Electrochemical Investigation on the Stable Iron Species in Molten FLINAK

Hao Peng¹², Miao Shen¹, Chenyang Wang¹, Yong Zuo¹ and Leidong Xie⁴

Abstract
The electrochemical behavior of Fe(III) in molten LiF–NaF–KF [46.5:11.5:42 (mol%)] (FLINAK) salt was studied by cyclic voltammetry (CV), chronopotentiometry (CP) and square wave voltammetry (SWV) at 600°C. It was found that Fe(III) was initially reduced to Fe(II) at +2.0 V (vs. alkalis) followed by reduction of Fe(II) to Fe at +1.4 V (vs. alkalis) and both reduction processes were controlled by ion diffusion. Diffusion coefficients of Fe(III) in molten FLINAK were calculated through CV and CP. The reduction peak of Fe(III)/Fe(II) was still observed in SWVs even though only FeF₂ was added to FLINAK. This result showed that Fe(II) was converted to Fe(III), which exists stably in FLINAK melts.

Keywords: Molten fluorides; Stable iron valence; Cyclic voltammetry; Chronopotentiometry; Square wave voltammetry

Introduction
Molten fluorides are suitable for use as coolants of molten salt reactors because these materials present excellent heat transfer properties [1-3]. However, the residual oxidation of impurities in fluorides, such as absorbed water and HF(g) [4,5], are corrosive to the structural materials at high temperature [6-9], resulting in the dissolution of Fe in those materials [10], such as Hastelloy.

According to the investigations described by Oak Ridge National Laboratory (ORNL) [11], the corrosion valence state of Fe in molten fluorides is determined by the acid-base properties of the molten fluoride employed; here, a Lewis acid is defined as a fluoride ion acceptor, and a Lewis base is a fluoride ion donor. Pure FLINAK consisting of LiF, NaF, and KF [LiF:NaF:KF, 46.5:11.5:42 (mol%)] is known to be a strongly basic solvent that tends to stabilize the Fe(III) valence state [11]. According to the theory of non-electric transfer described by Ozeryanaya [12], Fe may firstly dissolve in FLINAK melts as a form of Fe(II), which would further convert to Fe(III). Unfortunately, no relevant studies have yet been published to prove this conversion.

By using cyclic voltammetry (CV), Bing [13] found that Fe(III) could be converted to Fe(II) in KCl–CaCl₂–NaCl–MgCl₂ melts. With the same method, Manning [14] indicated that O²⁻ and O₃²⁻ ions stayed stable in LiF–BeF₂–ZrF₄ and LiF–BeF₂–ThF₄ melts whereas O²⁻ was unstable in these eutectics. Recently, Nourry [15] found that U(III) could be oxidized to U(IV) in LiF–CaF₂–UF₅ melts through CV and SWV. Cassayre and Pakhui [16,17] claimed that Fe(III) could be converted to Fe(II) in KCl–CaCl₂ melts. According to the investigations described by Oak Ridge National Laboratory (ORNL) [11], the corrosion valence state of Fe in molten fluorides is determined by the acid-base properties of the molten fluoride employed; here, a Lewis acid is defined as a fluoride ion acceptor, and a Lewis base is a fluoride ion donor. Pure FLINAK consisting of LiF, NaF, and KF [LiF:NaF:KF, 46.5:11.5:42 (mol%)] is known to be a strongly basic solvent that tends to stabilize the Fe(III) valence state [11]. According to the theory of non-electric transfer described by Ozeryanaya [12], Fe may firstly dissolve in FLINAK melts as a form of Fe(II), which would further convert to Fe(III). Unfortunately, no relevant studies have yet been published to prove this conversion.

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Th(IV) is the only stable species in LiCl–KCl melts at 420–550 °C by involving CV, CP, SWV and chronamperometry (CA). Reports thus far [13-19] suggest that the electrochemical method can be used to investigate the stable valence of electro-active species because the technique offers quick responses and in-situ monitoring. The aim of the present work is to determine the stable valence state of Fe in FLINAK melts through CV, CP and SWV.

Experimental Methods
Highly-purified LiF–NaF–KF [46.5:11.5:42 (mol%)] (FLINAK) eutectic salt was used as the experimental fluorides. A known amount of Fe(III) and Fe(II) were introduced to FLINAK salt as the form of FeF₃ (Strem Chemicals, 99.9%) and FeF₂ (Alfa Aesar, 99%), respectively. Then the fluorides system was melted at 600°C in a vitreous carbon crucible placed in a stainless steel cell inside an electric furnace. The temperature of the melts was measured by a nickel-chromium thermocouple positioned just outside the crucible.

A platinum wire (Φ=1.0 mm) served as the working electrode, whose surface area was determined by measuring the immersion depth in the melts. A graphite rod (Φ=6.0 mm) was used as...
the auxiliary electrode with a large surface area (2.50 cm²). All potentials were referred to a platinum wire (Φ=1.0 mm) that had been proven to function as a quasi-reference electrode Pt/PtOx/O₂, with a stable potential when the O₂ concentration is constant [20,21]. The entire apparatus was placed inside a glove box with dry argon atmosphere (99.99 wt%), as shown in Figure 1, and the typical concentrations of moisture and oxygen in glove box were generally below 2 ppm. All electrochemical measurements were performed with a computer-controlled AUTOLAB digital electrochemical analyzer (Metrohm AutoLab Co. Ltd.).

Results and Discussion

Electrochemical behavior of Fe(III) in FLINAK melts

Cyclic voltammetry: The typical cyclic voltammograms of FLINAK-Fe(III) (484 ppm) melts on a Pt electrode at 600°C and different scan rates are shown in Figure 2. Two reduction peaks, A and B, at 1.97 V (vs. alkalis) and 1.42 V (vs. alkalis), respectively, in the cathodic run and two anodic counter-peaks, A' and B', at 2.15 V (vs. alkalis) and 1.52 V (vs. alkalis), respectively, can be observed. As the Fe(III) concentration increases, the current densities of peak A and B (ip_A and ip_B) increase accordingly, as shown in Figure 3. Thus, the reduction of Fe(III) proceeds in two steps.

A/A' redox system: The cathodic current density of peak A (ip_A) obtained after subtracting the background current increases linearly with the square root of the scan rate (ν^{1/2}) as shown in Figure 4a, indicating that the first reduction step of Fe(III) is controlled by ion diffusion. In addition to the almost invariable peak potential (Ep_A) in the range of 0.1 to 1.0 V/s, the ratio of |ip_A'/ip_A| is approximately equal to 1, as shown in Table 1. These results suggest that the first step of Fe(III) reduction is considered reversible over the studied scan rates.

For a reversible system, the diffusion coefficient of Fe(III) in the melts can be calculated according to the Randles-Sevcik equation [24]:

\[
 ip = -0.4463nFSC \left( \frac{nF^2}{RT} \right)^{1/2} D^{1/2} \nu^{1/2}
\]  (1)

Where \( ip \) is the peak current (A), \( n \) the number of exchanged electrons, \( F \) the Faraday constant (96,485 C mol⁻¹), \( S \) the electrode surface area (cm²), \( C \) the Fe(III) concentration (mol cm⁻³), \( \nu \) the universal gas constant (8.314 J mol⁻¹ K⁻¹), \( T \) the absolute temperature of the melts (K), \( D \) the diffusion coefficient.
The slope of $ip$ versus $v^{1/2}$ attributed to peak A obtained in Figure 4a is:

$$\frac{ip}{v^{1/2}} = -0.00529 A s^{-1/2} V^{-1/2} cm^{-2}$$  \hspace{1cm} (2)

at $T=600^\circ$C and $C=1.73 \times 10^{-5}$ mol cm$^{-3}$.

**B'//B' redox system**: The sharp oxidation peak B' and the ratios of $|ip_{B'}/ip_A|>1$ imply the couple B'/B may be attributed to the deposition and dissolution of Fe [25,26]. Since the peak potential $E_p$ remains at about 1.42 V (vs. alkalis) and the cathodic peak current density $ip$ linearly increases with $v^{1/2}$ as shown in Figure 4b, the reduction peak B is a quasi-reversible reaction controlled by ion diffusion.

**Chronopotentiometry**

A typical chronopotentiogram of FLINAK-Fe(III) (997 ppm) melts obtained for an applied current of -3.5 mA on a Pt electrode at 600°C is shown in Figure 5. Two plateaus, A and B, at about 1.9 V (vs. alkalis) and 1.5 V (vs. alkalis), respectively, can be observed, which confirms the two-step reduction mechanism of Fe(III) previously evidenced by CV.

The validity of the Sand’s law [Eq. (3)] is verified in Figure 6, since the $i^{1/2}$ plotted versus the applied current (I) is constant [Eq. (4), (5)]. The two reduction processes of Fe(III) are thus controlled by ion diffusion in molten FLINAK. The diffusion coefficient of Fe(III) can be determined using the Sand’s law [24]:

$$i^{1/2} = \frac{nFSD^{1/2}A^{1/2}}{2}$$  \hspace{1cm} (3)

Where $i$ is the applied current (A), $r$ the transition time (s), $C$ the Fe(III) concentration (here, $C=3.56 \times 10^{-5}$ mol cm$^{-3}$), $n$ the number of exchanged electrons, $F$ the Faraday constant (96,485 C mol$^{-1}$), $D$ the electrode surface area (cm$^2$) and $D$ the diffusion coefficient (cm$^2$ s$^{-1}$).

Peak A: $i^{1/2} = -0.00395 A s^{-1/2}$ \hspace{1cm} (4)

Peak B: $i^{1/2} = -0.01242 A s^{-1/2}$ \hspace{1cm} (5)

**Number of exchanged electrons**

The Fe(III) reduction mechanism was finally evidenced by calculating the number of exchanged electrons. Combining CV and CP measurements, the exchanged electron number of peak A was...
obtained to be 0.87 by coupling Eq. (1)-(4). Thus, Fe(III) reduction proceeded in two steps: initial Fe(III) reduction to Fe(II) followed by subsequent reduction of Fe(II) to Fe. For the reversible Fe(III)/Fe(II) couple, Fe(III) diffusion coefficient is determined to be $3.80 \times 10^{-6}$ cm$^2$ s$^{-1}$ from CV measurement [Eq. (1)] and to be $4.38 \times 10^{-6}$ cm$^2$ s$^{-1}$ from CP measurement [Eq. (3)].

### Square wave voltammetry

The typical square wave voltammograms of FLINAK-Fe(III) (190 ppm) melts at 30-70 Hz on a Pt electrode are shown in **Figure 7**. Two reduction peaks, A and B, at about 2.03 V (vs. alkalis) and 1.43 V (vs. alkalis), respectively, can be observed. The mathematical analysis of the peak yields a simple equation associating the width of the half peak ($W_{1/2}$) and the electron transfer number $n$.

$$W_{1/2} = 3.52 \times \frac{RT}{nF}$$  \hspace{1cm} (6)

Eq. (6) is theoretical valid for a reversible system, which can be extended to other systems as far as the criterion of linearity between the peak intensity and the square root of the frequency signal is respected [29-33]. As shown in **Figure 8**, the reduction peak current densities ($\delta_{ip}$ and $\delta_{ip}$) show a linear relationship with the square root of the frequency. Calculated according to Eq. (6), the electron transfer number for peaks A and B are 1.04 and 1.77, respectively, as shown in **Table 2**. Thus, peaks A and B are corresponding to the reductions of Fe(III)/Fe(II) and Fe(II)/Fe, respectively. These results are in accordance with those obtained through CV and CP.

### Electrochemical behavior of Fe(II) in FLINAK melts

After 740 ppm of Fe(II) was introduced into FLINAK melts in the form of FeF$_2$, the square wave voltammograms obtained on a Pt electrode at 600°C and different holding times are shown in **Figure 9**. Two reduction peaks, A and B, at about 2.1 V and 1.5 V (vs. alkalis), attributed to the reductions of Fe(III)/Fe(II) and Fe(II)/Fe, respectively, can be observed. Peak A assigned to the reduction of Fe(III)/Fe(II) also appeared even though only FeF$_2$ was added to FLINAK, indicating the conversion of Fe(II) to Fe(III).

Plot of current density of peak A ($\delta_{ip}$) vs. different holding times at 600°C in FLINAK-Fe(II) (740 ppm) melts is shown in **Figure 10**. $\delta_{ip}$ increases from $-1.22$ mA cm$^{-2}$ to $-5.64$ mA cm$^{-2}$ and then reaches a plateau after 130 min. The increase of $\delta_{ip}$ before 130 min is attributed to the conversion of Fe(II) to Fe(III). After the conversion equilibrium is achieved at 130 min, the Fe(III) concentration in molten FLINAK remains constant, resulting in an unchangeable $\delta_{ip}$ value.
Table 2 Reduction reactions and electron transfer numbers of peak A and B.

<table>
<thead>
<tr>
<th>Reduction peak</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduction potential vs. alkalis</td>
<td>2.03 V</td>
<td>1.43 V</td>
</tr>
<tr>
<td>Value of $W_{1/2}$</td>
<td>253 mV</td>
<td>150 mV</td>
</tr>
<tr>
<td>Exchanged electron numbers</td>
<td>1.04</td>
<td>1.77</td>
</tr>
<tr>
<td>Corresponding reaction</td>
<td>Fe(III)+e=Fe(II)</td>
<td>Fe(II)+2e=Fe</td>
</tr>
</tbody>
</table>

Figure 8 Plots of peak current density ($\delta ip$) and peak potential ($Ep$) vs. the square root of the frequency ($f^{1/2}$) for cathodic peaks A and B in FLINAK-Fe(III) (190 ppm) melts at 600°C. Pulse height: 20 mV, step potential: 2 mV. Working electrode: Pt (0.62 cm$^2$); auxiliary electrode: Graphite; reference electrode: Pt.

Figure 9 Square wave voltammograms of the FLINAK-Fe(II) (740 ppm) melts recorded on a Pt electrode at 600°C and different holding times. Pulse height: 20 mV, step potential: 2 mV, frequency: 10 Hz. Working electrode: Pt (0.62 cm$^2$); auxiliary electrode: Graphite; reference electrode: Pt.

Figure 10 Plot of the current density of peak A vs. holding time at 600°C as measured from the SWVs of FLINAK-Fe(II) (740 ppm) melts. Pulse height: 20 mV, step potential: 2 mV, frequency: 10 Hz. Working electrodes: Pt (0.62 cm$^2$); auxiliary electrode: Graphite; reference electrode: Pt.

Conclusion

In this work, the electrochemical behavior of Fe(III) in molten FLINAK was studied by CV, CP and SWV. The results showed that Fe(III) was initially reduced to Fe(II), which was subsequently reduced to Fe. Both Fe(III)/Fe(II) and Fe(II)/Fe reductions were controlled by ion diffusion. The diffusion coefficient of Fe(III) was $3.80 \times 10^{-6}$ cm$^2$ s$^{-1}$ obtained by Randles-Sevcik equation and was $4.38 \times 10^{-6}$ cm$^2$ s$^{-1}$ obtained by Sand's law. The electrochemical behavior of Fe(II) was then investigated by SWV. Two cathodic peaks attributed to the reductions of Fe(III)/Fe(II) and Fe(II)/Fe, can be observed. This result indicated that Fe(II) was converted to Fe(III), which is more stable in FLINAK melts.

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References


