Determination of Diffusion Coefficients of Mg²⁺ Ions from Molten LiCl-KCl-MgCl₂†

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The diffusion coefficients of Mg²⁺ ions at molybdenum electrode in molten LiCl-KCl-MgCl₂ at 670 ℃ were determined using the cyclic voltammetry, chronoamperometry and chronopotentiometry, which were calculated to be 1.47×10^{-6}, 1.23×10^{-6} and 1.67×10^{-6} cm²/s, respectively. The activation energy for the diffusion process of Mg²⁺ ions was found to be 106.3 kJ/mol. The underpotential deposition (UPD) of Li⁺ ions on the pre-deposited Mg and the codeposition of Mg²⁺ and Li⁺ ions led a formation of liquid Mg-Li solution at a more positive potential than a potential for Li deposition.

Keywords: Magnesium, Diffusion coefficient, Activation energy, LiCl-KCl-MgCl₂.

INTRODUCTION

Recently, molten salt electrolysis has been considered to be an important method for preparing light metals and alloys due to its simplicity and economic advantages[1,2]. The basic data such as diffusion coefficient, activation energy, *etc.* are important in developing this technology more efficiently[3]. Several studies have reported on the electrode process of Mg²⁺ ions in molten chlorides[4-7]. However, due to the variations in the experimental conditions such as salt composition and temperature in the molten salt, the basic data reported in previous publications differ considerably[8-10]. Therefore, the diffusion coefficients of Mg²⁺ ions need to be further investigated.

In the present study, electrochemical techniques including cyclic voltammetry (CV), chronoamperometry (CA) and chronopotentiometry (CP) were used to determine the diffusion coefficients of Mg²⁺ ions at an inert molybdenum electrode in a molten LiCl-KCl-MgCl₂ system at 670 ℃. Also, the activation energy for the diffusion process of Mg²⁺ ions was calculated by Arrhenius equation.

EXPERIMENTAL

Anhydrous LiCl (98.2 % purity; Samchun Chemicals, Korea), KCl (99 % purity; Samchun Chemicals, Korea) and MgCl₂ (96 % purity; Samchun Chemicals, Korea) were used as electrolytes in this study. A molybdenum wire (0.5 mm in diameter), graphite rod (13 mm in diameter) and Ag/AgCl electrode were used as the working electrode, counter electrode
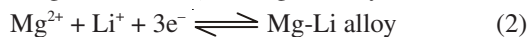
and reference electrode, respectively. The reference electrode was fabricated as follows: AgCl (1 wt %) was added in a mixture of LiCl-KCl (60 : 40 in mole percent) and the salt was put in a mullite tube with a closed end. A silver wire (0.5 mm in diameter) was immersed to salt inside the tube. A LiCl-KCl mixture of 300 g that contained various MgCl₂ concentrations was placed in the MgO crucible and then heated and maintained at 670 ℃. A potentiostat (PGSTAT302N, Metrohm Autolab, Netherlands) was used to conduct three electrochemical techniques. In the cyclic voltammetry experiments, the diffusion coefficient of Mg²⁺ ions is calculated at various temperatures between 670 and 710 ℃. The chronoamperometry measurement was conducted through applying a potential in a range from -2.2 to -3.0 V to the cell. The chronopotentiometry measurement was also conducted through applying a current between 25 and 225 mA to the cell.

RESULTS AND DISCUSSION

Cyclic voltammetry: Fig. 1(a) shows the cyclic voltammograms of a molybdenum wire at various MgCl₂ concentrations in the LiCl-KCl molten salt. In the eutectic LiCl-KCl, the sharp increase in the cathodic/anodic current is caused from a redox couple of Li⁺/Li. After the addition of 5 wt % MgCl₂, a cathodic current peak at -1.7 V (*vs.* Ag/AgCl) appeared due to the reduction of Mg²⁺ ions to Mg metal (Mg²⁺/Mg). It is clear that the electrode process of Mg²⁺ ions is controlled by the diffusion rate and mass transfer[11]. The cathodic current at -2.1 V (*vs.* Ag/AgCl) probably corresponds to the formation of a

liquid Mg-Li solution which is formed by underpotential deposition (UPD) of lithium on the liquid Mg already deposited on the molybdenum electrode[11] and codeposition of Mg^{2+} and Li^+ ions. The corresponding reaction can be understood as follows:

$$Mg + Li^+ + e^- \rightleftharpoons Mg\text{-}Li \text{ alloy} \qquad (1)$$

$$Mg^{2+} + Li^+ + 3e^- \rightleftharpoons Mg\text{-}Li \text{ alloy} \qquad (2)$$

In the reverse scans, two re-oxidation peaks associated with the dissolution of Li and Mg metals were observed. When the $MgCl_2$ concentration was increased to 10 wt %, more reduction reactions of Mg^{2+} ions occurred due to the increase in the $MgCl_2$ concentration. Fig. 1(b) shows the cyclic voltammetric graphs at various scan rates (100-350 mV/s) in LiCl-KCl-$MgCl_2$ (5 wt %). An increase in the current with an increase in the scan rates was observed, which indicates that a fast electrode reaction occurred at higher scan rates through the thin diffusion layer. Fig. 1(c) shows a plot of the current density against the inverse square root of the scan rate for the cyclic voltammetric graphs at various temperatures (670-710 °C). The plot of i *vs.* $v^{-1/2}$ exhibited a linear relationship at a given temperature window over the scan rate ranges (100-350 mV/s). The diffusion coefficient was calculated using the Randles- Sevcik equation, as follows:

$$i_p = 0.61\left(\frac{F^3}{RT}\right)^{1/2} n^{3/2} A D^{1/2} C_O v^{1/2} \qquad (3)$$

where i_p is the reduction peak current (A), A is the electrode surface area (cm^2), C_O is the Mg^{2+} concentration (mol/cm^3), D is the diffusion coefficient (cm^2/s), F is Faraday's constant (96,485 C/mol) and í is the scan rate. The diffusion coefficient of Mg^{2+} ions was 1.47×10^{-6} cm^2/s at 670 °C. Table-1 summarized the diffusion coefficients of Mg^{2+} ions at various temperatures between 670 and 710 °C. As the temperature of the molten salt increased, the diffusion coefficient also increased due to the temperature dependence on the diffusion of electro-active species. Fig. 1(d) shows an Arrhenius plot of the diffusion coefficients of Mg^{2+} ions and the reciprocal of temperature. The plot of ln D *vs.* T^{-1} exhibited a linear relationship over the range of temperatures. The activation energy for the diffusion processes of Mg^{2+} ions was calculated using the Arrhenius equation. The values of the activation energy and pre-exponential factor were 106.3 kJ/mol and 1.134, respectively.

Chronoamperometry: Fig. 2(a) shows the chronoamperograms of a molybdenum wire with different applied potentials from -1.6 to -2.6 V in LiCl-KCl-$MgCl_2$ (5 wt %) at 760 °C. The current curves exhibited a typical tendency in the chrono-amperometry experiments, which indicated that the reduction of Mg^{2+} ions was a diffusion-controlled reaction. At an applied potential of -1.8 V, the current increased sharply due to the reduction of Mg^{2+} ions. When the applied potential changed from -2.0 to -2.1 V, the current increased sharply again, which probably indicated that the reduction of Li^+ ions was accompanied
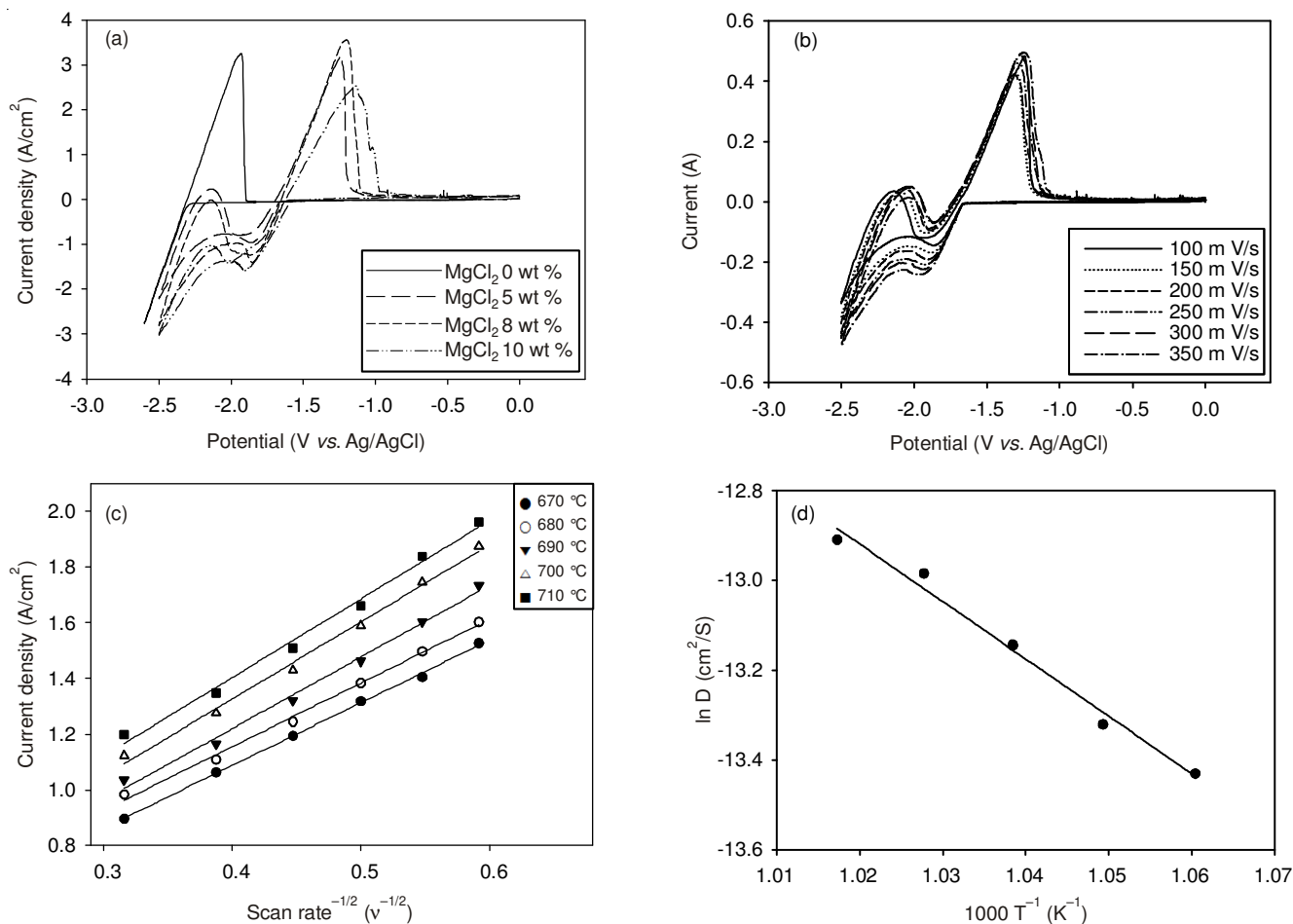

Fig. 1. (a) CV graphs of a Mo wire at 100 mV/s in LiCl-KCl-$MgCl_2$ ($MgCl_2$ = 0, 5, 8 and 10 wt %), (b) CV graphs of a Mo wire at various scan rates (100-350 mV/s), (c) plot of the current density against the inverse square root of time at between 670 and 710 °C and (d) plot of the diffusion coefficient of Mg^{2+} ions and the reciprocal of temperature

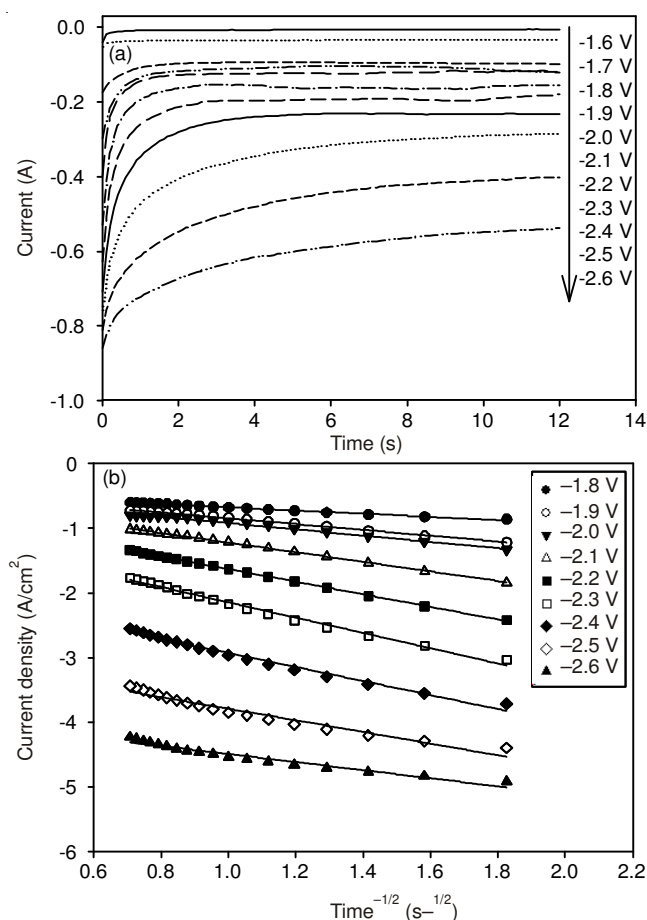| TABLE-1					
DIFFUSION COEFFICIENTS OF Mg^{2+} IONS AT VARIOUS TEMPERATURES					
Melt temperature (°C)	670	680	690	700	710
Diffusion coefficient of Mg^{2+} ions (cm^2/s)	1.47×10^{-6}	1.64×10^{-6}	1.96×10^{-6}	2.30×10^{-6}	2.47×10^{-6}

Fig. 2. (a) Chronoamperograms of a molybdenum wire at various applied potentials (-1.6 to -2.6 V) and (b) plot of the current density against the inverse square root of time
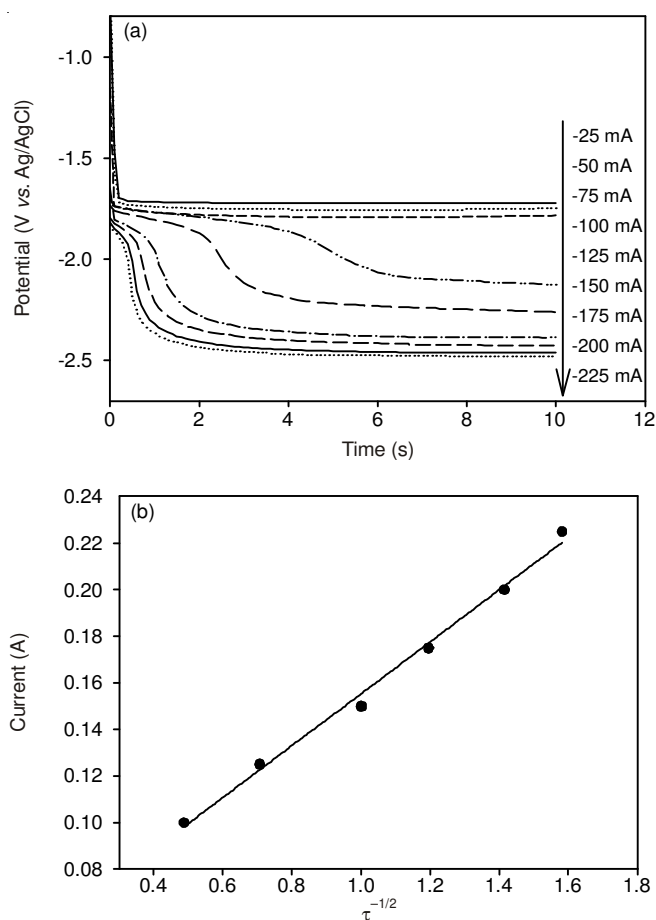

Fig. 3. (a) Chronopotentiograms of a molybdenum wire at various applied currents (25-225 mA) and (b) plot of the current against the inverse square root of transition time (T)

with that of Mg^{2+} ions. Accordingly, the co-deposition of Mg^{2+} and Li$^+$ ions occurred at negative values lower than -2.1 V. Fig. 2(b) shows the plot of the current density against the inverse square root of time for the chronoamperometry graphs. The plot of i *vs.* t$^{-1/2}$ exhibited a linear relationship for a period of time (0.3-2 s) over the range of applied potentials, where the diffusion coefficient can be calculated using the Cottrell equation, as follows:

$$i(t) = \frac{nFAD_O^{1/2}C_O}{\pi^{1/2}t^{1/2}} \qquad (4)$$

where i is the reduction current (A), A is the electrode surface area (cm^2), C$_o$ is the Mg^{2+} concentration (mol/cm^3), F is Faraday's constant (96,485 C/mol) and D is the diffusion coefficient (cm^2/s). The diffusion coefficient of Mg^{2+} ions at between -1.8 and -2.0 V was 1.23×10^{-6} cm^2/s at 670 °C. At an applied potential between -2.1 and -2.6 V where the co-deposition of Mg^{2+} and Li$^+$ ions occurs as shown in cyclic voltammetric experiment.

Chronopotentiometry: Fig. 3(a) shows the chronopotentiograms of a Mo wire at various applied currents (25-225 mA) in LiCl-KCl-MgCl$_2$ (5 wt %) at 760 °C. At a current lower than 100 mA, the current curves exhibited two potential plateaus

that are associated with the reduction of Mg^{2+} ions (Plateaus 1) and Li$^+$ ions (Plateaus 2). The flux of Mg^{2+} ions to the electrode surface was not sufficiently large and thus the potential is shifted to a more negative value where the co-deposition of Mg^{2+} and Li$^+$ ions takes place. This result suggests that the electrode process of Mg^{2+} ions was a diffusion-controlled reaction[12,13]. Fig. 3(b) shows the plot of the current against the inverse square root of transition time (τ) from the chrono-amperometry graphs. The plot of i *vs.* $\tau^{-1/2}$ exhibited a linear relationship over the range of applied currents. The diffusion coefficient of Mg^{2+} ions was calculated using the Sand's equation, as follows:

$$i\tau^{1/2} = \frac{nFAC_oD^{1/2}\pi^{1/2}}{2} \qquad (5)$$

where i is the reduction current (A), F is Faraday's constant (96,485 C/mol), τ is the transition time (s), A is the surface area (cm^2), C$_o$ is the Mg^{2+} concentrations (mol/cm^3) and D is the diffusion coefficient (cm^2/s). The diffusion coefficient of Mg^{2+} ions on a molybdenum wire was 1.67×10^{-6} cm^2/s at 670 °C. The values of diffusion coefficients exhibit a similar level regardless of the analytical techniques.

Conclusion

The cyclic voltammetry, chronoamperometry and chrono-potentiometry were conducted to determine the diffusion coefficients of Mg^{2+} ions at a molybdenum electrode in molten LiCl-KCl-MgCl$_2$ at 670 ºC, which was found to be 1.47×10^{-6}, 1.23×10^{-6} and 1.67×10^{-6} cm^2/s, respectively. The temperature dependence on diffusion coefficients was investigated and the activation energy for the diffusion process of Mg^{2+} ions was calculated to be 106.3 kJ/mol. The electrode process of Mg^{2+} ions was a diffusion-controlled reaction. Also, the underpotential deposition (UPD) of Li^+ ions on the pre-deposited Mg and the codeposition of Mg^{2+} and Li^+ ions led a formation of liquid Mg-Li solution at a more positive potential than a potential for Li deposition.

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