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# Electrolytic reduction of CrF<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> in molten fluoride salt

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The electrochemical behavior of Cr<sup>3+</sup> in molten LiF–NaF–KF (46.5 : 11.5 : 42 mol%) (FLiNaK) was studied by cyclic voltammetry (CV) at 600 °C. With an acceptable solubility and a relatively positive reduction potential of solute Cr<sup>3+</sup>, the electrolytic reduction of chromium in FLiNaK–CrF<sub>3</sub> melt was performed on a tungsten electrode by potentiostatic electrolysis. After electrolysis for 21.5 h, the Cr<sup>3+</sup> in the melt was effectively removed as confirmed by ICP-OES and CV. Then, the solubility of Cr<sub>2</sub>O<sub>3</sub> in FLiNaK with ZrF<sub>4</sub> additive was analyzed by CV. The results showed that the solubility of Cr<sub>2</sub>O<sub>3</sub> was greatly promoted by ZrF<sub>4</sub> and the reduction potential of zirconium is far more negative than that of chromium, which makes the electrolysis of chromium from Cr<sub>2</sub>O<sub>3</sub> material possible. Thus, the electrolytic reduction of Cr in a FLiNaK–Cr<sub>2</sub>O<sub>3</sub>–ZrF<sub>4</sub> system was further performed by potentiostatic electrolysis on a nickel electrode. After electrolysis for 5 h, a thin layer of chromium metal (with a thickness of *c.a.* 20 μm) was deposited on the electrode, as confirmed by SEM-EDS and XRD techniques. This study verified the feasibility of electroextraction of Cr from the FLiNaK–CrF<sub>3</sub> and FLiNaK–Cr<sub>2</sub>O<sub>3</sub>–ZrF<sub>4</sub> molten salt systems.

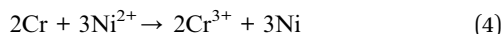
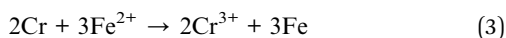
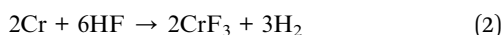
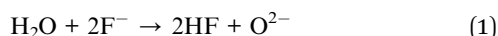
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## 1. Introduction

Molten fluorides are particularly appropriate as the coolant of molten salt reactors (MSR) because of their excellent heat transfer properties.<sup>1–3</sup> However, the oxidizing impurities contained in fluoride salts,<sup>4</sup> including adsorbed H<sub>2</sub>O, dissolved HF, and metal impurity ions (Fe<sup>2+</sup>, Ni<sup>2+</sup>) are corrosive to structural materials,<sup>5–8</sup> particularly to the most vulnerable element Cr in those materials [eqn (1)–(4)].<sup>9–11</sup> The corrosion reactions lead to dissolution of Cr into the molten salt. Despite this problem, high temperature Cr-bearing alloys, such as Hastelloy, still have been used in molten fluorides because of their acceptable, time-tested, and overall high temperature properties.<sup>12,13</sup>



By periodic sampling and off-line chemical analysis, the Oak Ridge National Laboratory (ORNL)<sup>14</sup> found that chromium concentration was less than 150 ppm during the normal

operation of molten salt reactor experiment (MSRE), and 70–80 ppm of chromium kept in molten fluorides will help to reduce the material corrosion. However, considering its neutron absorption, chromium needs to be removed when its concentration approaches to 300 ppm. Hence, developing a fast method to remove chromium in molten fluorides is necessary. The electrochemical methods are proposed to separate those impurities which have lower theoretical decomposition voltages than that of salt component. As one of the most important impurities in FLiNaK melt, Cr<sup>3+</sup> in the form of CrF<sub>3</sub> presents a much lower theoretical decomposition voltage than LiF, NaF, and KF, thus it is supposed that Cr can be electrodeposited and separated from the FLiNaK–Cr<sup>3+</sup> melts by electrolysis. Actually, the electrochemical behavior of Cr<sup>3+</sup> in molten fluorides was widely studied. Our previous studies<sup>4</sup> found that the reduction of Cr<sup>3+</sup> ions in molten FLiNaK was a two-step process by cyclic voltammetry (CV) and square wave voltammetry (SWV), namely, the initial Cr(III) reduction to Cr(II) followed by subsequent reduction to Cr. The first reduction step of Cr(III)/Cr(II) was reversible and the second reduction step of Cr(II)/Cr was quasi-reversible over the studied scan rates (0.05–0.4 V s<sup>−1</sup>). Since the kinetics of chromium deposition in molten FLiNaK by electrochemical techniques is controlled by diffusion according to T. Yoko,<sup>15</sup> R. A. Bailey,<sup>16</sup> D. Ludwig,<sup>17</sup> and our previous studies.<sup>4</sup> Therefore, the most concern is that if Cr<sup>3+</sup> ion can be efficiently removed from the melts by electrolytic reduction method and how long the process will take.

However, due to the hygrometric nature of fluorine salt and the pyro-hydrolysis of adsorbed water (eqn (1)), the oxide impurity (O<sup>2−</sup>) in molten salt is unavoidable.<sup>18–22</sup> The Cr<sup>3+</sup>

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exhibits a high sensitivity towards  $O^{2-}$  ions and the interaction between the two would probably produce solid oxide compound (e.g.  $Cr_2O_3$ ) with high melting point and low solubility. Therefore, the  $Cr^{3+}$  impurity in molten fluorides should generally exist in two forms: chromium(III) fluoride (e.g.  $CrF_3$ ) and chromium(III) oxide (e.g.  $Cr_2O_3$ ).

With the purpose of  $Cr^{3+}$  removal, electrolysis of chromium from both the  $CrF_3$  and  $Cr_2O_3$  raw materials should be performed. The reported high solubility of  $CrF_3$ <sup>4,15–17</sup> in molten FLiNaK makes its electrolysis feasible. However, with respect to the FLiNaK- $Cr_2O_3$  system, the solubility of  $Cr_2O_3$  in FLiNaK is a key factor affecting chromium electroextraction. Our previous investigation and related reports<sup>23–25</sup> pointed out that the  $Cr_2O_3$  solubility in molten fluorides was relatively low. For example, the solubility of  $Cr_2O_3$  in molten FLiNaK and FLiBe at 600 °C was as low as 122 ppm and 183 ppm, respectively,<sup>23</sup> which makes the electrolysis difficult and challenging. Therefore, it is necessary to find suitable additives to increase  $Cr_2O_3$  solubility in molten fluorides.  $ZrF_4$  might be a good choice, which has a strong affinity towards oxide. Peng and Shen *et al.*<sup>19,21,26</sup> found that Zr(IV) could readily combine with  $O^{2-}$  to produce zirconium oxide (e.g.  $ZrO_2$ ) or zirconium oxy-fluoride species (e.g.  $ZrOF_2$  and  $Zr_2OF_{10}^{4-}$ ) in FLiNaK and FLiBe molten fluoride systems.<sup>16,17</sup> Besides, Gibilaro *et al.*<sup>27</sup> also found the interactions between  $Zr^{4+}$  and  $O^{2-}$  in LiF-CaF<sub>2</sub> would lead to the formation of  $ZrO_2$  and  $ZrO_{1.3}F_{1.4}$ . These studies confirmed that  $ZrF_4$  is a good oxide collector that can easily capture  $O^{2-}$  in molten fluorides.

Therefore, it is reasonably supposed that  $ZrF_4$  can improve the solubility of solid oxides in melt through the reaction of Zr(IV) and oxygen in these oxides. Song *et al.*<sup>23</sup> studied the dissolution behavior of  $Cr_2O_3$  in various molten fluorides by combining electrochemical and chemical methods (including CV, ICP-OES, Raman, and XRD techniques), and found that the  $ZrF_4$  additive significantly increased the solubility of  $Cr_2O_3$  by 19 and 2 times in FLiNaK and FLiBe molten fluoride salts, respectively, with yielding the dissolution product of  $Cr^{3+}$  and  $[ZrO_xF_y]^{4-2x-y}$  complex species through the dissolution mechanism of  $Cr_2O_3 + ZrF_4 + F^- \rightarrow CrF_3 + ZrO_xF_y^{4-2x-y}$ . Specifically, the solubility of  $Cr_2O_3$  increased from 122 ppm to 2300 ppm in FLiNaK and increased from 183 ppm to 320 ppm in FLiBe by  $ZrF_4$  at 600 °C. Besides, Peng *et al.*<sup>18–21</sup> studied the dissolution-precipitation behaviors of  $UO_2$  in FLiNaK and FLiBe with  $ZrF_4$  additive, and found that  $ZrF_4$  can greatly improve the solubility of  $UO_2$  in both systems. Particularly, their results showed that the maximum solubility of  $UO_2$  in FLiNaK was increased by a factor of 5.76 when the added  $ZrF_4$  concentration was up to 2.91 wt%, and  $UO_2$  was dissolved as  $UOF_2$  and  $ZrOF_2$  species.<sup>19</sup> These studies demonstrated that  $ZrF_4$  can effectively improve the solubility of oxides in molten fluorides. Moreover,  $ZrF_4$  has a low neutron-absorption cross-section, which allows it to be used in the carrier media of MSR. Meanwhile, the theoretical decomposition potential difference between zirconium and chromium is significant. From the above,  $ZrF_4$  is probably an ideal additive for improving the solubility of  $Cr_2O_3$  in molten fluorides, which make the electrolysis of chromium from  $Cr_2O_3$  material possible.

In this paper, with analysis of the reduction potentials of solute  $Cr^{3+}$  by cyclic voltammetry (CV), the feasibility of electrolyzing chromium from the FLiNaK- $CrF_3$  melt was verified. Then, the solubility of  $Cr_2O_3$  in FLiNaK with  $ZrF_4$  additive was analyzed by CV. The results showed that the solubility of  $Cr_2O_3$  was greatly facilitated by  $ZrF_4$ , which make the electrolysis of chromium from this system possible. Furthermore, the electrolytic reduction of Cr in the FLiNaK- $CrF_3$  and FLiNaK- $Cr_2O_3$ - $ZrF_4$  systems were performed by potentiostatic electrolysis on W and Ni electrodes, respectively. The removal rate of  $Cr^{3+}$  was examined by ICP-OES and CV, and the electrolytic product was characterized by SEM-EDS and XRD. The results showed that the  $Cr^{3+}$  in the melt was effectively removed after electrolysis of both systems. This study successfully verified the feasibility of electrolytic extraction of Cr from the FLiNaK- $CrF_3$  and FLiNaK- $Cr_2O_3$ - $ZrF_4$  molten salt systems.

## 2. Experimental

### 2.1 Chemicals and molten salt systems

Before use, the highly-purified FLiNaK [LiF-NaF-KF (46.5 : 11.5 : 42 mol%)] eutectic salt was dehydrated by heating under vacuum from ambient temperature up to its melting point for 72 h. The main impurities contained in FLiNaK salt were analyzed by ICP-OES and shown in Table 1. Then, 300 g of dehydrated FLiNaK salt was weighed and loaded into a vitreous carbon crucible ( $\Phi 70 \times H 100$  mm). During the electrolysis experiment of FLiNaK- $CrF_3$  system, a certain amount of  $Cr^{3+}$  solute was introduced into FLiNaK salt in the form of  $CrF_3$  (Sigma-Aldrich, 99.99%), and the electrolysis of  $Cr^{3+}$  was then conducted in this prepared FLiNaK- $CrF_3$  electrolyte, as shown in Fig. 1(a). While in the electrolysis of FLiNaK- $Cr_2O_3$ - $ZrF_4$  system, an excess of  $Cr_2O_3$  powder (ca. 10 g, Sigma-Aldrich, 99.9%) was added into FLiNaK salt, and the  $Cr_2O_3$  ( $\rho = 5.21 \text{ g cm}^{-3}$ ) would deposited at the bottom of the molten bath ( $\rho \approx 2 \text{ g cm}^{-3}$ ) when balanced. Then a known amount of  $ZrF_4$  (Sigma-Aldrich, 99.99%) was gradually introduced into the FLiNaK- $Cr_2O_3$  melt to promote the solubility of  $Cr_2O_3$ , and the electrolysis of  $Cr^{3+}$  by  $Cr_2O_3$  dissolution was then conducted in this prepared FLiNaK- $Cr_2O_3$ - $ZrF_4$  electrolyte, as shown in Fig. 1(b).

### 2.2 Chemical analysis

Concentrations of the solute chromium in molten fluoride electrolytes were determined by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) technique. Firstly, samples of the melt were siphoned by dipping a nickel tube ( $\Phi 6$

Table 1 The main impurities contained in the FLiNaK salt analyzed by ICP-OES

| Impurities | Content/ppm |
|------------|-------------|
| Fe         | 78          |
| Cr         | 38          |
| Ni         | 8           |
| Ca         | 20          |
| Mg         | 9           |
| W          | 15          |



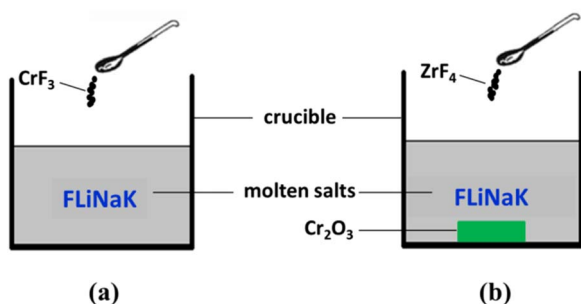


Fig. 1 Schematic diagram of the experimental systems for (a) FLiNaK- $\text{CrF}_3$  electrolysis and (b) FLiNaK- $\text{ZrF}_4$ - $\text{Cr}_2\text{O}_3$  electrolysis.

mm) into the supernatant of the melt without touching the bottom precipitates. 0.1 g of finely pulverized sample was weighed-in a glove box. Then, the sample was dissolved in diluted 20% (v : v)  $\text{HNO}_3$  and heated at 80 °C for *ca.* 30 min until the sample was completely dissolved. After cooling, the sample solution was transferred to a 50 ml flask and further diluted with deionized water. For each sample, duplicate decomposition tests of the sample were made. Chromium in the dissolved sample was then determined by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES, Arcos, Spectro Co., Ltd). With the obtained results, we can compare the chromium content in the bath before and after electrolysis, and the removal efficiency of Cr is thus evaluated.

### 2.3 Electrochemical measurements

(1) **Electrochemical analysis and apparatus.** The crucible loaded with molten salts was transferred to a stainless steel cell inside an electric furnace. Then the salt was heated, melted, and kept at 600 °C for electrochemical measurements. The temperature was measured with a nickel–chromium thermocouple positioned just outside the crucible. The whole experiment was conducted in a glove box protected by dry argon gas atmosphere (99.999%), and the oxygen and moisture contents in the glove box were both strictly controlled below 0.5 ppm. The experimental apparatus used in present work has also been described in our previous studies.<sup>4,18–22</sup>

The electrochemical behaviors of  $\text{CrF}_3$  and dissolved chromium species caused by  $\text{Cr}_2\text{O}_3$  dissolution in molten fluorides with  $\text{ZrF}_4$  additive were investigated by cyclic voltammetry (CV). The schematic diagram of the electrochemical set-up used in this study is shown in Fig. 2. The electrochemical cyclic voltammetry (CV) measurements were carried out with a three-electrode system connected to an electrochemical analyzer. A tungsten or nickel wire (1.0 mm diameter) was used as the working electrode; the surface area of this wire was determined by measuring the immersion depth in the melts after completion of the experiment. The auxiliary electrode was a graphite rod (6.0 mm diameter) with a large surface area (2.5  $\text{cm}^2$ ). The reference electrode was a platinum wire (1.0 mm diameter), which was proved to act as a quasi-reference electrode  $\text{Pt}/\text{PtO}_x/\text{O}^{2-}$ .<sup>28,29</sup> All potentials in this paper were measured with respect to this reference electrode and then transferred to *vs.*  $\text{K}/\text{K}^+$

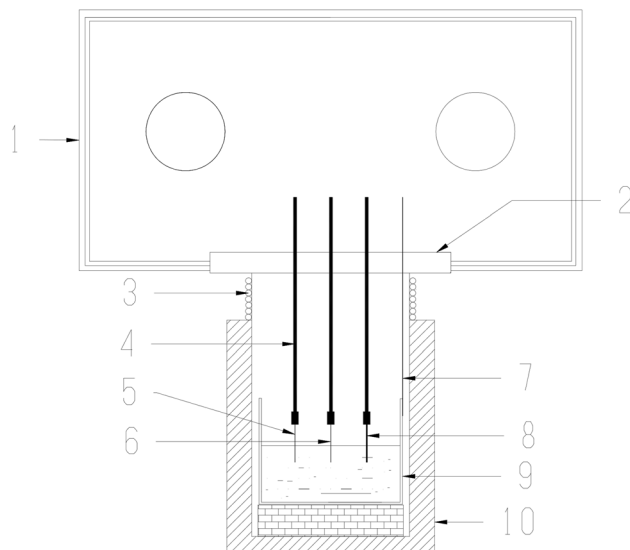


Fig. 2 Drawing of the electrochemical set-up used in this study. 1: Glove box. 2: Transition cover. 3: Water cooling coil. 4: Alumina insulation tubes. 5: Working electrode. 6: Reference electrode. 7: Thermocouple. 8: Auxiliary electrode. 9: Vitreous carbon crucible and molten salt. 10: Electric furnace.

reference electrode according to literature.<sup>30,31</sup> An electrochemical analyzer, AUTOLAB (Ecochemie, NL), was used as the source of signal and for storage of data.

(2) **Electrolysis and electrolysis products.** During FLiNaK- $\text{CrF}_3$  electrolysis experiment,  $\text{CrF}_3$  was the active component and electrolysis raw material. A potentiostatic mode was used for electrolysis. A tungsten wire (1.0 mm diameter) and graphite rod (spectral pure; 6.0 mm diameter) were employed as cathode and anode respectively, and the reference electrode was a platinum wire (1.0 mm diameter). The applied electrolytic potential was controlled at a constant value of 1.0 V *vs.*  $\text{K}/\text{K}^+$  in the whole electrolysis process.

During FLiNaK- $\text{ZrF}_4$ - $\text{Cr}_2\text{O}_3$  electrolysis experiment,  $\text{Cr}_2\text{O}_3$  was the active component and electrolysis raw material. A potentiostatic mode was used for electrolysis. The cathode and anode were Ni plate (1.5 cm × 2.0 cm) and graphite rod (spectral pure; 6.0 mm diameter), respectively. And the reference electrode was a platinum wire (1.0 mm diameter) as well. A constant potential of 1.0 V *vs.*  $\text{K}/\text{K}^+$  was used in the potentiostatic mode.

After electrolysis, the cathodic deposits were characterized by the techniques of X-ray diffraction (XRD; DY3614, PANzlytical Co., Ltd) and scanning electron microscopy (SEM; Merlin compact-60-83) equipped with an energy dispersive X-ray spectroscopy (EDS).

## 3. Results and discussion

### 3.1 Electrochemical behavior of $\text{Cr}^{3+}$ in FLiNaK melt

The typical cyclic voltammograms obtained on a W electrode in FLiNaK melt at 600 °C after addition of 345.30 ppm  $\text{Cr}^{3+}$  is shown in Fig. 3(a). Evidently, one couple of cathodic/anodic



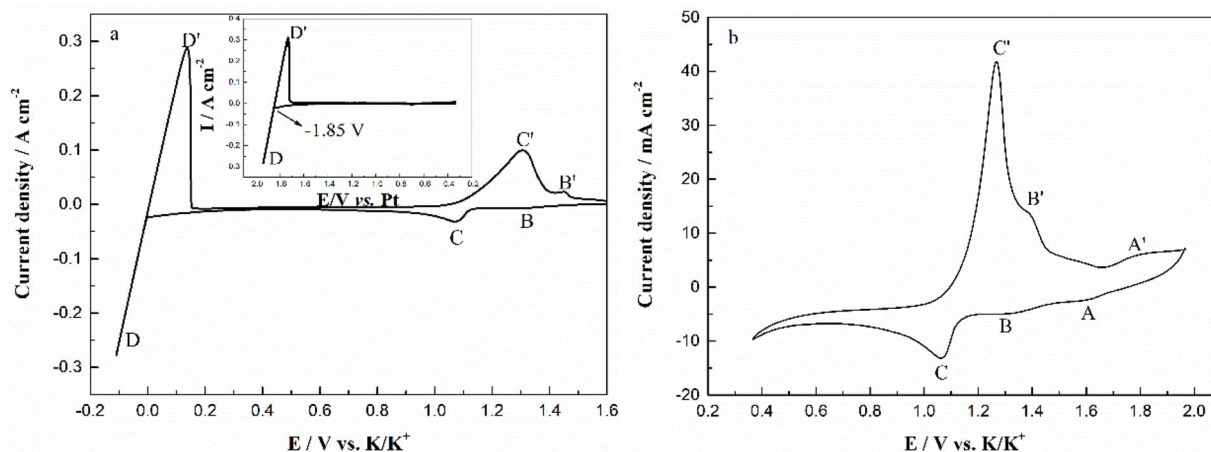
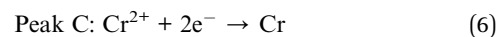
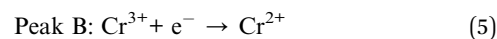


Fig. 3 (a) CV of the FLiNaK-CrF<sub>3</sub> (345.30 ppm Cr<sup>3+</sup>) melt in the potential range of 1.60 V to -0.10 V vs. K/K<sup>+</sup>. Inset: CV of the blank FLiNaK melt. (b) CV of the same FLiNaK-CrF<sub>3</sub> melt in the potential range of 1.90 V to 0.40 V vs. K/K<sup>+</sup>. Working EL.: W (S = 1.13 cm<sup>2</sup>); auxiliary EL.: graphite; reference EL.: Pt; temperature: 600 °C; scan rate: 0.1 V s<sup>-1</sup>.

signals D and D' corresponding to the deposition and dissolution of one of the melt components can be observed. According to heats of formation data for fluorides given by Baes<sup>32</sup> and the investigation of Gabriela,<sup>31</sup> it can be presumed that the signal D corresponds to the electrodeposition of potassium, while the oxidation signal D' is attributed to the dissolution of potassium (KF → K, 4.97 V vs. F<sub>2</sub>/F<sup>-</sup>; NaF → Na 5.03 V vs. F<sub>2</sub>/F<sup>-</sup>; LiF → Li, 5.52 V vs. F<sub>2</sub>/F<sup>-</sup> at 600 °C). The reduction signal D at -1.85 V vs. Pt is shown in inset from Fig. 3(a). Thus, all potentials referenced to a platinum wire can be converted to vs. K/K<sup>+</sup>. Besides the couple of D and D', two reduction peaks B and C at 1.27 V and 1.07 V vs. K/K<sup>+</sup> in the cathodic run and two anodic counter-peaks B' and C' at 1.45 V and 1.31 V vs. K/K<sup>+</sup> can be observed.

In order to exhibit the details of the redox signals, Fig. 3(b) shows the cyclic voltammogram of the same FLiNaK-Cr<sup>3+</sup> (345.30 ppm) melt on a W electrode in a relatively narrow potential range (from 1.90 V to 0.40 V vs. K/K<sup>+</sup>) also at 600 °C and scan rate of 0.1 V s<sup>-1</sup>. In this figure, the two reduction peaks B (1.27 V vs. K/K<sup>+</sup>) and C (1.07 V vs. K/K<sup>+</sup>), as well as their counter-oxidation peaks B' (1.45 V vs. K/K<sup>+</sup>) and C' (1.31 V vs. K/K<sup>+</sup>) also can be clearly observed. Since the deposition potential of Cr is more positive than that of alkali metal in a fluoride system and the peak current density for B and C linearly increases with the Cr<sup>3+</sup> concentration (see Fig. 4), the observed peaks B and C should be attributed to the reduction of Cr<sup>3+</sup>. According to our previous studies and other relevant reports, the reduction of Cr<sup>3+</sup> in molten fluorides proceeds in two steps: the first reduction of Cr<sup>3+</sup> to Cr<sup>2+</sup> and the subsequent reduction of Cr<sup>2+</sup> to metal Cr, denoted as B and C shown in eqn (5) and (6), respectively. What is worth mentioning, except for B/B' and C/C' couples, a new weak reduction signal A at around 1.60 V vs. K/K<sup>+</sup> associated with its counter-anodic signal A' (1.80 V vs. K/K<sup>+</sup>) can be observed in Fig. 3(b). Its peak current density is constant even if the concentration of Cr<sup>3+</sup> increases. Thus, it is probably linked to the impurity Fe contained in the original FLiNaK eutectics (see Table 1). The attribution of the redox couple A/A' will be discussed later.



### 3.2 Electrolysis removal of Cr<sup>3+</sup> from FLiNaK-CrF<sub>3</sub> melt

According to the theory of A. J. Bard,<sup>33</sup> the minimum potential difference for successful quantitative separation was considered to be 200 mV. From above analysis, the potential difference between Cr<sup>3+</sup> and alkaline ions is approximately equal to 1.3 V, indicating that the Cr<sup>3+</sup> can be theoretically removed from FLiNaK melt by potentiostatic electrolysis. Thus, potentiostatic electrolysis of the FLiNaK-CrF<sub>3</sub> system was carried out. After electrolysis, the system was on-line sampled at 600 °C and the concentration of Cr<sup>3+</sup> remaining in melt was analyzed by ICP-OES.

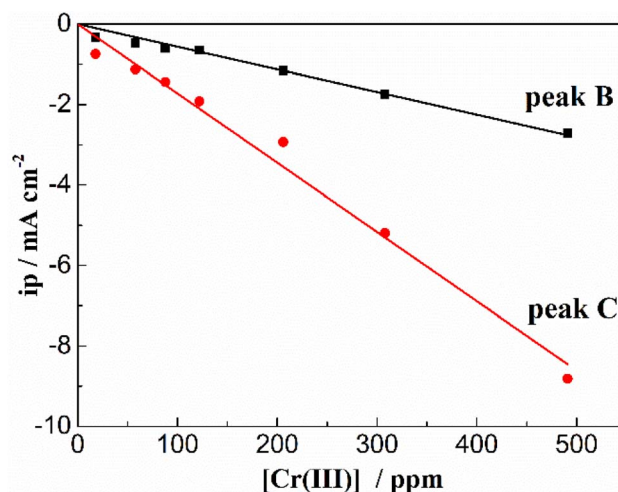


Fig. 4 Linear relationship between the peak current density and the Cr<sup>3+</sup> concentration in FLiNaK melt at 600 °C at the scan rate of 0.1 V s<sup>-1</sup> for both cathodic peak A and B. Working EL.: W (S = 1.13 cm<sup>2</sup>); auxiliary EL.: graphite; reference EL. Pt.



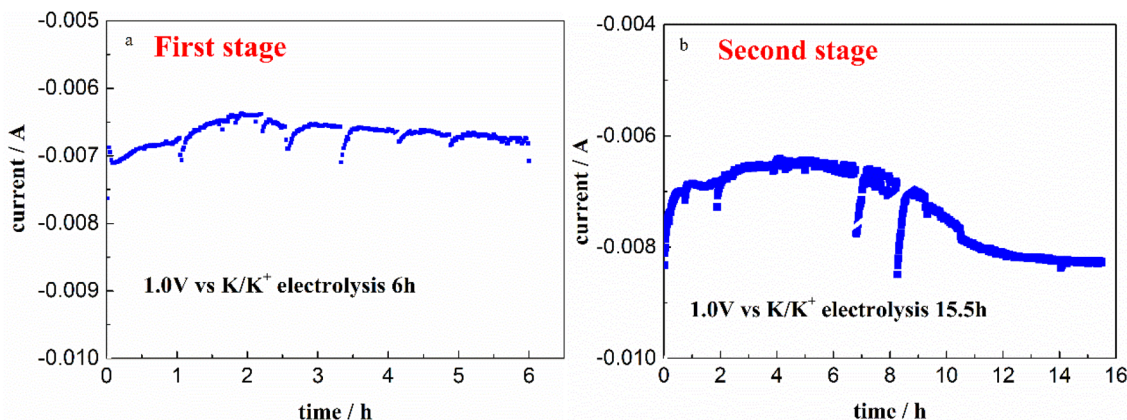


Fig. 5 Variations of the current on W cathode during the electrolysis at 1.0 V vs.  $K/K^+$  and 600 °C for both two stages in FLiNaK- $Cr^{3+}$  (345.30 ppm) melt. (a): The first stage; (b): the second stage. Working EL: W ( $S = 1.13 \text{ cm}^2$ ); auxiliary EL: spectral pure graphite; reference EL: Pt.

**3.2.1 First stage electrolysis.** The current response vs. electrolysis time on a W electrode at 1.0 V vs.  $K/K^+$  in FLiNaK- $Cr^{3+}$  (345.30 ppm) melt for successive electrolysis of 6 h was recorded and shown in Fig. 5(a). The current decreased from  $-7 \text{ mA}$  to  $-6.4 \text{ mA}$  in the first 2 h, and then gradually increased to  $-6.6 \text{ mA}$  for the following 4 h. Stable and continuous current output indicates that the  $Cr^{3+}$  ions are continuously being electrodeposited. After electrolysis, the remaining  $Cr^{3+}$  decreased from the initial 345.30 ppm to 108.61 ppm, which was analyzed by ICP-OES. That means, the decrement of  $Cr^{3+}$  was 236.69 ppm, as shown in Table 2. It is reasonable to speculate that the  $Cr^{3+}$  can be successfully removed by electrochemical reduction. However, the remaining  $Cr^{3+}$  content was still high as 108.61 ppm after this time of electrolysis for 6 h.

**3.2.2 Second stage electrolysis.** In order to further decrease the  $Cr^{3+}$  concentration, continual electrolysis was carried out on a W electrode at 1.0 V vs.  $K/K^+$  for another 15.5 h. The relation between current and electrolysis time was given in Fig. 5(b). The current decreased from 8 mA to 6.5 mA in the first 3 h, then gradually increased to 8 mA in the following 8 h and eventually reached a plateau. After electrolysis for 15.5 h, the remaining  $Cr^{3+}$  further decreased from 108.61 ppm to 13.12 ppm. That means, the decrement of  $Cr^{3+}$  in this electrolysis stage was 95.49 ppm, as shown in Table 2.

Therefore, after the whole electrolysis of 21.5 h, the  $Cr^{3+}$  in melt successfully decreased from the initial 345.30 ppm to a sufficiently low concentration level of 13.12 ppm, with the practical removal content of 332.18 ppm (Table 2). This result confirmed that the  $Cr^{3+}$  in melt can be almost removed through electrolysis method. Besides, it should be noted that the

impurity Fe ions in molten FLiNaK analyzed by ICP-OES also continuously decreased from 78.19 ppm to below the detection limit after the overall electrolysis duration for 21.5 h. This result indicates that a certain amount of charges were used for Fe deposition. The current fluctuation in electrolytic process may be caused by the absorption and desorption of the electrodeposited products, resulting in a change in the electrode surface area.

According to the CV theory, the peak current density of the electroactive solute (in this case the  $Cr^{3+}$ ) is fundamentally proportional to its concentration for an electrode process controlled by diffusion (Fig. 5). Thus, the variation of the  $Cr^{3+}$  concentration remaining in the melts can be monitored by CV measurements throughout the electrolysis process. Fig. 6 shows the cyclic voltammograms of FLiNaK- $Cr^{3+}$  melts before electrolysis, after 6 h and 21.5 h electrolysis on W cathode at 1.0 V vs.  $K/K^+$ . Obviously, the reduction peak current density of  $Cr^{3+}$  ( $Cr^{3+}/Cr^{2+}$  reduction for peak B and  $Cr^{2+}/Cr$  reduction for peak C) gradually decreased as the electrolysis progressed, and eventually no reduction peak current density can be detected on cyclic voltammogram after electrolysis for 21.5 h. This result indicates a decreasing  $Cr^{3+}$  concentration during electrolysis and until it drops to below the detection limit of CV, which agreed well with the result obtained from ICP-OES. It should be noted that the cathodic peak A attributed to Fe reduction also decreased after electrolysis, indicating the trace impurity of Fe ions was electrochemically removed as well. Therefore, the reduction peak A corresponds to the reduction of  $Fe^{2+}$  to iron metal ( $Fe^{2+} + 2e^- \rightarrow Fe$ ), and the oxidation peak A' corresponds to the oxidation of Fe metal to iron ions ( $Fe - 2e^- \rightarrow Fe^{2+}$ ).

Table 2 The concentration of Cr in FLiNaK melt before and after electrolysis

| Samples  | Before electrolysis | Electrolysis for 6 h | Electrolysis for 21.5 h |
|--|---------------------|----------------------|-------------------------|
| Electrolysis potential (V)                             | —                   | 1.0 vs. $K/K^+$      | 1.0 vs. $K/K^+$         |
| Cr concentration in melt analyzed by ICP-OES (ppm)     | 345.30              | 108.61               | 13.12                   |
| Cr practical removal content analyzed by ICP-OES (ppm) | —                   | 236.69               | 332.18                  |
| Fe concentration analyzed by ICP-OES (ppm)             | 78.19               | 7.43                 | <–0.04                  |



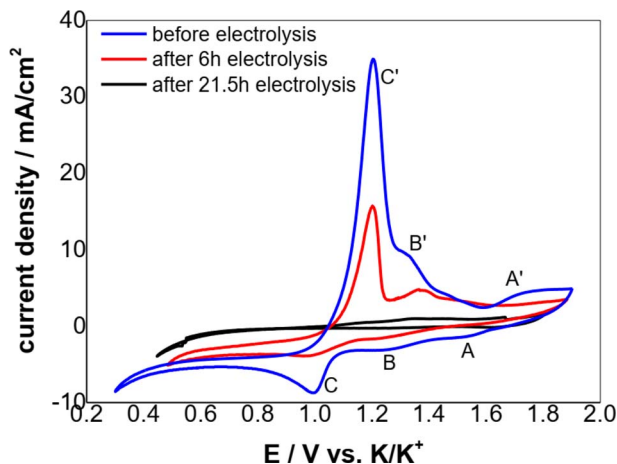


Fig. 6 Typical CVs of the FLiNaK- $\text{Cr}^{3+}$  (345.30 ppm) melts before and after electrolysis on W cathode at 600 °C. Scan rate:  $0.1 \text{ V s}^{-1}$ ; working El.: W ( $S = 1.13 \text{ cm}^2$ ); auxiliary El.: graphite; reference El.: Pt.

### 3.3 Solubility of $\text{Cr}_2\text{O}_3$ in molten FLiNaK with $\text{ZrF}_4$ additive

**3.3.1 Solubility of  $\text{Cr}_2\text{O}_3$  in pure FLiNaK melt.** The solubility of  $\text{Cr}_2\text{O}_3$  in molten FLiNaK was firstly studied by cyclic voltammetry method. The cyclic voltammograms of FLiNaK and FLiNaK- $\text{Cr}_2\text{O}_3$  systems were measured on tungsten electrode at 600 °C with scan rate of  $0.1 \text{ V s}^{-1}$ , and overlap of the two results were presented in Fig. 7. Obviously, only one couple of cathodic/anodic signals D and D' corresponding to the deposition and dissolution of K was observed in the pure FLiNaK (dotted black line). After addition of  $\text{Cr}_2\text{O}_3$  into FLiNaK melts, the voltammogram of the system on tungsten electrode was featureless (solid red line). No reduction and oxidation signals or processes can be detected prior to the deposition of potassium metal (signal D), and the obtained CV curve is almost the same as that in the pure FLiNaK melt. The similarity of the CVs between FLiNaK and FLiNaK- $\text{Cr}_2\text{O}_3$  systems indicates that the solubility of  $\text{Cr}_2\text{O}_3$  in FLiNaK was low enough that the dissolved

chromium species cannot be detected by CV. Actually, the accurate value of  $\text{Cr}_2\text{O}_3$  solubility in FLiNaK was determined to be 122 ppm at 600 °C through dissolved chromium content determination (83 ppm  $\text{Cr}^{3+}$ ) by chemical analysis (ICP-OES).<sup>23</sup> Herein, the electrochemical CV results agreed well with that obtained by ICP-OES, and both techniques revealed that the solubility of  $\text{Cr}_2\text{O}_3$  in the FLiNaK melt is quite low (122 ppm).

**3.3.2 Solubility of  $\text{Cr}_2\text{O}_3$  in FLiNaK- $\text{ZrF}_4$  melt.** After addition of 2.14 wt%  $\text{ZrF}_4$  into FLiNaK- $\text{Cr}_2\text{O}_3$  melts, the cyclic voltammogram of FLiNaK- $\text{Cr}_2\text{O}_3$ - $\text{ZrF}_4$  (2.14 wt%) was measured on W electrode and the result was shown as dotted red line in Fig. 8. Besides one couple of cathodic/anodic signals D and D' corresponding to the deposition and dissolution of potassium metal, three reduction peaks, B, C and R at 1.27, 1.07 V and 0.24 V vs.  $\text{K/K}^+$ , respectively, in the cathodic run can be observed. Obviously, the locations of the peaks B and C are consistent with that obtained in FLiNaK- $\text{CrF}_3$  melt (solid black line), also with a potential difference of  $\sim 0.2 \text{ V}$ . Thus, the two peaks B and C in this case corresponded to the reductions of  $\text{Cr}^{3+}/\text{Cr}^{2+}$  and  $\text{Cr}^{2+}/\text{Cr}$ , respectively. The same nature of the two peaks B and C in FLiNaK- $\text{CrF}_3$  and FLiNaK- $\text{ZrF}_4$ - $\text{Cr}_2\text{O}_3$  systems proves that  $\text{Cr}_2\text{O}_3$  dissolves into molten salt in the form of  $\text{CrF}_3$  species. This result indicated the dissolution mechanism of  $\text{Cr}_2\text{O}_3$  in FLiNaK- $\text{ZrF}_4$  melt was attributed to the reaction between  $\text{ZrF}_4$  and oxygen in  $\text{Cr}_2\text{O}_3$ , with releasing  $\text{Cr}^{3+}$  as the form of  $\text{CrF}_3$  that dissolves into molten salt. Moreover, compared with the FLiNaK- $\text{Cr}_2\text{O}_3$  system, the CV curve in FLiNaK- $\text{ZrF}_4$ - $\text{Cr}_2\text{O}_3$  showed a significant current enhancement for peaks B ( $\text{Cr}^{3+}/\text{Cr}^{2+}$ ) and C ( $\text{Cr}^{2+}/\text{Cr}$ ). Hence, it can be concluded that the solubility of  $\text{Cr}_2\text{O}_3$  in FLiNaK melt was greatly facilitated by  $\text{ZrF}_4$  addition, and the  $\text{Cr}_2\text{O}_3$  was dissolved as the form of  $\text{CrF}_3$ , which was consistent with that reported by Song *et al.*<sup>23</sup> In fact, Song *et al.*<sup>23</sup> proved that the dissolution product of  $\text{Cr}_2\text{O}_3$  in molten FLiNaK- $\text{ZrF}_4$  system corresponded to  $\text{CrF}_3$  and  $\text{Zr(IV)}$  oxyfluoride through the reaction of  $\text{Cr}_2\text{O}_3 + \text{ZrF}_4 + \text{F}^- \rightarrow \text{CrF}_3 + \text{ZrO}_x\text{F}_y^{4-2x-y}$ , as determined by XRD technique and chemical analysis. It should be noted that, the newly appeared peak R at

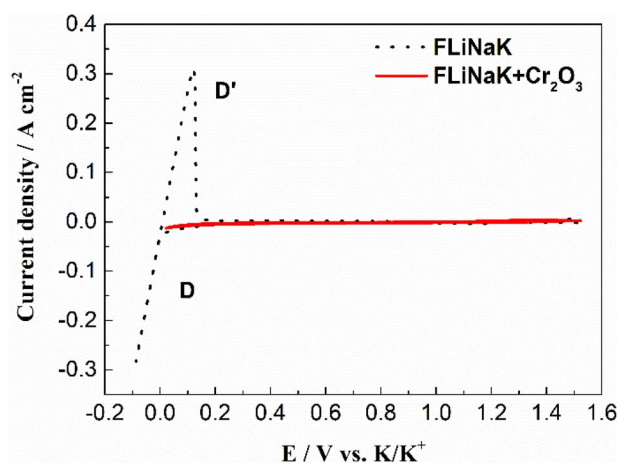


Fig. 7 CVs of FLiNaK and FLiNaK- $\text{Cr}_2\text{O}_3$  systems at 600 °C and scan rate of  $0.1 \text{ V s}^{-1}$ . Working El.: W ( $S = 1.13 \text{ cm}^2$ ); auxiliary El.: graphite; reference El.: Pt.

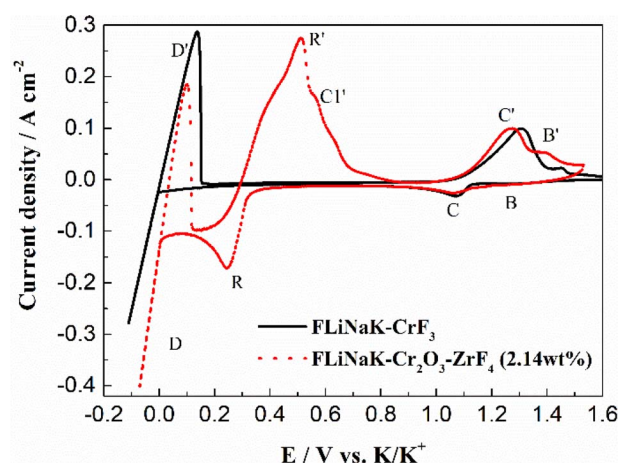


Fig. 8 The CVs of FLiNaK- $\text{CrF}_3$  and FLiNaK- $\text{ZrF}_4$ - $\text{Cr}_2\text{O}_3$  melt at 600 °C and scan rate of  $0.1 \text{ V s}^{-1}$ . Working El.: W ( $S = 1.13 \text{ cm}^2$ ); auxiliary El.: graphite; reference El.: Pt.



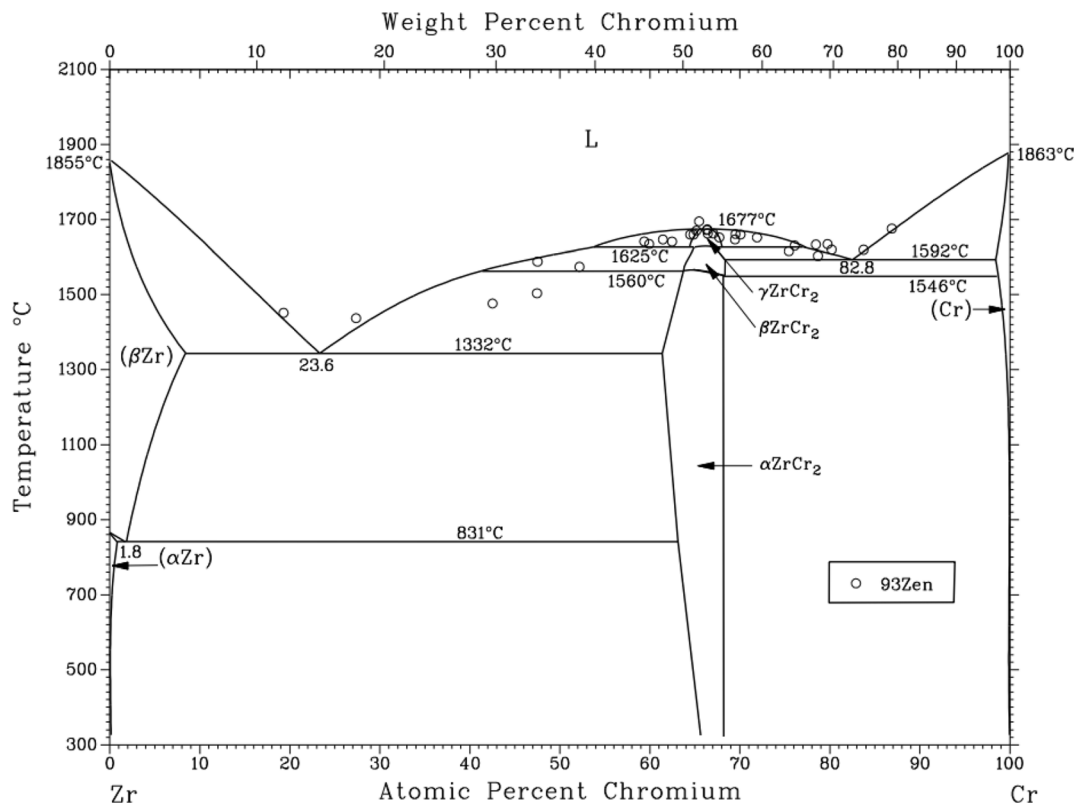


Fig. 9 Cr-Zr binary phase diagram.

0.24 V vs.  $K/K^+$  should be attributed to the reduction of  $Zr^{4+}/Zr$  with a four-electron exchanging process<sup>27</sup> since the deposition potential of zirconium is more negative than that of chromium metal in a fluoride system. The anode signal R' corresponding to the dissolution of Zr metal. Besides, according to the Cr-Zr binary phase diagram (Fig. 9), it is easy to form intermetallic compounds or alloys between chromium and zirconium metals. Thus, the signal C1' should be arisen from the dissolution of Zr-

Cr alloys formed in the cathodic run. The obtained CV results in present study was highly consistent with that reported by Song *et al.*<sup>23</sup> in the same system (FLiNaK-ZrF<sub>4</sub>-Cr<sub>2</sub>O<sub>3</sub>).

It should be noted that, although Song *et al.*<sup>23</sup> also studied the electrochemical behavior of the FLiNaK-ZrF<sub>4</sub>-Cr<sub>2</sub>O<sub>3</sub> system, they only focused on the attribution of peaks at a single concentration, and did not systematically study the electrochemical law at different ZrF<sub>4</sub> concentrations. Meanwhile, ref.

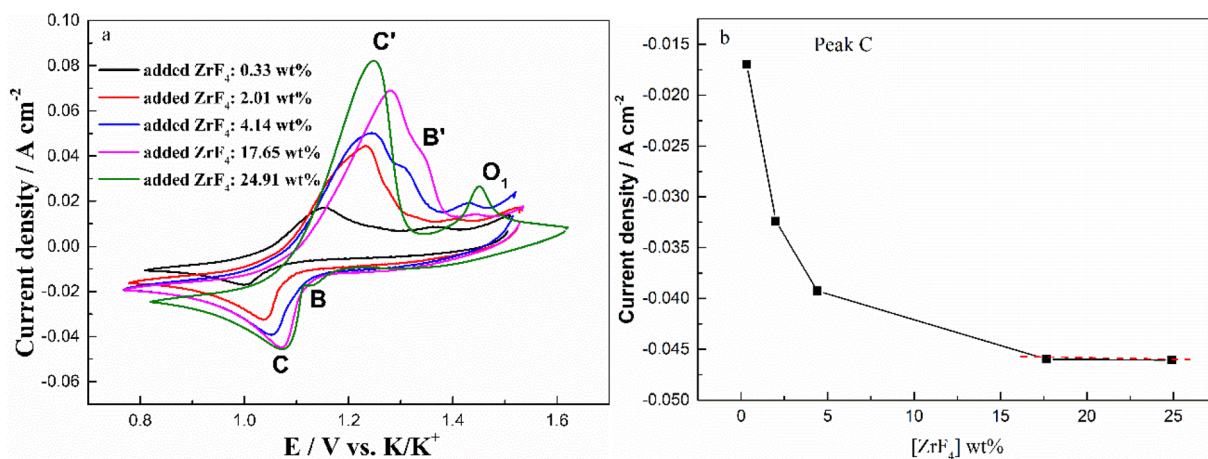


Fig. 10 (a) Typical CVs recorded on a tungsten electrode in the FLiNaK-Cr<sub>2</sub>O<sub>3</sub> melt with different concentrations of added ZrF<sub>4</sub> at 600 °C and scan rate of 0.1 V s<sup>-1</sup>. Working El.: W ( $S = 1.13 \text{ cm}^2$ ); Auxiliary El.: graphite; reference El.: Pt. (b) ZrF<sub>4</sub> concentration vs. peak current density (peak C).

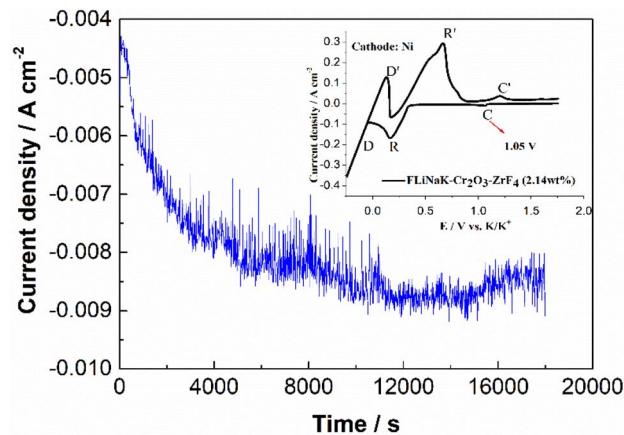


Fig. 11 Current-variation curve during the potentiostatic electrolysis of FLiNaK-Cr<sub>2</sub>O<sub>3</sub>-ZrF<sub>4</sub> (17.65 wt%) system at 1.0 V (vs. K/K<sup>+</sup>) and 600 °C on Ni electrode. Inset: CV of FLiNaK-ZrF<sub>4</sub>-Cr<sub>2</sub>O<sub>3</sub> melt at 600 °C and scan rate of 0.1 V s<sup>-1</sup>. Working El.: Ni; auxiliary El.: graphite; reference El.: Pt.

23 did not focus on the electrolytic removal of chromium. Therefore, the electrochemical measurement of FLiNaK-Cr<sub>2</sub>O<sub>3</sub> under different ZrF<sub>4</sub> conditions and the further electrolytic extraction of chromium will be studied subsequently.

To further investigate the effect of ZrF<sub>4</sub> concentration on the solubility of Cr<sub>2</sub>O<sub>3</sub>, the cyclic voltammograms of FLiNaK-Cr<sub>2</sub>O<sub>3</sub> melt with different concentrations of ZrF<sub>4</sub> were recorded and the results were shown in Fig. 10(a). As can be seen in Fig. 10(a), the current densities of reduction peaks B (Cr<sup>3+</sup>/Cr<sup>2+</sup>) and C (Cr<sup>2+</sup>/Cr) both gradually increased with ZrF<sub>4</sub> additions. When the concentration of ZrF<sub>4</sub> increased from 0.33 to 4.14 wt%, the reduction current density of peak C assigned to the reduction of Cr<sup>2+</sup> to Cr distinctly increased from 0.016 to 0.044 A cm<sup>-2</sup>, while the reduction current density of B for Cr<sup>3+</sup> to Cr<sup>2+</sup> increased from 0.004 to 0.009 A cm<sup>-2</sup>. This result implied that the dissolved chromium ions caused by Cr<sub>2</sub>O<sub>3</sub> dissolution gradually increased with ZrF<sub>4</sub> additions, since the peak current density is proportional to the concentration of the electroactive species.

In addition to the redox peaks B/B' and C/C', a new oxidation peak O<sub>1</sub> appeared (within the potential range 1.35–1.50 V vs. K/K<sup>+</sup>). The formation of oxidation peak O<sub>1</sub> may be related to the formation of zirconium oxy-fluoride species in the FLiNaK-ZrF<sub>4</sub>-Cr<sub>2</sub>O<sub>3</sub> melt. Previous studies<sup>19,21,23,26</sup> also confirmed the existence of stable Zr(IV) oxy-fluoride species in molten fluoride media. The reasons for the formation of zirconium oxy-fluoride have been described in detail in previous text. Moreover, it was found that as the concentration of ZrF<sub>4</sub> increased, the oxidation peak O<sub>1</sub> current gradually increased, indicating that the concentration of the formed zirconium oxy-fluoride species also gradually increased.

Fig. 10(b) shows the relationship between the added ZrF<sub>4</sub> concentration and peak current density (peak C). It can be clearly observed that the peak current density of Cr<sup>2+</sup> to Cr gradually increases with the addition of ZrF<sub>4</sub>. When ZrF<sub>4</sub> increases to 17.65 wt% and 24.91 wt%, the curve approaches the plateau as shown in Fig. 10(b). These observations indicate that ZrF<sub>4</sub> can promote solubility of Cr<sub>2</sub>O<sub>3</sub> in FLiNaK to a certain extent, and its maximum solubility can be achieved when the added concentration of ZrF<sub>4</sub> corresponded to 17.65 wt%.

It should be noted that the solubility of Cr<sub>2</sub>O<sub>3</sub> in molten FLiNaK with ZrF<sub>4</sub> additive has already been determined by ICP-OES, as reported by Song *et al.*<sup>23</sup> Actually, they found that the specific value of Cr<sub>2</sub>O<sub>3</sub> solubility in FLiNaK can greatly increase from 122 ppm to 2300 ppm level (by 19 times) through ZrF<sub>4</sub> additive, which agreed well with the results obtained by electrochemical analysis in case of present study. Besides, the theoretical decomposition voltage of zirconium is far more negative than that of chromium, and in this case the potential difference between Cr<sup>2+</sup>/Cr and Zr<sup>4+</sup>/Zr reductions is 0.83 V vs. K/K<sup>+</sup>, which is much larger than the minimum value of 200 mV required for electrolytic separation. Therefore, it is feasible to electrolyze chromium with Cr<sub>2</sub>O<sub>3</sub> raw material from FLiNaK-ZrF<sub>4</sub> melt.

#### 3.4 Electrolysis of chromium from molten FLiNaK-ZrF<sub>4</sub>-Cr<sub>2</sub>O<sub>3</sub> system

The CV of FLiNaK-Cr<sub>2</sub>O<sub>3</sub>-ZrF<sub>4</sub> (2.14 wt%) was measured on Ni electrode at 600 °C, as shown in inset from Fig. 11. Compared

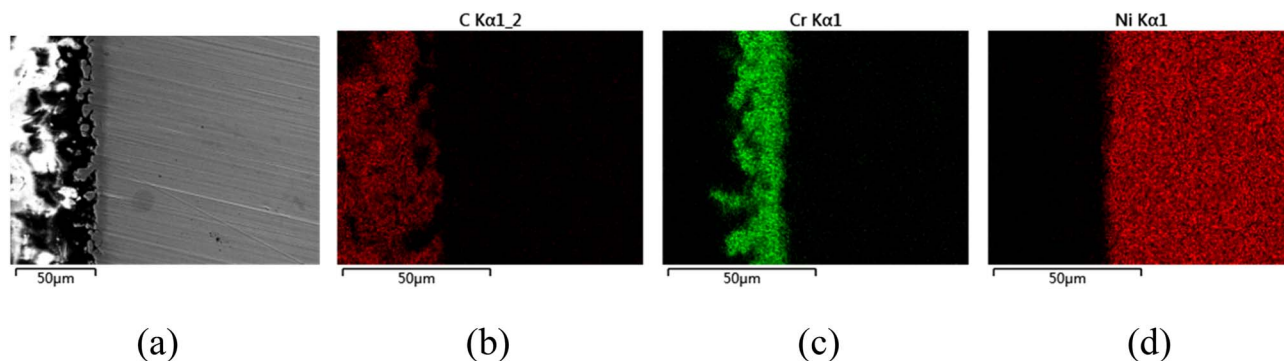


Fig. 12 (a) SEM photo of the cross-section of the cathodic deposits obtained by potentiostatic electrolysis at 1.0 V (vs. K/K<sup>+</sup>) on a Ni electrode in FLiNaK-Cr<sub>2</sub>O<sub>3</sub>-ZrF<sub>4</sub> (17.65 wt%) system for 5 h at 600 °C. (b), (c), and (d) the corresponding EDS mapping patterns images for C (from the SEM inlay material: epoxy resin), Cr (electrolytic product) and Ni (cathode substrate) elements analysis.





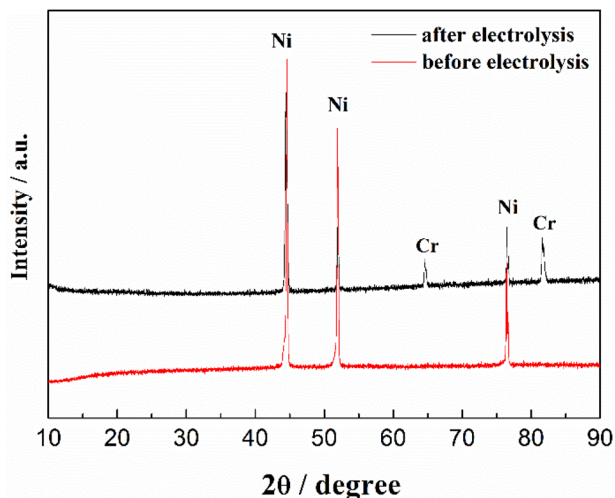


Fig. 13 XRD pattern of the cathodic deposits in FLiNaK-Cr<sub>2</sub>O<sub>3</sub>-ZrF<sub>4</sub> (17.65 wt%) system on Ni electrode. Red line: pure substrate of Ni electrode before electrolysis; black line: Ni electrode with cathodic deposits (Cr metal) after electrolysis.

with the W electrode, the signal of Cr<sup>2+</sup> reduction to metallic Cr can still be observed on the Ni electrode, and the potential is basically consistent at 1.05 V vs. K/K<sup>+</sup>. Based on the analysis results in Fig. 8, 10 and inset (from Fig. 11), the potentiostatic electrolysis of FLiNaK-Cr<sub>2</sub>O<sub>3</sub>-ZrF<sub>4</sub> (17.65 wt%) system was further performed on a Ni plate at the constant potential of 1.0 V (vs. K/K<sup>+</sup>) for 5 h. The current density varied in the range of 4–9 mA cm<sup>-2</sup> in the whole electrolysis duration, as shown in Fig. 11. The time-current density curve fluctuates significantly, which possibly due to the continuous deposition of electrolytic products on the cathode Ni plate during the electrolysis process and a coating of uneven thickness is formed. After electrolysis, the electrode was cleaned, cut, embedded, polished, and the electro-deposits on Ni electrode were analyzed by SEM-EDS (Fig. 12(a–d)). The results showed that a chromium layer with the thickness of ca. 20 μm was formed and coated on the surface of Ni electrode, as shown in Fig. 12(c). XRD analysis further confirmed this layer corresponded to Cr metal (Fig. 13).

Potentiostatic electrolysis in FLiNaK-Cr<sub>2</sub>O<sub>3</sub>-ZrF<sub>4</sub> system can successfully produce Cr metal as the form of electro-deposited coating. These results prove the feasibility of electrolyzing chromium from Cr<sub>2</sub>O<sub>3</sub> raw materials in molten fluorides containing ZrF<sub>4</sub>, and thus achieving the goal of chromium extraction.

## 4. Conclusion

The electrochemical behavior of Cr<sup>3+</sup> was studied in the FLiNaK melts using W electrode at 600 °C by cyclic voltammetry. For a W electrode, the reduction of CrF<sub>3</sub> in FLiNaK melts is two steps reaction: Cr<sup>3+</sup> + e<sup>-</sup> → Cr<sup>2+</sup> and Cr<sup>2+</sup> + 2e<sup>-</sup> → Cr. Then, potentiostatic electrolysis of Cr in the FLiNaK-CrF<sub>3</sub> melt was performed on W electrode for 21.5 h. The ICP-OES results showed that Cr<sup>3+</sup> in melt decreased from the initial 345.30 ppm to 13.12 ppm, indicating an effective removal of Cr<sup>3+</sup> with the

practical removal content of 332.18 ppm. Moreover, the CV results showed a gradual decrease of reduction peak current for Cr<sup>3+</sup> during electrolysis, and the reduction peaks B (Cr<sup>3+</sup>/Cr<sup>2+</sup>) and C (Cr<sup>2+</sup>/Cr) almost could not be detected by cyclic voltammetry after electrolysis. This result indicates a decreasing Cr<sup>3+</sup> concentration and until to below the detection limit of CV.

The CV of FLiNaK-Cr<sub>2</sub>O<sub>3</sub> system was similar with that of blank FLiNaK, indicating that the solubility of Cr<sub>2</sub>O<sub>3</sub> is quite low in FLiNaK melt. The electrochemical behavior of Cr<sub>2</sub>O<sub>3</sub> after adding ZrF<sub>4</sub> was studied in FLiNaK molten salt system on W electrode at 600 °C by cyclic voltammetry. The reduction peak current of Cr<sup>3+</sup> obviously increases with ZrF<sub>4</sub> addition, indicating that the solubility of Cr<sub>2</sub>O<sub>3</sub> in FLiNaK can be greatly promoted by ZrF<sub>4</sub> additive. When the concentration of ZrF<sub>4</sub> added reaches 17.65 wt%, the solubility of Cr<sub>2</sub>O<sub>3</sub> in FLiNaK salt reaches its maximum value. These results make the electro-extraction of Cr with Cr<sub>2</sub>O<sub>3</sub> from ZrF<sub>4</sub>-containing molten fluorides possible. Therefore, the potentiostatic electrolysis of FLiNaK-Cr<sub>2</sub>O<sub>3</sub>-ZrF<sub>4</sub> (17.65 wt%) system was further performed on a Ni plate at the constant potential of 1.0 V (vs. K/K<sup>+</sup>) for 5 h. Characterization of the electrolytic product by SEM-EDS and XRD revealed that metallic Cr can be successfully obtained on the surface of Ni plate. This study verified the feasibility of electroextraction of Cr from CrF<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> in molten fluorides.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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