FLUKA, p.a.) was dried and heated under vacuum. The experiments were performed in glassy carbon crucibles, with increasing additions of MgO from 0 to 0.39wt%. The actual content of oxide was also determined by iodometric titration of samples taken from the melt, quenched at room temperature, and analyzed.

Electrochemical cell
The cell consisted of a cylindrical quartz container placed in a transparent gold mirror furnace (Trans Temp Co.). The working and quasi-reference electrodes were, respectively, a rod made of glassy carbon (3mm diameter) and a platinum wire directly immersed in the bath. A glassy carbon crucible served as a melt container and worked as the counter-electrode. The temperature of the melt was controlled by using a Pt-PtRh (10%) thermocouple. The uncertainty in the temperature measurements was found less than ±1°C. The electrode area which was about 0.94 cm² was checked by changing the depth of immersion in the electrolyte during voltammetry at constant sweep rate. All measurements were performed at a temperature of 1023K.

Instrumentation
Cyclic voltammetry and square-wave voltammetry were carried out using a Princeton Applied Research (PAR) Model 273 potentiostat/galvanostat under computer control via a personal computer executing M270/250 research electrochemistry version 4.11 software supplied by PAR.

In SWV, the potentiostat applies a series of forward and reverse pulses superimposed on a linear scan of constant height, the step height \( \Delta E_s \). Both the pulse height and the square-wave amplitude \( E_{sw} \) and the step height are constant throughout the experiment. The width of the pulses are inversely related to the frequency \( f \) of the applied pulse sequence, i.e., pulse width \( \tau_p = \frac{1}{2\pi f} \). The potentiostat samples the current at the end of both the forward and reverse pulses. Like this, the capacitive currents are negligible and faster scan rates than in conventional cyclic voltammetry may be applied. A typical response curve for the difference current displays a flat baseline with peaks corresponding to the electroactive species. The peak height is directly related to the
concentration of these species. The theoretical curve of the differential current vs. potential is Gaussian in the case of a reversible system involving soluble species. The peak is centered at a potential close to the half-wave potential for the ionized species. The width of the net peak current voltammogram at half height, $W_{1/2}$, depends on the number of electrons exchanged and on the temperature, according to the relation (11-12):

$$W_{1/2} = 3.52 \frac{RT}{nF}$$

Calculations and simulations

Experimental square wave voltammograms were compared directly with the exact numerical solution for the boundary value problem by means of the Model 271 COOL Kinetic Analysis Software 4.01 Beta, which is described elsewhere (13-15). They were analyzed according to a slow charge transfer mechanism (Eq.1). This mechanistic model supposes the presence of a single electroactive species in solution. This species is further assumed to exhibit only one redox couple and the charge transfer process is slow enough to be detectable on the time scale of the experiment. Three model variables are accessible during calculation: the reversible half-wave potential, $E_{1/2}$, of the redox process, the charge transfer coefficient, $\alpha$, and the log($\kappa \cdot \tau^{1/2}$) which is related to the apparent standard rate constant, $k_0^0$, through equation 2.

$$A \xrightarrow{k_0^0} B + ne$$

$$\kappa = \frac{k_0^0}{\sqrt{D_O^{1-\alpha} D_R^\alpha}}$$

where $D_O$ and $D_R$ are the diffusion coefficients of the oxidized and reduced forms, respectively.

RESULTS AND DISCUSSION

Cyclic Voltammetry

Cyclic voltammograms exhibit a well-defined anodic current peak labeled A, at about 0.8V. Upon reversing the direction of the potential sweep, current continued to flow in the anodic direction, suggesting that the electrochemical process was (to some extent) irreversible. Typical voltammograms obtained with 0.08wt% MgO and in the potential range 0V to 1V are shown in Fig. 1. The main anodic wave that starts at about 1V is due to chlorine evolution. The peak current of peak A as a function of sweep rate is illustrated in Fig. 2. The peak current appears to be linear with the square root of the sweep rate and has an intercept of 2.9mA. Values of $I_{pA}/(Sv^{1/2})$ were plotted as a function of $v$ in order to investigate possible chemical reactions coupled to the charge transfer (Fig. 3). Invariance of $I_{pA}/(Sv^{1/2})$ with $v$ would indicate charge transfer with no chemical complication (16). The results show that the $I_{pA}/(Sv^{1/2})$ parameter slightly decreases as the potential sweep rate
increases at sweep rates below 0.4 V s\(^{-1}\), which is interpreted as a chemical reaction coupled to the electrode reaction. However, the chemical reaction will not influence to a significant extent as the scan rate is increased. The anodic peak potential, \(E_p\), corrected from the ohmic drop \(R_e\) (\(R_e=1.38\Omega\), measured by AC-impedance spectroscopy) was found to be proportional to the logarithm of the sweep rate up to 0.7 V s\(^{-1}\) (Fig. 4). The slope obtained with the best linear fit is equal to 0.048 V, implying that \(\alpha n\) is equal to 0.92 (16). Therefore, assuming \(n=2\) yields \(\alpha=0.46\). The evolution of the peak current, \(I_{pa}\), as a function of the MgO concentration is summarized in Table I. At concentration of MgO up to 0.19 wt%, the \(I_{pa}\) increased with increasing \(C_{MgO}\). The peak current did not increase with a further addition of oxide. The reason for this is most likely that the solubility of oxide in this melt, at this temperature, is about 0.19 wt%, which is in agreement with solubility data reported by Boghosian et al. (17).

| \(C_{MgO}\) wt% | \(I_{pa}\) A | \(I_{pa}\) A |
|---|---|---|
| 0.08 | 0.021 | 0.023 |
| 0.19 | 0.028 | 0.031 |
| 0.28 | 0.029 | 0.031 |
| 0.39 | 0.028 | 0.030 |

**Table I.** The anodic current peak for process A as function of the magnesium content

Diffusion coefficient for the \(O_2^-\) containing specie. Using the well-known relationship for a reaction of irreversible charge transfer (16), one can write:

\[
\frac{I_p}{v^{1/2}S} = 0.496nF\left[\frac{\alpha n \alpha F D}{RT}\right]^{1/2}
\]  

By means of constant \(I_{pa}/(v^{1/2}S)\) (found for sweep rates higher than 0.4 V s\(^{-1}\)) and taking \(n=2, \alpha=0.46\), we obtain \(D_{O_2^-} = 6.65 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}\). The value of the diffusion coefficient is directly linked to the structural mean radius of the electroactive particle \(i\) by the well-known relation of Stokes-Einstein relation (18):

\[
R_i = \frac{kT}{6\pi\eta D_i}
\]

where \(\eta\) represents the dynamic viscosity of the medium in which the particle \(i\) is contained. We assume that in the concentration range used during this investigation, \(\eta\) corresponds to the value of pure MgCl\(_2\) at 1023K, 2.008 mNsm\(^{-2}\). Consequently, \(R_i=5.61 \text{ Å}\) whereas \(R_{O_2^-}=1.32\text{ Å}\) (19). This result probably reflects the degree of complexing of the \(O_2^-\) ion in the bulk of the solution. Solubility measurements and cryoscopy together with model
calculations reported by Boghosian et al. (17) indicated the presence of the complex Mg$_2$OCl$_2$ in molten MgCl$_2$ containing dissolved MgO.

Square-wave voltammetry

Various experimental conditions of $\Delta E_S$, $E_{SW}$ and $f$ were evaluated in order to obtain the best parameters for SWV studies of the behaviour of the dissolved oxides. A typical SW-voltammogram run at $f=25$Hz, $\Delta E_S=2$mV and $E_{SW}=20$mV is shown in Fig. 5. It exhibits a well-defined anodic current peak at about 0.8V. The main anodic wave that starts at about 1V is due to chlorine evolution. No cathodic peak was observed during the reverse current, which indicates that the reaction is irreversible. These results are in agreement with results from cyclic voltammetry (Fig.1). A significant advantage of the square-wave mode over the cyclic voltammetry is the superiority of discrimination against background current. This is clearly seen by comparing Fig. 5 and Fig. 1, particularly in the potential region of the anodic limit.

Numerical calculation

We have tried to analyze the data by considering different reaction mechanisms, the one step reversible, the CE and the EC mechanisms. None of these models seems to yield satisfactory results. The model that most correctly describes our results is the one represented by Eq. 1. An example of a good fit between the experimental data and the theoretical voltammograms is presented in Fig. 6 (for visualization of the quality of the fit we show curves recorded at some SW-frequencies) and the derived kinetic parameters are tabulated in Table II. The region of confidence at the 95% confidence interval for these parameters is also shown in Table II. The quality of the fits to the theoretical model is very satisfactory and clearly demonstrates that the model is valid. We must emphasize that because of the use of a quasi-reference electrode, the degeneracy in $E_{1/2}$ and $\kappa$ was removed in all our calculations by choosing an arbitrary reference potential, $E_r$. The systematic effect of this degeneracy is that small errors in potential propagate exponentially to the calculated rate constant, which also depends upon the experimental choice of the reference electrode. Thus, the initial estimate of $E_{1/2}$ was then chosen to be $E_r$. This value was fixed to 0.7 V, which corresponds to the half-wave potential in the square-wave voltammogram, and by selecting a step size of zero in that dimension during the calculation. With assumed $E_r$, only two non-linear parameters, $k_0^0$ and $\alpha$ (referenced to $E_r$) remain to be determined.

As shown in Table II, the correlation coefficient($R$) is excellent over wide range of experimental conditions. The charge transfer coefficient varies around 0.46, which is in perfect agreement with the results from cyclic voltammetry. The value of the rate constant increases with increasing frequency and tends to be about $5.27 \times 10^{-4}$ cm s$^{-1}$ at low frequency. Note that the uncompensated resistance does not decrease the quality of the fit to the model, which is excellent in all cases, but rather manifests itself by a frequency dependence of the rate constant.
Table II. Values of kinetic parameters and their 95% confidence intervals obtained using the COOL algorithm. $E_{SW}=15$ mV, $\Delta E_{S}=2$ mV, $D^{-2}_{O^{-}}=6.65 \times 10^{-6}$ cm$^2$ s$^{-1}$

| Frequency/Hz | Correlation coefficient, $R$ | $\alpha$ | log ($k_s/\nu^{1/2}$) | $k_s^0 \times 10^4$/cm s$^{-1}$ |
|--------------|------------------------------|----------|------------------------|---------------------------------|
| 5            | 0.9997                       | 0.44±0.0033 | -1.19±0.0052           | 5.27                            |
| 10           | 0.9993                       | 0.46±0.0039 | -1.30±0.0048           | 5.80                            |
| 15           | 0.9990                       | 0.47±0.0078 | -1.34±0.0099           | 6.47                            |
| 20           | 0.9993                       | 0.47±0.0054 | -1.38±0.0066           | 6.80                            |
| 25           | 0.9996                       | 0.46±0.0050 | -1.44±0.0060           | 6.64                            |
| 30           | 0.9990                       | 0.46±0.0069 | -1.45±0.0087           | 7.09                            |
| 40           | 0.9992                       | 0.46±0.0058 | -1.46±0.0075           | 8.05                            |
| 60           | 0.9997                       | 0.46±0.0071 | -1.49±0.0088           | 9.60                            |

**Electrode reaction mechanism**

Cyclic voltammetry recorded in oxide-free MgCl$_2$ within the potential range of 0--1 V has shown no distinct reaction occurring in this range. This clearly indicates that the peak A in Fig. 1 is due to oxygen containing ions. The dependence of the current peak A with $\nu^{1/2}$, makes it possible to assume that the electrode process is governed by diffusion. The shift of peak potential corrected from ohmic drop for $\nu<0.7$ V s$^{-1}$ could be due to the effect of cylindrical diffusion, or more likely to irreversibility of the process. Linear diffusion [20] may be assumed if the quantity $(l/r)(D/n\nu)^{0.5}$ is less than 0.2, where $r$ is the radius of the electrode, $D$ the diffusion coefficient of the electroactive species and $n$ is the number of electrons transferred. In our experimental conditions, $r=0.15$ cm. Assuming $n=2$, and $D=6.65 \times 10^{-6}$ cm$^2$ s$^{-1}$, the lowest sweep rate used was 0.1 V s$^{-1}$, which satisfies the above condition. We therefore conclude that the shift of peak potential with $\nu$ at low sweep rates is due to some irreversibility of the process. It was also observed that $I_pA/(\nu^{1/2}S)$ showed a decrease although insignificant with increasing the sweep rate up to 0.4 V s$^{-1}$. This could be due to the presence of a chemical reaction preceding the charge transfer. As it was suggested in the CaO-CaCl$_2$ system [2], there is a very likely possibility of a dissociation of an oxychloride, in this case presumably Mg$_2$OCl$_2$. At high sweep rates the $I_pA/(\nu^{1/2}S)$ keeps a constant value, a behaviour expected for diffusion control.

A large difference between the system under study and the CaO-CaCl$_2$ system [2] is of course the solubility of oxides in their respective pure chlorides. The molar solubility limit of MgO in MgCl$_2$ is about $8 \times 10^{-5}$ mol cm$^{-3}$. This is however, within the range of concentrations we used in the CaO-CaCl$_2$ system: $3.3 \times 10^{-5}$--$2.7 \times 10^{-5}$ mol cm$^{-3}$. In the present work, the range of concentration of MgO used was from 0.08 wt%--0.19 wt% (8.4 $\times 10^{-5}$--1.6 $\times 10^{-4}$ mol cm$^{-3}$). We have observed that the limiting solubility of MgO was 0.19 wt% (8 $\times 10^{-5}$ mol cm$^{-3}$) in very good agreement with the literature. The results from the two chloride systems are compared in Table III. The diffusion coefficient in the MgO-MgCl$_2$ is 3 times superior to the one in the CaO-CaCl$_2$.
system, while the $\alpha$-values are close to the same. This probably means that the complex is much larger in the latter case. In the MgO-MgCl$_2$ system we only see one charge transfer step with a charge number of 2, while the calcium system most probably exhibit a two step mechanism. This could mean that we in the magnesium chloride case only see the first step corresponding to the adsorption of the product and that the final CO$_2$(gas) forming step takes place in the chlorine evolution region.

Table III. Comparison of the electrochemical behaviour of carbon electrodes in different oxide melts systems.

|                      | MgO-MgCl$_2$(750°C) | CaO-CaCl$_2$(850°C) |
|----------------------|---------------------|---------------------|
| $D_\text{O}_2^-$ /cm$^2$s$^{-1}$ | 6.65x10$^{-6}$      | 2.1x10$^{-6}$       |
| $\alpha$             | 0.46                | 0.43                |
| $k_s$ /cm s$^{-1}$    | 10$^{-4}$           | 1.8x10$^{-5}$       |
| Mechanism            | One step: $n_\alpha=2$ | Two steps: $n=2+2$ |

CONCLUSION

The results of the electrochemical investigations the discharge of MgO at the glassy carbon electrode showed the existence of one electrochemical step. The electrode process is governed by charge transfer or mixed kinetics that includes diffusion control where complex oxide ions move towards the electrode surface, as well as the charge transfer stage. The number of electron exchanged, the diffusion coefficient, the charge transfer coefficient and the rate constant were evaluated. The value of the diffusion coefficient suggests a large structure of the electroactive species, i.e., the diffusing species are complexes probably rather than simple O$_2^-$ ion. Although the reaction obviously involves at least one chemical step, the results presented here show that a single two-electron charge transfer step describes the response precisely. As it was seen above, the correlation between the theoretically predicted curves and the experimental voltammograms is excellent over a wide range of SW-frequencies.

ACKNOWLEDGMENTS

The authors thank the Norsk Hydro A/S and The Norwegian Research Council for supporting this work.
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Fig. 1 Cyclic voltammograms run at various scan rates. [MgO]=0.08 wt%, T=1023K. Scan rates : 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, and 0.8 Vs⁻¹.

Fig. 2 Dependence of the current related to peak A shown in Fig. 1 on the square root of the scan rate. C_{MgO}=0.08wt%, T=1023K.
Fig. 4 Dependence of the peak potential of process A on the logarithm of the scan rate.

Fig. 3 Variation of the \( \left( \frac{I_p}{\sqrt{v}} \right) \) criterion with the scan rate.
Fig. 5  Typical square-net voltammogram for the oxidation of MgO in molten MgCl$_2$ at a glassy carbon electrode (0.94 cm$^2$).

$[\text{MgO}]=0.08$ wt%, $T=1023\text{K}$, $\Delta E_s=2$ mV, $E_{sw}=20$ mV and $f=25$ Hz.

Fig. 6  Square-wave net voltammograms recorded at various frequencies. $\Delta E_s=2$ mV, $E_{sw}=15$ mV.

Frequencies in ascending order are, 5, 10, 15, 20 and 25 Hz. Lines are best fit calculated with COOL algorithm.