ACADEMIA ROMÂNĂ
Revue Roumaine de Chimie
http://web.icf.ro/rrch/

Rev. Roum. Chim.,
2011, *56*(8), 763-769

CYCLIC VOLTAMMETRY OF IRON IONS IN MOLTEN HALIDES ELECTROLYTES

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Received April 27, 2010

The cyclic voltammetry method was applied using Mo electrode to study the Fe electrodeposition by dissol-ving Fe_2O_3 or $FeCl_2$ in molten alkaline-earth and/or alkali metal halides at a constant temperature 1123 K. Two molten electrolytes were tested as solvents; chlorides ($CaCl_2$ - NaCl) and chlorides-fluoride (NaCl-KCl-NaF) mixtures, respectively. Both cathodic processes of iron(III) and iron(II) have been found to exhibit only one reduction step to the iron metal. However, the electroreduction of Fe(III) on Mo electrode in $CaCl_2$ – NaCl melt is a reversible process with diffusion control, whereas the electroreduction of Fe(II) in NaCl-KCl-NaF melt is an irreversible process.

INTRODUCTION

The electrochemical behaviour of iron compounds in high temperature molten alkali halide electrolytes has been described in a number of publications.[1-4] Gaur and Jindal[5] found that the electroreduction is accompanied by the formation of iron dendrites and cannot be described in the terms of diffusion-controlled process complying with the equation Heyrovsky-Illkovic. Chryssolakis and coworkers[6] obtained cyclic voltammograms with the peak potential clearly dependent on the scan rate. In addition, the electrochemical studies of the behaviour of iron in glass and enamel were mainly studied by square wave voltammetry,[7-10] as well as by voltammetry with linear[11, 12] and cyclic[13-15] potential variations.

The objective of the present work is to study the electrochemistry and electrodeposition processes of two compounds of iron dissolved in molten salt electrolytes, namely Fe_2O_3 in $CaCl_2$ – NaCl melt and $FeCl_2$ in NaCl-KCl-NaF melt. In this way, we will investigate both the Fe(III)/Fe(II) and Fe(II)/Fe(0) couple systems in order to obtain some information about their mechanisms useful for the last stage of the molten salt process for iron extractive metallurgy.

EXPERIMENTAL

The electrochemical experiments, storage and handling of all melts were carried out in a protective atmosphere under purified argon atmosphere.

Anhydrous KCl, NaF (+99.5% purity), purchased from Riedel-deHaen and Fe_2O_3 (Merck, +99.5% purity) were used as received without any treatment. Anhydrous $CaCl_2$ (Aldrich) and NaCl (CHIMACTIV) of analytical reagent grade were carefully dried at 500 K and 700 K for 4 and 2 hours separately, in air. The $CaCl_2 \cdot 10H_2O$ (Aldrich) was dehydrated in air at 373 K for 2 hours, heated slowly to 600 K, and then held at 600 K for 8 hours. $FeCl_3 \cdot 6H_2O$ from Merck (+ 99.5 % purity) was dried in vacuum at 300 K for 4-10 hours and then was stored in protective atmosphere.

All molten salt experiments were performed in a stainless steel crucible placed in a sealed stainless steel container which was continuously purged with argon. The working temperature was measured with a Pt-Pt/Rh (type S) thermocouple protected by an Inconel tube inserted into the melt. Pre-electrolysis for removing moisture from molten electrolyte was carried out at 1.2-1.5 V for 2 hours, using the graphite anode and the crucible (cathode) as electrodes.

The electrochemical technique used, *i.e.*, cyclic voltammetry, was applied using a computer-controlled potentiostat model Tacussel PRT 20-10X. The electrochemical cell was a three-electrode set-up. In the cyclic voltammetry, the potential was changed cathodically from the open-circuit value with a sweep rate ranging from 10mV to 1500 mV/s. The cyclic voltammograms were registered using Linseis recorder LY 1600.

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In case of studies of electrochemical behaviour of the Fe_2O_3 in $CaCl_2$ – NaCl molten electrolytes, the working electrode was a high purity molybdenum wire (surface area $7.8 \cdot 10^{-3}$ cm^2) encased in a BN tube. The counter electrode rod was prepared from Fe_3O_4 powder by axially pressed and sintered under argon atmosphere at 1200 K for 2 h; its electrical conductivity was about 360 $\Omega^{-1}m^{-1}$ at room temperature. The reference electrode was a Ag wire immersed in $CaCl_2$ – NaCl melt. In studies of the electrochemistry of $FeCl_2$ dissolved in molten electrolyte the inert working electrode was the same Mo wire with a surface area of $7.8 \cdot 10^{-3}$ cm^2 exposed to the molten electrolyte. Because Fe(III) chloride is not stable at the experimental temperature in the molten alkali halide (reaction $Fe^{3+} + Cl^- \rightarrow Fe^{2+} + 1/2Cl_2$ occurs) the electroactive species containing Fe(II) in molten electrolyte was prepared by iron salt precursor ($FeCl_3 \cdot 6\ H_2O$) in the following mode: the iron precursor was mixed with the solid electrolyte components and the mixture was dried under vacuum at 310–320 K for 1 h. After completing the drying, the mixture was melted at 1000 K for two hours, in order to quantitatively reduce Fe(III) species to divalent Fe ions.[6, 16] An 8 mm diameter graphite rod served as the counter electrode. The reference electrode was a silver wire dipped in a melt of AgCl in KCl-NaCl-NaF ($1.12 \cdot 10^{-3}$ mol/cm^3 AgCl) separated from the working electrolyte by a thin BN diaphragm. All the potentials and potential ranges are described with respect to this reference electrode.

RESULTS AND DISCUSSION

The cyclic voltammograms on Mo electrode with $1.7 \cdot 10^{-3}$ mol/cm^3 Fe_2O_3 (0.28 wt.%) additions in $CaCl_2$ - NaCl at different sweep rates have the shape quite typical for a metal deposition process (Fig. 1):

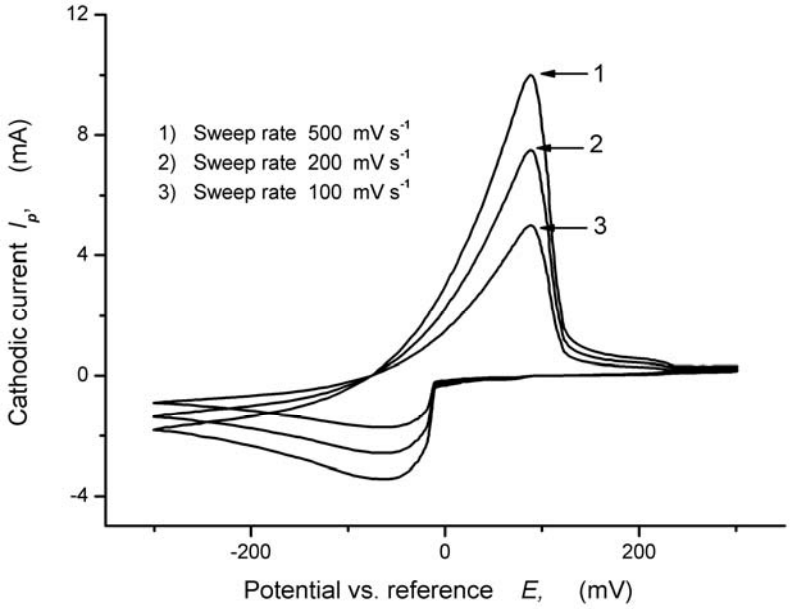

Fig. 1 – Cyclic voltammograms of iron (III) ion deposition on Mo at 1123 K in $CaCl_2$-NaCl molten electrolyte; C_{Fe2O3} = 1.70 mmol·cm^{-3}.

All voltammograms show a single couple of peaks, corresponding to the iron deposition and dissolution of iron metal.

Theoretically, iron deposition from the molten electrolyte should be tested if the control consists in either diffusion of dissolved electroactive species from bulk electrolyte to electrode surface or charge transfer at electrode. Diffusion control of deposition reaction, is proving when plotting the cathodic peak current as a function of the square root of the sweep rate, the following linear relationship is obtained:[17]

$$i_p \quad 0.61\,(nF)^{3/2}\,[\frac{D}{RT}]^{1/2}\, c\ v^{1/2} \qquad (1)$$

where i_p, n, F, D, R, T, c, and v are the cathodic peak current density, number of electron transferred, Faraday constant, diffusion coefficient of iron species Fe(III), ideal gas constant, absolute temperature, concentration of iron species Fe(III) in the bulk electrolyte and sweep rate, respectively.

In molten electrolyte containing 0.28% % Fe_2O_3 only well-defined reduction wave is observed with a peak potential in range – 50 ÷ – 65 mV vs. Ag reference. This wave can be attributed to the direct reduction of Fe(III) to Fe(O):

$$Fe(III) + 3e^- \rightarrow Fe(O) \qquad (2)$$

Experimental voltammograms recorded for the electroreduction of Fe(III) on molybdenum electrode in $CaCl_2$-NaCl molten electrolyte confirm the reversibility of process (2).[18-20] The reversibility criteria were the followings:

A linear relationship between the logarithm of peak cathodic current and the logarithm of polarization rate in cyclic voltammograms. The relationship should result in a slope of 0.5. (criterion 1)

The peak potential is quite independent of sweep rate. (criterion 2)

The difference between the cathodic peak potential and its half-wave potential should be constant (2.2RT/nF). For a 3 electrons process, this difference should be equal to 70.9 mV for 1123 K. (criterion 3)

The difference between the anodic and cathodic peak potentials should be a constant and equal to 116.2 mV at 1123 K for a three electrons exchange. (criterion 4)

The ratio of the anodic and cathodic peak currents obtained in cyclic voltammetry should be independent of polarization rate and more than 1. (criterion 5)

The experimental values of $E_p - E_{p/2}$ and $E_{p,a} - E_{p,c}$ differences (criterion 4) are in good agreement with those predicted from theory for a reversible process that exchanges three electrons. In addition, the data verify the criteria 1 (Fig. 2), 2 (Table 1), 3 (Table 1) and 5 (a 2.85 ratio is the experimental value).

Table 1

Cyclic voltammetry data for reduction of Fe_2O_3 at molybdenum electrode in $CaCl_2$ - NaCl melt at 1123 K; $C_{Fe2O3} = 1.70$ mmol·cm^{-3}

v (mV s^{-1})	$i_{p,c}$ (mA)	$E_{p,c}$ vs. Ag (mV)	$E_{p,a}$ vs. Ag (mV)	**n**	$E_{p,c} - E_{p/2}$ (mV)
100	1.74	- 54.7	87.27	2.96	- 26.1
200	2.55	- 54.7	87.88	3.13	- 24.6
500	3.42	- 54.1	87.88	3.00	- 25.5

The results obtained show that all reversibility criteria are fulfilled, a fact which allows us to conclude that the Fe(III)/Fe(O) redox system behaves reversible, with an insoluble product obtained on electrode or in molten electrolyte.

The plot of the cathodic peak current as a function of the square root of the sweep rate is shown in Fig. 2 and as function of Fe(III) iron concentration is shown in Fig. 3.

The straight lines in both Figs. suggests that the electroreduction process of Fe(III) species on cathode is controlled by diffusion. The diffusion coefficient value of iron species Fe(III) in molten electrolyte at 1123 K calculated according to eq. (1) and using the slope value from Figs. 2 and 3 is (9.4 ± 0.7) · 10^{-5} cm^2·s^{-1}, in good agreement with literature.[16]

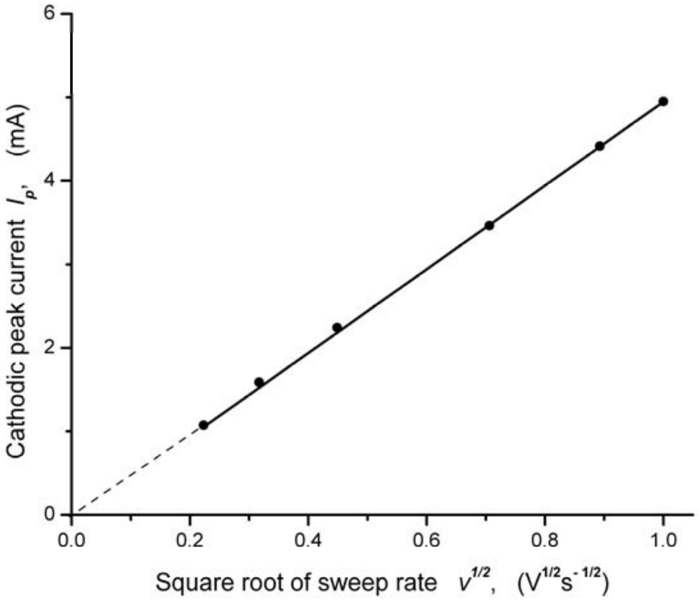

Fig. 2 – Dependence of cathodic peak current on the square root of sweep rate for electroreduction of Fe(III) ion in $CaCl_2$-NaCl electrolyte at 1123 K on Mo electrode; $C_{Fe2O3} = 1.70$ mmol·cm^{-3}.

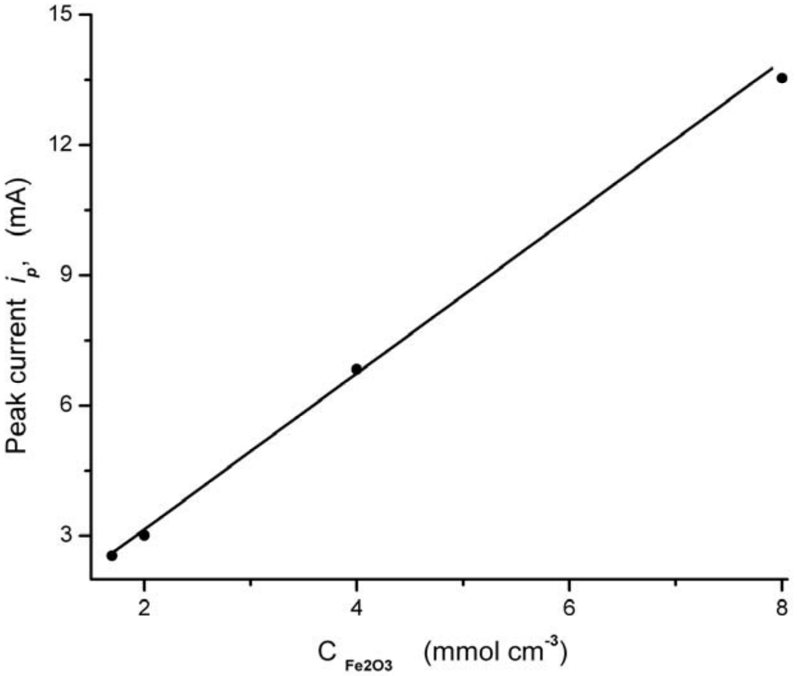

Fig. 3 – Dependence of cathodic peak current on the concentration of iron species at electroreduction of Fe(III) in a $CaCl_2$-NaCl molten electrolyte at 1123 K on Mo electrode.

Typical cyclic voltammograms for divalent ion species Fe(II) electrodeposition and its dissolution on molybdenum in chlorides-fluoride NaCl-KCl-NaF melt are shown in Fig. 4:

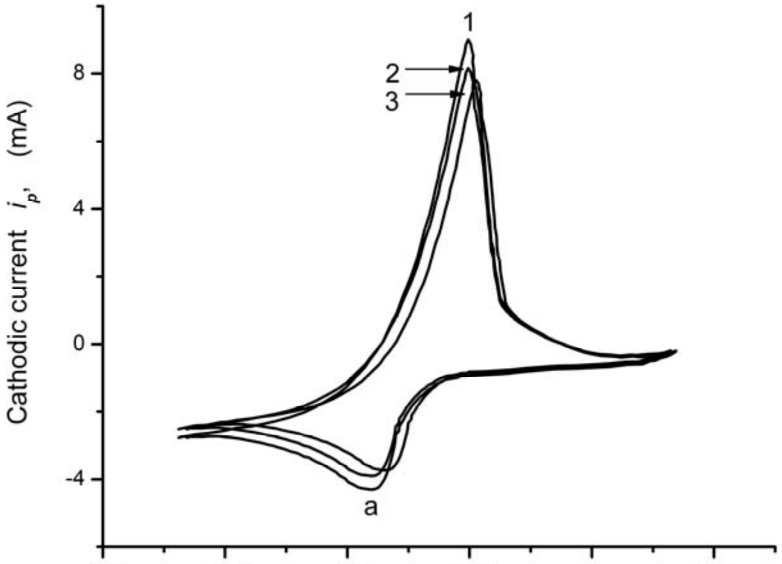

Fig. 4 – Typical cyclic voltammograms of Fe(II) ion on Mo at 1123 K in NaCl-KCl-NaF molten electrolyte; 1) v = 200 mVs^{-1}; 2) v = 100 mVs^{-1}; 3) v = 20 mVs^{-1}; C_{Fe2O3} = 1.70 mmol·cm^{-3}.

As seen from this Fig., the electrochemical process consists also in a single cathodic peak with a typical shape for metal electrodeposition. The potential corresponding to cathodic peak is – 361 mV vs. Ag reference for the sweep rate of 200 mVs^{-1} and concentration 3.4 mmol cm^{-3}. The peak currents plotted against the square root of sweep rates (such dependencies are traditionally referred to Randles-Sevcik equation[21]) demonstrate a linear behaviour (see Fig. 5). Another peculiarity of these dependences at various concentrations is their non-zero intercepts, which are all positive and grow as the concentration of Fe(II) increases. It is most probable that this behaviour is caused by Fe(II) ion adsorption, a process occurring in parallel to main faradaic process.[22]

The value of cathodic peak current denoted as “a” (see Fig. 4) clearly depends on the concentration of Fe(II) ion. Also, the cathodic peak potential shifts to more negative values as the sweep rate increases.

The cathodic peak potential, E_p, plotted vs. square root of sweep rate log v, gives a linear dependence, (Fig. 6), this dependence being characteristic for an irreversible electrochemical process.[23]

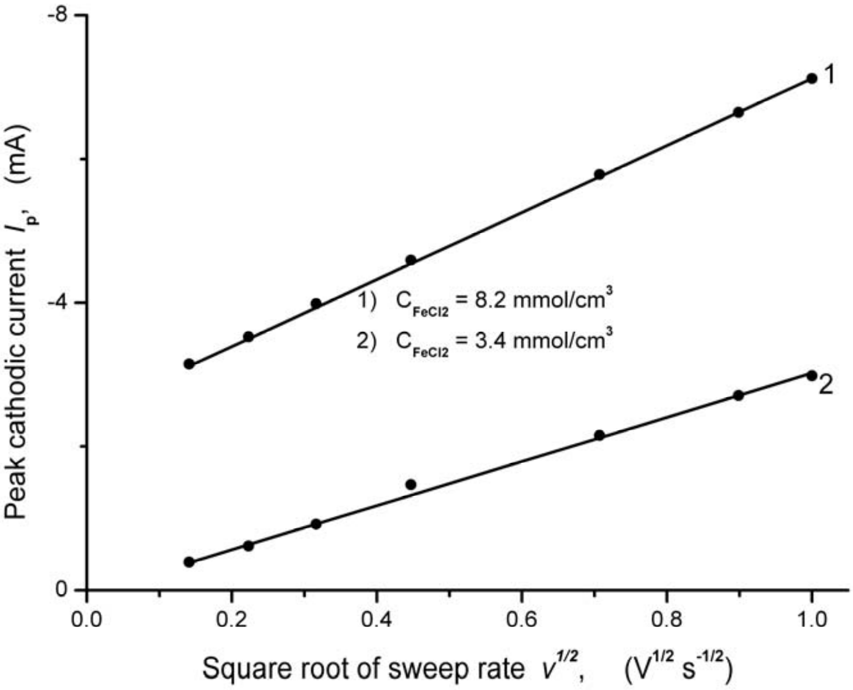

Fig. 5 – Randles-Sevcik plot for Fe(II) ion reduction on Mo in NaCl-KCl-NaF molten electrolyte at 1123 K for different concentrations of the dissolved $FeCl_2$.

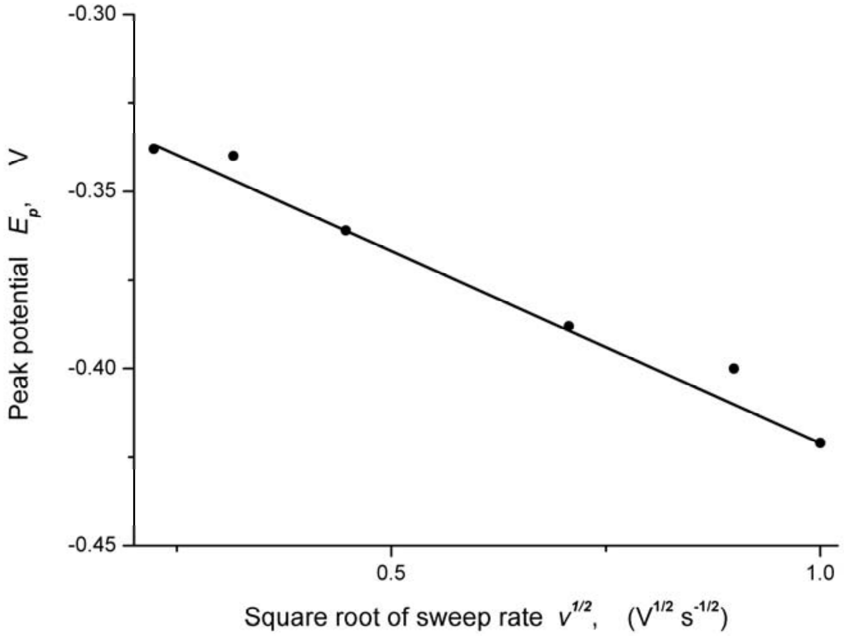

Fig. 6 – Dependence of cathodic peak potential on the square root of the sweep rate for Fe(II) ion reduction on Mo in a NaCl-KCl-NaF molten electrolyte at 1123 K; $C_{Fe2O3} = 1.70$ mmol·cm^{-3}.

If we treat Fe(II) ion electroreduction on molybdenum electrode in the alkali chlorides-fluoride molten electrolyte as an irreversible electrochemical process, one can evaluate the value of (α·n) from equation:[23, 24]

$$|E_p - E_{p/2}| = 1.857 \frac{R \cdot T}{\alpha n \cdot F} \qquad (3)$$

Thus, the calculated values of ($\alpha \cdot n$) parameter for the electrochemical process studied herein are all in the range of 1.08 ± 0.08, which is consistent with the two electrons transfer of Fe(II) electroreduction on Mo electrode; this value is also in good agreement with literature data.[25] Hence, the value of α is around 0.5, which may reflect a change transfer process with a symmetrical transition state as the rate determining step. Hence, it may reasonable to calculate appropriate diffusion coefficient for Fe(II) ions in the NaCl-KCl-NaF molten electrolyte from equation:[26, 27]

$$i_p \quad 0.4958\ (nF)^{3/2}\ D^{1/2}\ S\ (RT)^{\ 1/2}\ C\ (\ \ n\ )^{1/2}\ v^{1/2} \qquad (4)$$

where: $n_\alpha = (n \cdot F \cdot v)/R \cdot T$ is the number of electrons involved in the rate determining step and S is apparent area of cathode electrode. The approximate values obtained for *D* is around (2.1 ± 0.6) · 10^{-5} $cm^2 \cdot s^{-1}$ at 1123 K, which is in good agreement with those calculated for Fe(II) electrodeposition on tungsten.[16]

The irreversible character of Fe(II) electroreduction on a molybdenum electrode at high temperature in molten electrolyte is quite surprising, because it is expected that the elevated temperatures should facilitate surpassing the activation barriers for global electrochemical processes, thus promoting a relatively simple iron electroreduction and electrodeposition on a solid electrode with diffusion control.

The observed values of (α·n) close to 1 suggest that the change transfer occurs *via* a two electron process with a symmetrical transition state. Therefore, the following electrochemical mechanism can be proposed:

1. $(Fe^{2}\ )_{bulk\ electrolyte}$ *diffusion to Mo electrode*
2. $(Fe^{2}\ )_{bulk\ electrolyte}$ *on Mo electrode* $\overset{fast}{\quad}$ $Mo\,|\,Fe(II)_{ads}$
3. $Mo\,|\,Fe(II)_{ads} \quad 2e \quad \overset{slow}{\quad} \quad Fe(0)_{on\ Mo\ electrode}$

It should be noted that the second step can be considered as a process that resembles the well-known UPD processes,[28,29] namely, deposition of a mono-layer of a metal ion on another metallic substrate. We assume that at 1123 K, the stage 3 is the rate determining electroreduction step.

The rate determining electrochemical step cannot be iron ion diffusion from the bulk electrolyte to the electrode. In addition, one could not suggest that the electrochemical process studied in this work is a simple Fe(II) ion electroreduction to Fe(0) metal on electrode, because the electro-reduction and electrodeposition of Fe(II) on molybdenum electrodes in the same molten electrolyte, which is indeed a simple electro-reduction process, has an unambiguous diffusion control.[16]

CONCLUSIONS

The electrochemical behaviour of dissolved Fe_2O_3 in $CaCl_2$-NaCl molten electrolyte at 1123 K on molybdenum electrodes indicate that the electroreduction process is controlled by diffusion in the sweep rate range 0.050 $V \cdot s^{-1}$ – 1 $V \cdot s^{-1}$, and consequently the electrode process is reversible. At higher sweep rates, the electrochemical process becomes quasireversible. The charge transfer process occurs in a single step with a three electrons change.

The electroreduction of Fe(II) on molybdenum electrodes in NaCl-KCl-NaF molten electrolyte at 1123 K was studied by cyclic voltammetry and related kinetic analysis. This electroreduction process is essentially irreversible with a single step, probably because the rate determining step is related to a charge transfer with formation of a Fe mono layer on Mo electrode rather than to Fe(II) ion diffusion control.

The value of (α·n) found for Fe(II) ion electroreduction around unity indicates a relatively simple two electron charge transfer process with a symmetrical transition state, which is the rate determining step.

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