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## N°4 + Extraction of zirconium in the Molten Salt Fast Reactor

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### Abstract

The Molten Salt Fast Reactor is a GEN IV reactor which uses a liquid fuel salt constituted of a mixture of fluoride salts:  $\text{LiF-ThF}_4\text{-UF}_4$  (77.5- 18.5 – 4 mol%). The working temperature is close to 650°C. The design of MSFR integrates a continuous reprocessing in order to prevent the precipitation of insoluble compounds (fluorides, oxides and oxy-fluorides). In the previous European project EVOL, a reprocessing scheme has been recommended to treat the liquid fuel of the Molten Salt Fast Reactor but this reprocessing scheme do not propose any option to remove zirconium fluoride from the salt whereas this element is one of the more important produced in the core. The aim of this paper is to present the chemical behavior of zirconium in the fuel salt. The thermodynamic stability diagram of zirconium in a fluoride salt is calculated from the thermochemical data of pure compounds. This diagram shows two stable soluble compounds of zirconium,  $\text{ZrF}_2$  and  $\text{ZrF}_4$ . On the contrary, the experimental study evidences that only  $\text{ZrF}_4$  is stable in the salt, probably due to the low activity coefficients of zirconium fluoride which was determined equal to - 4.33. The reduction of  $\text{ZrF}_4$  to Zr metal occurs at a potential of 0.377 V against the potential  $\text{ThF}_4/\text{Th}$  which constitutes the limit of the electroactivity range of the fuel salt. Then, the electrochemical reduction on solid cathode is retained to perform Zr extraction from the salt.

### KEYWORDS:

*Molten salt reactor, zirconium, electrochemistry*

### Introduction

Since more than 15 years, the National Centre for Scientific Research (CNRS, France) has focused R&D efforts on the development of a new molten salt reactor concept called the Molten Salt Fast Reactor (MSFR) selected by the Generation-IV International Forum (GIF) due to its promising design and safety features [1]. The particularities of such a concept is to use a liquid fuel, to be both burner and breeder and to propose a reprocessing scheme [2] in order to separate the fission products from the actinides. The Molten Salt Fast Reactor is a GEN IV reactor which uses a liquid fuel salt constituted of a mixture of fluoride salts:  $\text{LiF-ThF}_4\text{-UF}_4$  (77.5- 18.5 – 4 mol%). The working temperature is close to 650°C. Zirconium is the main fission product contained in the core (followed by Ce, Ba, Y and Nd) [3]. Combined with oxide ions, zirconium can produce zirconium oxy-fluoride and zirconium oxide compounds which solubility are unknown. Therefore, it can form solid compounds in the reactor core that have to be removed. The chemistry and redox properties of zirconium have been already studied both in chlorides media and fluorides media. Some recent publications in chloride media [4-7] are focused on the influence of fluoride ions in these melt to stabilize zirconium (IV) in the salt,  $\text{ZrCl}_4$  being easy to sublime. In fluoride media, alkali salts have been mainly studied ( $\text{LiF-NaF-KF}$ ,  $\text{LiF-NaF}$ ,  $\text{LiF-KF}$ ) [8-14],  $\text{LiF-CaF}_2$  [15] and  $\text{KF-NaF-AlF}_3$  [16]. Except Liang Xu et al, who observed a stability of Zr(II), only Zr(IV) seems to be stable in the fluoride salts. This observation leads to reduce in one step Zr(IV) to Zr metal even if Zr is under oxide form  $\text{ZrO}_2$  [16]. Zr metal deposit quality is clearly improved by the presence of KF in the molten salt. On the contrary, Kipouros recommends to avoid use of KF fluorides because they observed K metal in the deposit and explained it by a chemical reaction between KF and Zr metal leading to the reduction of potassium and to an over-dissolution of Zr metal. Thermodynamically, this reaction is not possible. Electrolysis performed by Kipouros being realized by applying a current, it is more probable that K is co-deposited with Zr. No studies have been already realized in the molten salt  $\text{LiF-ThF}_4$ . The first step in the MSFR reprocessing is a fluorination step which leads to remove uranium, neptunium and other fission products from the molten salt. After this step the solvent is constituted mainly of  $\text{LiF-ThF}_4$ , the other constituents being solutes. Then, the electrochemical behavior of zirconium dissolved in  $\text{LiF-ThF}_4$  was studied in order to determine the redox and solvation properties of this element. The main results are given in this paper.

## I- Thermodynamic study of zirconium stability in LiF-ThF<sub>4</sub> (77.5-22.5 mol%) molten salt

Thermodynamic calculations of redox potentials are performed using the database and software HSC Chemistry for Windows 5.0 created by  $\Omega$  outokumpu (Finland). In molten salt chemistry, the thermodynamic approach consists in the calculation of potential-acidity diagrams which gives the stability domains of an element in several chemical forms. The calculation procedure, using the thermodynamic data of pure compounds (HSC database) has been described previously [17]. Two calculations were made: (i) the thermodynamic limits defined by the molten salt LiF-ThF<sub>4</sub> and (ii) the stability domains of zirconium in a fluoride media. Several compounds combining Zr and F can be obtained in LiF-ThF<sub>4</sub>. The thermochemical data reported in the literature concern ZrF<sub>4</sub>, ZrF<sub>2</sub> and Zr. Table 1 gives the reactions considered and the thermodynamical potential calculated from the data of pure compounds available in the literature (HSC database). The calculation of E° is derived from the calculation of the Gibbs enthalpy  $\Delta G^\circ$  of the chemical reaction given in the table 1 using the following relation:

$$E^\circ = - \Delta G^\circ / nF . \quad (1)$$

in which E° is the potential (V),  $\Delta G^\circ$  the Gibbs enthalpy (J), n the number of electrons exchanged in the chemical redox reaction and F the Faraday constant (F = 96485 C).

The redox electrochemical system F<sub>2</sub> (1atm)/F<sup>-</sup> (a=1) is taken as the potential reference and reference states are mole fractions for solid compounds and partial pressures for gaseous compounds. All the calculations are made for a temperature T of 650°C. Li<sub>2</sub>O is considered for calculations as the oxide donor because the activity of oxide is unknown in this molten salt.

Chemical reactions	$\Delta G^\circ$ (kJ)	E°(V)/ (F <sub>2</sub> /F)	log K	Relation E=pa(Li <sub>2</sub> O)
ThF <sub>4</sub> ↔ Th + 2F <sub>2</sub> (g)	1821.591	-4.72		$E = E^\circ + \frac{2.3RT}{4F} \log a(\text{ThF}_4)$
ThF <sub>4</sub> + 2Li <sub>2</sub> O ↔ ThO <sub>2</sub> + 4LiF			22.111	$pa(\text{li}_2\text{O}) = \frac{1}{2} \log \frac{K * a(\text{ThF}_4)}{a(\text{LiF})^4}$
O <sub>2</sub> (g) + 4LiF ↔ 2F <sub>2</sub> (g) + 2Li <sub>2</sub> O	1158.601	-3.00		$E = E^\circ + \frac{2.3RT}{4F} \log \frac{a(\text{LiF})^4 p_{\text{O}_2}}{a(\text{Li}_2\text{O})^2}$
ZrF <sub>4</sub> ↔ ZrF <sub>2</sub> + F <sub>2</sub> (g)	789.342	-4.09		$E = E^\circ + \frac{2.3RT}{2F} \log \frac{a(\text{ZrF}_4)}{a(\text{ZrF}_2)}$
ZrF <sub>2</sub> ↔ Zr + F <sub>2</sub> (g)	816.053	-4.23		$E = E^\circ + \frac{2.3RT}{2F} \log a(\text{ZrF}_2)$
ZrO <sub>2</sub> + 4LiF ↔ Zr + 2Li <sub>2</sub> O + 2F <sub>2</sub> (g)	2082.493	-5.40		$E = E^\circ + \frac{2.3RT}{4F} \log \frac{a(\text{LiF})^4}{a(\text{Li}_2\text{O})^2}$
ZrO <sub>2</sub> + 4LiF ↔ ZrF <sub>2</sub> + 2Li <sub>2</sub> O + F <sub>2</sub> (g)	1266.440	-6.56		$E = E^\circ + \frac{2.3RT}{2F} \log \frac{a(\text{LiF})^4}{a(\text{ZrF}_2)a(\text{Li}_2\text{O})^2}$
ZrF <sub>4</sub> + 2Li <sub>2</sub> O ↔ ZrO <sub>2</sub> + 4LiF			26.998	$pa(\text{li}_2\text{O}) = \frac{1}{2} \log \frac{K * a(\text{ZrF}_4)}{a(\text{LiF})^4}$

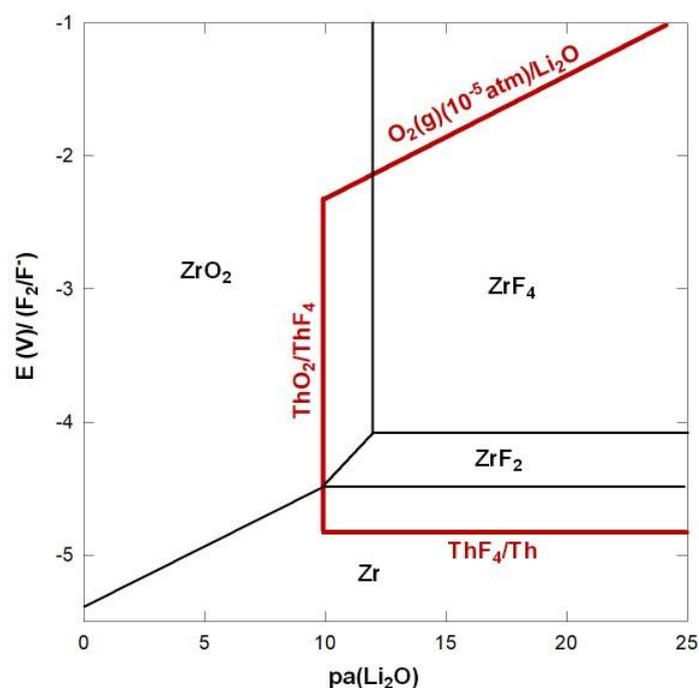
with  $pa(\text{Li}_2\text{O}) = - \log [a(\text{Li}_2\text{O})]$  and R the ideal gas constant

The activities of oxides compounds and metals are equal to 1.

**Table 1: Reactions considered to calculate the thermodynamic diagram of stability of zirconium in fluoride media and the thermodynamic limits of the fuel salt LiF-ThF<sub>4</sub>**

Figure 1 presents the overlay of thermodynamic diagrams of zirconium in fluoride salt and the fuel salt limits (in red). At low potential values, ThF<sub>4</sub> is reduced to Th metal, at high potential values, the limit corresponds to the O<sub>2</sub> and F<sub>2</sub> evolution (depending on pa(Li<sub>2</sub>O) value). The vertical line corresponds to the precipitation of ThO<sub>2</sub>. About zirconium, we observe including in the stability domain of the fuel salt,

the stability of two soluble compounds  $ZrF_2$  and  $ZrF_4$ . The precipitation of  $ZrO_2$  occurs in the fuel salt before the precipitation of  $ThO_2$ .



**Figure 1: Thermodynamic limits of LiF-ThF<sub>4</sub> fuel salt (red lines) at 650°C and stability domains of zirconium (black lines). Calculations are made using the relations given table 1 and considering a mole fraction of ZrF<sub>4</sub> of 10<sup>-3</sup> and an oxygen pressure of 10<sup>-5</sup>atm.**

## II- Experimental

The storage and handling of all the chemicals are carried out in a glove box in purified argon atmosphere because fluoride and chloride compounds have a tendency to absorb water molecules. Thorium fluoride powder is provided by SOLVAY and the other chemical products are provided by Sigma-Aldrich. Their purity is higher than 99 %. LiF and ThF<sub>4</sub> are dried and mixed in the glove box under argon before melting. The total weigh of the mixture is close to 100g. The solid salts are introduced in a glassy carbon crucible contained in an experimental cell. The cell is made of quartz and is constituted of two parts (top and bottom). The air tightness is maintained using a locking screw. The cell containing the mixture of salts prepared in the glove box under argon is transferred in a glove box under depressed atmosphere where the experiments are carried out. The melting procedure has been described previously [17]. The tubular furnace (80 cm diameter) used is connected to a regulation monitor provided by TANER/France. Inert argon gas flows in the cell during all the experiment. The electrodes are introduced through the cell top using tight joints. Potentiometric and voltammetric measurements are performed using a potentiostat Versastat 3F provided by AMETEK coupled with a PC computer using the software Versastudio. Working electrodes are prepared using Mo, Zr and Au wires (1 mm diameter, Goodfellow). A pseudo-reference electrode is used, constituted of a Pt wire (1 mm diameter, Goodfellow). The counter electrode is made of a glassy carbon rod (3 mm diameter, Carbone Lorraine).

## III- Electrochemical study of zirconium in LiF-ThF<sub>4</sub> molten salt

### III.1- Identification of the redox systems of zirconium

The experimental electroactivity range recorded in LiF-ThF<sub>4</sub> is given Figure 2. The anodic part is recorded using an Au working electrode while the cathodic part is done using a Mo working electrode. The electroactivity range is limited on cathodic size by the reduction of ThF<sub>4</sub> to Th metal and on anodic size by the oxidation of the gold electrode. We observe the presence of oxide ions under thorium oxifluoride ThOF<sub>2</sub> characterized by an anodic contribution corresponding to the oxidation of the oxides (included in

ThOF<sub>2</sub>) to oxygen O<sub>2</sub>.

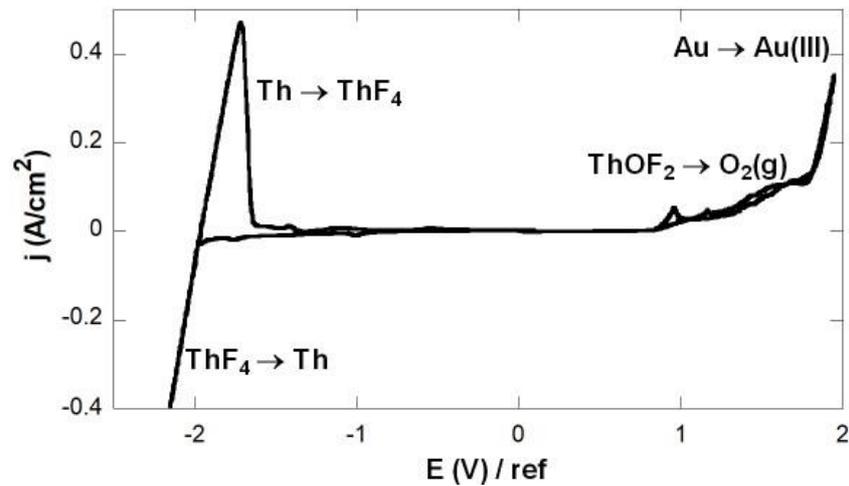


Figure 2: Electroactivity domain recorded at 0.1V/s in LiF-ThF<sub>4</sub> at 650°C on Mo working electrode (cathodic domain) and Au working electrode (anodic domain).

Cyclic voltammograms are recorded after several additions of ZrF<sub>4</sub> in the fuel salt in order to identify the redox systems characteristic of zirconium (Figure 3-left). We observe on the voltammograms recorded in cathodic scan a system at a potential close to -1.7V/Ref. The current peak increases linearly with the ZrF<sub>4</sub> concentration as shown in Figure 3-right. Therefore, the reduction process corresponds to the reduction of ZrF<sub>4</sub>. Only one electrochemical system is observed on the voltammograms which could be attributed, according to thermodynamic calculations, to the system ZrF<sub>4</sub>/ZrF<sub>2</sub> or ZrF<sub>4</sub>/Zr.

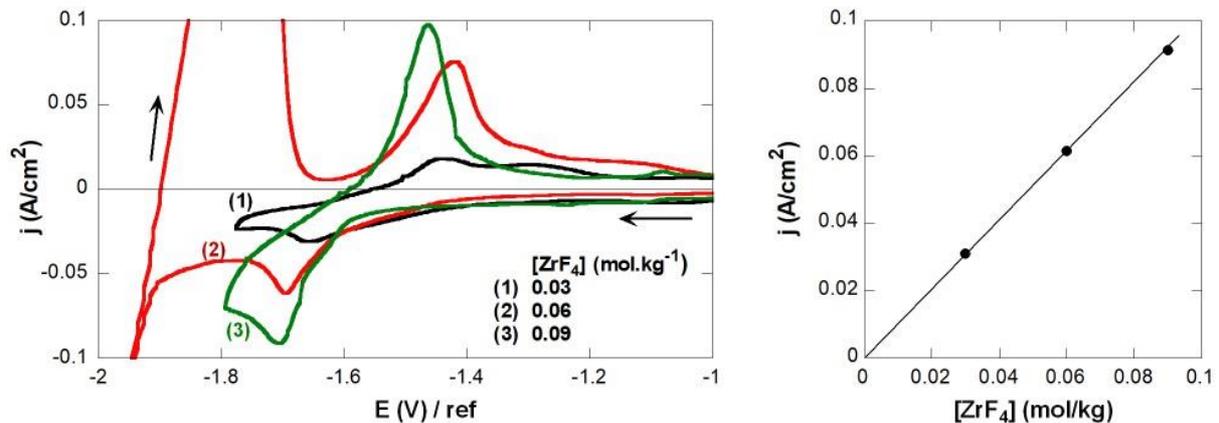
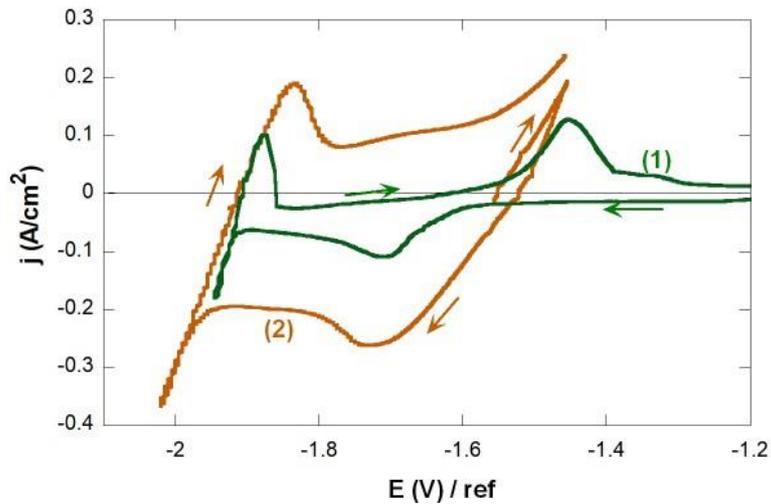


Figure 3: Left- cyclic voltammograms recorded on Mo electrode at 0.1V/s in LiF-ThF<sub>4</sub> at 650°C containing 0.03, 0.06 and 0.09 mol/kg of ZrF<sub>4</sub>.  
 Right- variation of the current peak density with the concentration of ZrF<sub>4</sub> introduced

The shape of the oxidation peak observed during the reverse scan is more consistent with the oxidation of a solid phase. Nevertheless, to confirm the reduction of ZrF<sub>4</sub> to Zr metal, cyclic voltammograms have been recorded using a Zr working electrode (Figure 4).

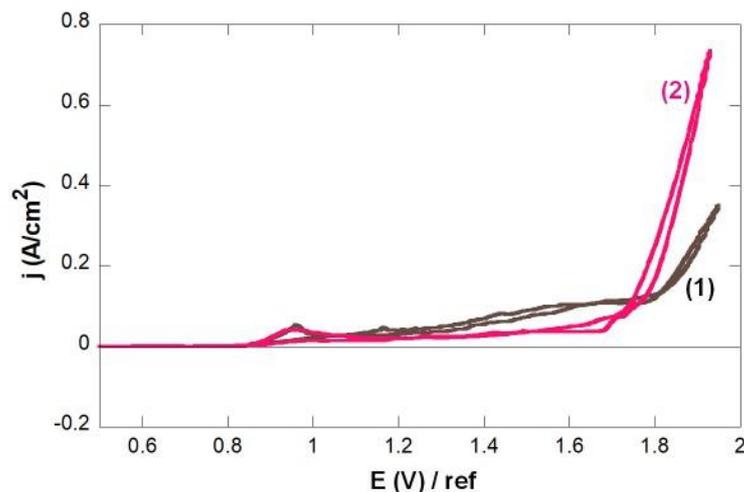


**Figure 4: Voltammograms recorded at 0.1V/s in LiF-ThF<sub>4</sub> at 650°C**  
 (1) on Mo working electrode in presence of 0.09 mol/kg of ZrF<sub>4</sub>.  
 (2) on Zr working electrode without ZrF<sub>4</sub> in the salt.

The comparison of these two curves shows that the oxidation of Zr metal (curve (2)) occurs at the same potential than the oxidation peak observed on the curve (1) during the reverse scan. Therefore, Zr metal is produced on Mo electrode when ZrF<sub>4</sub> is reduced. We can conclude that ZrF<sub>2</sub> is not stable in the molten salt LiF-ThF<sub>4</sub> at 650°C and that there is only one redox system, ZrF<sub>4</sub>/Zr.

### III.2- Reactivity of zirconium with oxide ions

A modification of the anodic part of the voltammograms (recorded on gold electrode) has been observed after the first addition of ZrF<sub>4</sub>. The oxidation of thorium oxifluoride disappears and a very low oxidation current density is measured before the anodic limit (Figure 5).



**Figure 5: Voltammograms recorded at 0.1V/s in LiF-ThF<sub>4</sub> at 650°C on Au working electrode before (1) and after (2) the addition of 0.03 mol/kg of ZrF<sub>4</sub>**

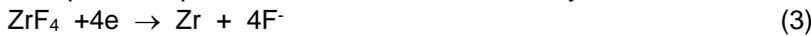
That can be explained by the strong affinity of Zr(IV) for oxide ions. We assume that the following reaction occurs:



the Gibbs energy of this reaction being negative ( $\Delta G = -83.316$  kJ). The voltammograms recorded on the gold electrode (anodic part of the electroactivity window) after the other additions of  $ZrF_4$  are strictly similar to the one recorded after the first addition. A part of  $ZrF_4$  is precipitated under solid oxide form. Nevertheless, this part is necessarily low because the evolution of the reduction current peak with  $ZrF_4$  concentration (shown in Figure 3-Right) is linear. Therefore, the concentration of  $ZrF_4$  is not significantly modified that indicates a low oxides content in the molten salt. A calibration of the anodic current characteristic of oxide oxidation will be done in order to determine the activity of oxide after introduction of  $ZrF_4$ . In this way we will be able to determine the solubility of  $ZrO_2$  in  $LiF-ThF_4$  salt.

### III.3- Determination of activity coefficient of zirconium

The principle of determination of the activity coefficient in molten salts is generally based on the difference between the redox potential of the pure element calculated from thermodynamic data and its experimental equilibrium potential. In the case of  $ZrF_4/Zr$  system, the electrochemical reaction is given by:



And the Nernst relation related to this reaction is:

$$E_{Zr/F} = E^\circ_{ZrF_4/Zr} + 2.3 \frac{RT}{4F} \log \frac{a(ZrF_4)}{a(Zr)a(F^-)^4} \quad (4)$$

$E_{Zr/F}$  is the experimental equilibrium potential of  $ZrF_4/Zr$  against the reference potential of  $F_2(1 \text{ atm})/F^-$  ( $a=1$ ) system. In the relation (4),  $E^\circ_{ZrF_4/Zr}$  is the standard potential calculated using the thermodynamic data of the pure compounds. In this calculation, the reference system chosen is  $F_2(1 \text{ atm})/F^-$  ( $a=1$ ). It is calculated from the Gibbs energy  $\Delta G_{ZrF_4/Zr}$  of the following chemical reaction:



$$E^\circ_{ZrF_4/Zr} = -\frac{\Delta G_{ZrF_4/Zr}}{4F} = -4.16V / (F_2(1 \text{ atm})/F^-(a=1)) \text{ at } 650^\circ\text{C} \quad (6)$$

In the relation (4),  $R$  is the ideal gas constant,  $T$  the temperature (in K),  $F$  the Faraday constant (96500C),  $a(i)$ , the activity of the compound  $i$ . By definition:

$$a(ZrF_4) = x(ZrF_4) \cdot \gamma(ZrF_4) \quad (7)$$

$x(ZrF_4)$  is the mole fraction of  $ZrF_4$  in the molten salt and  $\gamma(ZrF_4)$  its activity coefficient.

$a(Zr)$  represents the activity of zirconium metal. By definition,  $a(Zr)$  is equal to 1.

The determination of  $\gamma(ZrF_4)$  requires the knowledge of  $E_{Zr/F}$  and  $a(F^-)$ , the activity of fluorides in  $LiF-ThF_4$  molten salt. In previous works [18-19], the experimental potential  $E_{Th/F}$  of the redox system  $ThF_4/Th$  against the  $F_2(1 \text{ atm})/F^-$  ( $a=1$ ) system and the activity of fluoride ions  $a(F^-)$  have been determined. The scheme given Figure 6 shows how determine the experimental potential of  $ZrF_4/Zr$  system against  $F_2(1 \text{ atm})/F^-$  ( $a=1$ ) system.

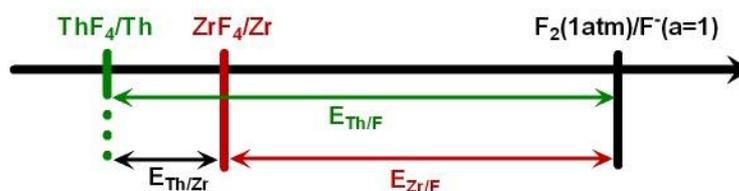
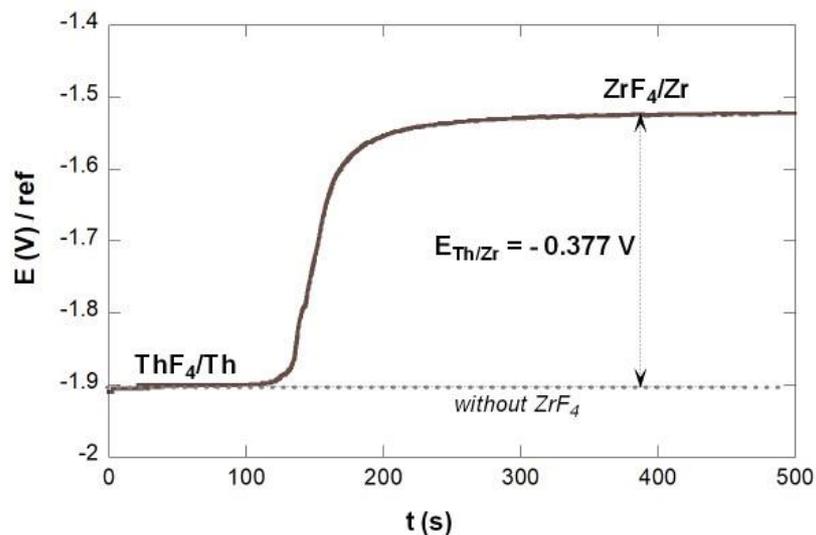


Figure 6: Scheme used for the determination of  $E_{Zr/F}$

The scheme of Figure 6 leads to the relation:

$$E_{Zr/F} = E_{Th/F} - E_{Zr/Th} \quad (8)$$

$E_{Zr/Th}$  is the experimental potential between the two redox systems  $ThF_4/Th$  and  $ZrF_4/Zr$ . This potential difference can be determined with high accuracy using a potentiometric method. That consists in applying a cathodic current on a Mo working electrode during a short time and to record the variation of the equilibrium potential during the relaxation time. During the pulse coulometry, thorium and zirconium metal are co-deposited on the working electrode. During the relaxation time, the deposited metals are naturally oxidized and the potential variation presents several steps corresponding to the several redox systems. In this case, two steps are observed corresponding respectively to  $ThF_4/Th$  and  $ZrF_4/Zr$  systems (Figure 7). The potential difference between the two plateaux corresponds to  $E_{Th/Zr}$  value.



**Figure 7: Potentiogram recorded after a pulse coulometry (applied current of -0.3A during 5s) realised on Mo working electrode in LiF-ThF<sub>4</sub> containing 0.06 mol/kg of ZrF<sub>4</sub>. The dotted line is obtained after a coulometry realized in the molten salt without ZrF<sub>4</sub>**

To be sure that the first plateau is characteristic of the system  $ThF_4/Th$  and not of an alloy  $Th/Zr$ , a preliminary study was done. A same experiment was realized in the molten salt without  $ZrF_4$ . In this case, only one plateau is recorded at -1.9V/Ref. The second plateau corresponds to the zirconium system as it was previously shown by cyclic voltammetry.

Combining the relations (4), (7) and (8), the general expression of  $\log \gamma(ZrF_4)$  is given by:

$$\log \gamma(ZrF_4) = \left[ E_{Th/F} - E_{Th/Zr} - E^{\circ}_{ZrF_4/Zr} \right] \frac{4F}{2.3RT} + 4 \log a(F^-) - \log x(ZrF_4) \quad (9)$$

Using the numerical values previously determined:  $E_{Th/F} = -4.277 V$ ;  $\log a(F^-) = -3.07$ ;  $E_{Th/Zr} = -0.377 V$ ;  $E^{\circ}_{ZrF_4/Zr} = -4.16 V$ ;  $x(ZrF_4) = 5.4 \cdot 10^{-3}$ , we calculate:

$$\log \gamma(ZrF_4) = -4.33$$

The chemical solvation of  $ZrF_4$  in LiF-ThF<sub>4</sub> seems similar to that of  $UF_4$  which activity coefficient was determined equal to -4.05 (in log unit) [19].

## Conclusion

The behavior of  $ZrF_4$  in LiF-ThF<sub>4</sub> at 650°C was examined in order to propose a selective extraction of this compound in the reprocessing scheme dedicated to the Molten Salt Fast Reactor. In contrast with thermodynamic calculations (which forecast the stability of  $ZrF_2$ ), the experimental measurements show that  $ZrF_4$  is reduced to Zr metal by only one direct step involving four electrons. The formation of  $ZrO_2$

was observed. That indicates a higher stability of  $ZrO_2$  compared to  $ThOF_2$ . Finally, potentiometric methodology leads to the determination of the activity coefficient of  $ZrF_4$  in the molten salt. Based on experimental results, the E-pa( $Li_2O$ ) stability diagram have been constructed in which the limits  $ThF_4/Th$ ,  $ZrF_4/Zr$  and  $O_2/O^{2-}$  are deduced from electrochemical measurements (Figure 8). The electroactivity range is lower than the thermodynamic one, due to the activity of fluorides involving in the reduction reaction  $ThF_4/Th$ .

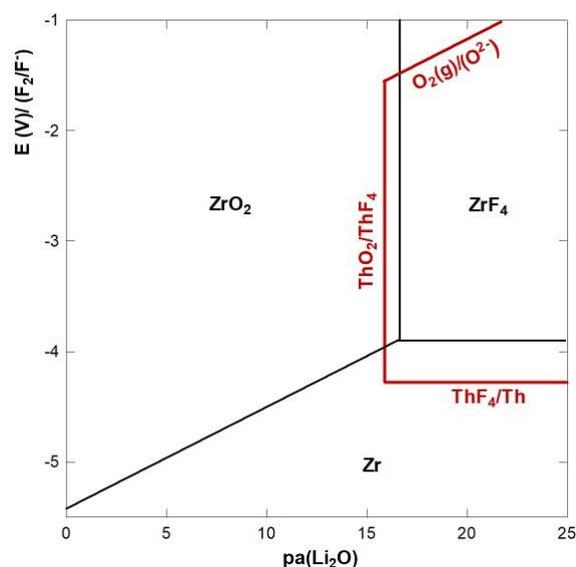


Figure 8: Stability limits of LiF-ThF<sub>4</sub> fuel salt (red lines) at 650°C and domain of zirconium (black lines) based on electrochemical measurements for  $x(ZrF_4) = 5.4 \cdot 10^{-3}$ .

All these results converge towards two possible extraction of zirconium. Due to its redox and solvation properties, zirconium produced in the molten salt reactor can be removed by electrolysis both on solid and by reductive extraction in a liquid metal phase. The reductive extraction on liquid cathode is interesting because it is a chemical redox reaction without applying a current or a potential. On the contrary, the low selectivity of this technique is a problem because actinides will be removed by the same way. Therefore, the best method seems to be the electrolysis on a solid cathode which leads to a good extraction efficiency and a good selectivity. The future work will be focused on the study of the efficiency of the method and on the choice of an anode electrode material which is a key issue in fluoride media because the anodes are generally soluble materials under polarization.

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