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# Generalized method for determining fluoroacidity by electrochemical diffusion coefficient measurement (application to HfF<sub>4</sub>)

M. Kergoat, M. Gibilaro\*, L. Massot, P. Chamelot

Université de Toulouse, UPS, CNRS, Laboratoire de Génie Chimique, 118 Route de Narbonne, F-31062 Toulouse, France

## ABSTRACT

A universal method for fluoroacidity evaluation was developed and based on a mass transport approach: it simply consists in measuring the diffusion coefficient of an electroactive species in various molten media. The reduction behaviour of Hf(IV) ions was investigated in molten fluorides and diffusion coefficients of Hf(IV) ions were measured. Results showed that diffusion coefficients decrease with fluoroacidity, due to the effect of solvent viscosity (which is linked to bridged fluorines). A global approach of mass transport in solution was then proposed, taking into account both solute and solvent. The Schmidt number (Sc) defined as the ratio between solvent viscosity and solute diffusivity was calculated in order to take into account these two parameters. Results showed that Sc increases with fluoroacidity, in a much more sensitive way than D. This universal method can be extended to all electroactive species and to all bath fluoroacidity.

**Keywords:**  
Fluoroacidity  
hafnium fluoride  
diffusion coefficient  
mass transport

## 1. Introduction

By analogy with aqueous solutions, notion of acidity in molten fluoride solvents is defined by fluoroacidity (pF) and based on the free fluorides exchange in molten mixtures as described in Eq. (1):



$$\text{pF} = -\log(a_{\text{F}^-}) \quad (2)$$

The activity of free fluorides ( $a_{\text{F}^-}$ ), which quantifies fluoroacidity, depends on the nature of the cations constituting the solvent, the composition and temperature, and influences solvation, ion stability and processes reaction. It therefore needs to be studied and quantified for a better understanding of physico-chemical properties of solvents and solutes.

Usual molten salts solvents are mixtures of alkaline and alkaline-earth fluorides (LiF, NaF, KF, MgF<sub>2</sub>, CaF<sub>2</sub> . . .) and the amount of free F<sup>-</sup> ions depends on their nature and composition: the more a molten salt contains free fluorides (i.e. fluorodonor), the higher its basicity is. As in aqueous media, the acidity is essential as it influences so many parameters; however pF values are not available yet since the F<sup>-</sup> activity can't be measured: only a relative fluoroacidity scale was established by indirect evaluations [1–3].

One electrochemical method to sort molten fluorides mixtures in regard of their fluoroacidity was proposed in our laboratory by Bieber et al. [4] and Kergoat et al. [5]. Based on silicon [4] and completed with boron [5], it consists in studying the equilibrium between a dissolved species and a gaseous compounds given by Eq. (3) for Si and Eq. (4) for B:



Thus, by definition, a fluorobasic bath (high [F<sup>-</sup>]<sub>free</sub>) stabilizes a species in solution, while a fluoroacid bath (low [F<sup>-</sup>]<sub>free</sub>) promotes the reaction of gaseous species release.

The study of these equilibria, moved by the free fluorides concentration, is then an indicator of fluoroacidity. Indeed the release of SiF<sub>4(g)</sub> or BF<sub>3(g)</sub> leads to a decrease of Si(IV) and B(III) ions concentrations respectively, controlled by in-situ electrochemical titrations.

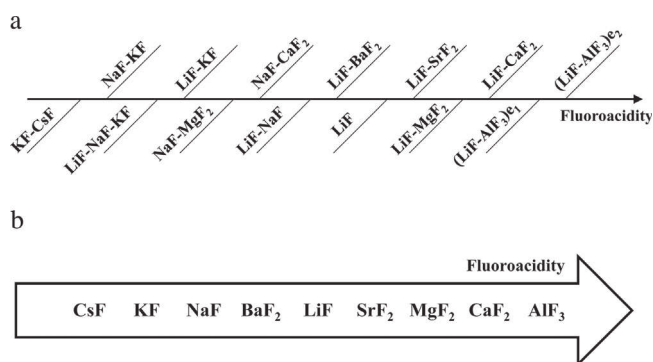
By calculating kinetic constants of silicon ( $k_{\text{Si}}$ ) and boron ( $k_{\text{B}}$ ) releases, ranking of various eutectic mixtures was established (Fig. 1a) and a fluoroacidity scale of fluoride compounds was proposed (Fig. 1b) [5].

However several limitations were pointed out:

- the choice of the solute is critical as it has to form a gaseous species and be in equilibrium with it,
- the solute must not react with the solvent,

\* corresponding author: Gibilaro Mathieu Tel.: +33 5 61 55 72 19 fax: +33 5 61 55 61 39

E-mail address: [gibilaro@chimie.ups-tlse.fr](mailto:gibilaro@chimie.ups-tlse.fr) (M. Gibilaro).



**Fig. 1.** Fluoroacidity scale of various eutectic mixtures. Fluoroacidity scale of fluoride compounds.

- has to be more acid than the solvent to capture free fluorides,
- for the most acidic baths, the gaseous species release is too fast to determine the kinetic constants.

To avoid these drastic conditions, a universal method for fluoroacidity evaluation was developed and based on a mass transport approach: it simply consists in measuring the diffusion coefficient of a species in various molten media [5]. However, small differences were observed between the diffusion coefficients and the discrimination was complicated by a lack of selectivity. A global approach of mass transport in solution was then proposed, taking into account both solute and solvent.

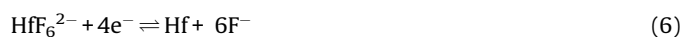
Several authors already showed that an increase of fluoroacidity directly impacts the chemical structure of the molten salt [6–8] and leads to a decrease of the free  $F^-$  which are involved in coordination of one complex. For the most acidic baths, complexes shares fluorines by forming bridges leading to a structure as a network-like liquid [9–11]. This chemical behaviour (coordination and bridging) affects physico-chemical parameters as solute solubility, vapor pressure and viscosity [12].

By measuring the diffusion coefficients of Si(IV) and B(III) ions and calculating the Schmidt number ( $Sc$ ), defined as the ration between solvent kinematic viscosity  $\nu$  (in  $m^2s^{-1}$ ) and solute diffusivity  $D$  (in  $m^2s^{-1}$ ) in various molten fluorides mixtures, it was shown that  $D$  decreases and  $Sc$  ( $Sc=\nu/D$ ) increases with acidity validating the previous scale obtained.

This novel approach is easier to set up than kinetic rates determination, as an accurate measurement could be performed by electrochemical techniques; moreover, it could be certainly extended to all electroactive species and to all bath fluoroacidity.

In order to confirm this assumption, hafnium tetrafluoride  $HfF_4$  solute was selected: it is stable in solution, inert to the solvent constituents, and do not form gaseous species in our experimental conditions.

Only few studies of the electrochemical behaviour of Hf(IV) ions are presented in the bibliography. The available results were mainly acquired in molten chlorides or chloro-fluorides media. In molten chlorides, Poinso et al. [13,14] and Adhoum et al. [15] did not agree on the on Hf(IV) ion reduction mechanism in NaCl-KCl mixture. Spink et al. [16] in CsCl, showed that Hf(IV) ions reduction is a one step process exchanging 4 electrons leading to the formation of Hf metal. Quite the contrary, Guang-Sen et al. [17] and Serrano [18] demonstrated in NaCl-KCl that reduction of Hf(IV) ions takes place in a two stages process, Hf(IV) to Hf(II) to Hf(0). However, all these authors agree that fluoride ions addition in molten chlorides stabilizes Hf(IV) ions to form hafnium fluoride complex  $HfF_6^{2-}$  (Eq. (5)) in molten chloro-fluorides media, as the reduction of Hf(IV) ions to Hf(0) is performed in a single 4 electrons reversible step under diffusion control (Eq. (6)):



In the first part of this paper, the reduction behaviour of Hf(IV) ions was investigated in molten eutectic LiF-NaF (61–39 mol.%) at 750 °C by cyclic voltammetry, square wave voltammetry and chronopotentiometric methods. Then, diffusion coefficients of Hf(IV) ions were determined in different conditions validating the previous obtained fluoroacidity scale.

In a second part, measurements of diffusion coefficients of Hf(IV) ions were performed in two others molten media: LiF-NaF-KF and LiF-CaF<sub>2</sub> selected in regards of their fluoroacidity (the first one is more basic and the second one more acid than LiF-NaF: cf. Fig. 1 a), in the 800–900 °C temperature range. Results obtained were correlated to solvent viscosity thanks to the Schmidt number previously defined. Relationships between  $D$ ,  $Sc$  and fluoroacidity previously demonstrated were confirmed with this electrochemical species.

This global mass transport approach is validated with a simple determination of a diffusion coefficient, and is a powerful tool in order to determine fluoroacidity.

## 2. Experimental

The cell consisted in a vitreous carbon crucible placed in a cylindrical vessel made of refractory steel and closed by a stainless steel lid cooled down by circulating water. The inner part of the wall was protected against fluoride vapours by a graphite liner. This cell has already been described in previous work [19]. The experiments were performed under an inert argon atmosphere. The cell was heated using a programmable furnace and the temperatures were measured using a chromel-alumel thermocouple.

Three eutectic mixtures (Carlo Erba Reagents 99.99%) were used as electrolyte and selected according to their fluoroacidity and relative easy handling:

- a basic bath: LiF-NaF-KF (46.5-11.5-42 mol%, melting point 452 °C),
- an acid bath: LiF-CaF<sub>2</sub> (79.2-20.8 mol%, melting point 767 °C),
- an intermediate bath: LiF-NaF (61-39 mol%, melting point 652 °C).

All the solvents were initially dehydrated by heating under vacuum from ambient temperature up to their melting point during 4 days. Hafnium ions were introduced into the bath in the form of hafnium tetrafluoride  $HfF_4$  powder (Sigma Aldrich 99.9%).

Silver wires (1 mm diameter, Goodfellow) were used as working electrode. The surface area of the working electrode was determined after each experiment by measuring the immersion depth in the bath. The auxiliary electrode was a vitreous carbon rod (V25, 3 mm diameter) with a large surface area (2.5 cm<sup>2</sup>). The potentials were referred to a platinum wire (0.5 mm diameter, Goodfellow) acting as a quasi-reference electrode  $Pt/PtO_x/O^{2-}$  [20].

All the electrochemical studies were performed with an Autolab PGSTAT30 potentiostat/galvanostat controlled by a computer using the research software GPES 4.9.

## 3. Results and discussion

### 3.1. Hf(IV) reduction mechanism

#### 3.1.1. Cyclic voltammetry

Hf(IV) ions reduction behaviour was investigated in molten LiF-NaF in the 750-900 °C temperature range. As hafnium and silver

are not miscible at operating temperature, silver was selected as an inert working electrode [21].

Fig. 2 shows typical cyclic voltammogram of LiF-NaF-HfF<sub>4</sub> (0.69 mol kg<sup>-1</sup>) on silver at 750 °C and 100 mV s<sup>-1</sup>. Only one reduction peak and its corresponding reoxidation peak are observed at -1.43 and -1.25 V vs. Pt respectively. The signal crossing between forward and backward scans is typical of the formation of a solid phase at the electrode (crossover). In addition, the asymmetrical shape of the reoxidation peak is characteristics of a metal deposited dissolution in the cathodic run (stripping peak). As presented in the inset of Fig. 2, no variations of peak potential at different scan rate proved that Hf(IV) electrochemical reduction process is reversible [22]. Thus, according to equations of cyclic voltammetry for a reversible soluble/insoluble system, the number of exchanged electrons can be calculated by measuring the difference between the potential peak and the half peak potential [22]:

$$|E_p - \frac{E_p}{2}| = 0.77 \frac{RT}{nF} \quad (7)$$

where  $E_p$  is the peak potential (V) and  $E_{p/2}$  is the half peak potential (V),  $R$  the ideal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>),  $T$  as the absolute temperature (K),  $n$  the number of exchanged electrons and  $F$  the Faraday constant (C mol<sup>-1</sup>).

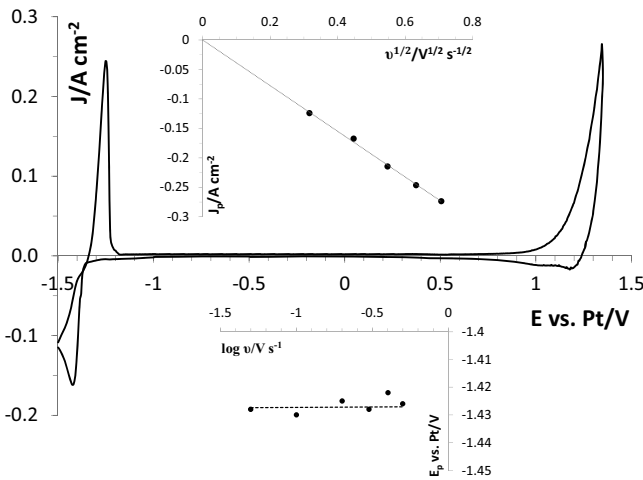
In this study, the difference was found to be  $18 \pm 2$  mV, corresponding to a value of  $3.8 \pm 0.3$  exchanged electrons.

The linear relationship between Hf(IV) reduction peak current density at -1.43 V vs. Pt and the square root of the scan rate presented in the inset of Fig. 2, proved that electrochemical reduction process is controlled by Hf(IV) diffusion [22]. Diffusion coefficients were determined using Berzins-Delahay equation (Eq. (8)) for a reversible soluble/insoluble system [23]:

$$J_p = 0.61 n F C \left( \frac{n F D v}{RT} \right)^{1/2} \quad (8)$$

where  $J_p$  is the peak current density (A m<sup>-2</sup>),  $C$  the solute concentration (mol m<sup>-3</sup>),  $D$  the diffusion coefficient (m<sup>2</sup> s<sup>-1</sup>) and  $v$  the potential scan rate (V s<sup>-1</sup>).

At 750 °C, a value of  $(3.5 \pm 0.3) \times 10^{-9}$  m<sup>2</sup> s<sup>-1</sup> for  $D$  was found. Serrano [18] and Poinso [13] found a Hf(IV) ions diffusion coefficient in NaCl-KCl-NaF at 750 °C equal to 2.2 and  $4.9 \times 10^{-9}$  m<sup>2</sup> s<sup>-1</sup> respectively.



**Fig. 2.** Cyclic voltammogram of LiF-NaF-HfF<sub>4</sub> (0.69 mol kg<sup>-1</sup>) at 100 mV s<sup>-1</sup> and  $T = 750$  °C Working El.: Ag; Auxiliary El.: vitreous carbon; Reference El.: Pt Insets: Linear relationship of Hf(IV) reduction peak current density versus the square root of the scanning potential rate. Hf(IV) reduction peak potential versus the logarithm of the scanning potential rate.

Diffusion coefficients were determined in LiF-NaF in the 800–900 °C temperature range and are presented in Table 1. Results showed that  $D$  and  $T$  follow an Arrhenius law type, the relationship is expressed as follows:

$$\ln D = -\frac{E_A}{RT} + \ln D_0 = -\frac{7863.4}{T} - 11.8 \quad (9)$$

From Eq. (9), the activation energy is found to be  $65.4 \pm 0.7$  kJ mol<sup>-1</sup>. This value is by the same order of magnitude with previous studies, as for instance 213 kJ mol<sup>-1</sup> for Si(IV) ions [4] or 48.9 kJ mol<sup>-1</sup> for Nd(III) ions [24].

### 3.1.2. Square wave voltammetry

The square wave voltammetry was used to confirm more accurately the number of exchanged electrons of Hf(IV) reduction than cyclic voltammetry.

Fig. 3 shows a square wave voltammogram of the LiF-NaF-HfF<sub>4</sub> (0.69 mol kg<sup>-1</sup>) system on silver electrode at 750 °C and 9 Hz. A single peak around -1.40 V vs. Pt is observed, in agreement with cyclic voltammetry and presenting an asymmetric Gaussian shape characteristic of a soluble/insoluble system [25].

The asymmetry of the peak is due to the currentless nucleation overvoltage needed for the formation of the first crystals of metallic hafnium at the electrode surface. This phenomenon delays the appearance of the faradic current, leading to a signal distortion [26]. The nucleation overvoltage  $\eta$  (V) can be determined by measuring the width at mid-height of the two half peaks using Eq. (10):

$$\eta = 2(10)(W_2 - W_1) \quad (10)$$

The obtained value,  $\eta = 32 \pm 2$  mV, is in agreement with previous overvoltage values for metals deposition available in the literature [27].

After checking in the frequency domain that the reduction reaction of Hf(IV) has a reversible behavior (linear variation of the peak differential current density with the square root of frequency (cf. inset Fig. 3)), the number of exchanged electrons was determined from the measurement of the width at mid-height  $W_{1/2}$  (V) carried out on an isolated peak.

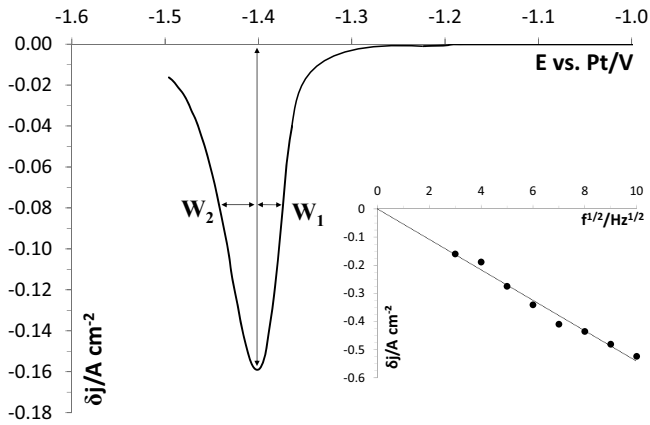
However, to get rid of the nucleation process, the width at mid-height  $W_{1/2}$  measurement has been determined by doubling the half-width at mid-height  $W_2$  (V) of the Gaussian curve (Eq. (11)). This methodology has already been validated in molten fluorides for different metals studies [24].

$$W_{1/2} = 2W_2 = 3.52 \frac{RT}{nF} \quad (11)$$

**Table 1**

Diffusion coefficient ( $D$ ), kinematic viscosity ( $\nu$ ) and Schmidt number ( $Sc$ ) of Hf(IV) ions for different fluoride media at different temperature.

| T (°C)                                       | LiF-NaF-KF   | LiF-NaF | LiF-CaF <sub>2</sub> |
|--|--------------|---------|----------------------|
| Molar comp.                                  | 46.5–11.5–42 | 61–39   | 79.2–20.8            |
| $10^9 D$ (m <sup>2</sup> s <sup>-1</sup> )   |              |         |                      |
| 800  | 5.34         | 4.96    | 1.49                 |
| 850  | 9.25         | 6.80    | 1.94                 |
| 900  | 16.66        | 9.46    | 2.48                 |
| $10^7 \nu$ (m <sup>2</sup> s <sup>-1</sup> ) |              |         |                      |
| 800  | 7.8          | 12.1    | 30.2                 |
| 850  | 6.5          | 10.8    | 29.6                 |
| 900  | 5.6          | 9.7     | 29.2                 |
| $Sc = \nu/D$                                 |              |         |                      |
| 800  | 145          | 245     | 2028                 |
| 850  | 71           | 158     | 1528                 |
| 900  | 34           | 102     | 1178                 |



**Fig. 3.** Square wave voltammogram of LiF-NaF-HfF<sub>4</sub> (0.69 mol kg<sup>-1</sup>) at frequency = 9 Hz and T = 750 °C Working EL: Ag; Auxiliary EL: vitreous carbon; Reference EL: Pt Inset: Linear relationship of Hf(IV) reduction peak current density versus the square root of the frequency.

82 ± 4 mV was found for W<sub>1/2</sub>, corresponding to a number of exchanged electrons of 3.8 ± 0.2.

The results obtained by cyclic and square wave voltammeteries allow concluding that Hf(IV) ions reduction in molten fluorides is a one-step process exchanging 4 electrons under diffusion control.

### 3.1.3. Chronopotentiometry

To confirm the diffusion-controlled process of the Hf(IV) electrochemical reduction, chronopotentiograms were performed. Fig. 4 shows the variation of the chronopotentiograms of HfF<sub>4</sub> with the applied current on silver electrode at 750 °C in LiF-NaF-HfF<sub>4</sub> (0.05 mol kg<sup>-1</sup>). These curves exhibit a single wave, obviously associated to the reduction of hafnium ions in the potential range (≈ -1.4 V vs. Pt) already observed on voltammograms.

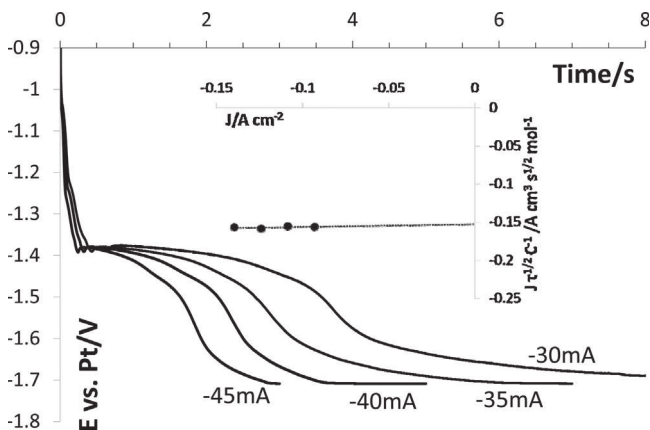
According to the data plotted in the inset of Fig. 4, Sand's equation (Eq. (12)) was verified [22]:

$$\frac{I\tau^{1/2}}{C} = \frac{nFSD^{1/2}\pi^{1/2}}{2} = \text{constant} \quad (12)$$

$$= 0.160 \pm 0.004 \text{ A cm}^3 \text{ s}^{-1/2} \text{ mol}^{-1}$$

where I is the applied current (A), τ the transition time (s), and S the immersed electrode surface area (m<sup>2</sup>).

Thus hafnium reduction process was confirmed to be limited by the diffusion of Hf(IV) ions in solution. Its diffusion coefficient calculated using Eq. (12) and assuming that n = 4 is: (3.3 ± 0.2)



**Fig. 4.** Typical chronopotentiograms with the intensity of the system LiF-NaF-HfF<sub>4</sub> (0.05 mol kg<sup>-1</sup>) at T = 750 °C Working EL: Ag; Auxiliary EL: vitreous carbon; Reference EL: Pt.

× 10<sup>-9</sup> m<sup>2</sup> s<sup>-1</sup> at 750 °C, in accordance with our previous result by cyclic voltammetry ((3.5 ± 0.3) × 10<sup>-9</sup> m<sup>2</sup> s<sup>-1</sup>).

The reversal chronopotentiogram presented in Fig. 5 proves that an insoluble compound is formed on silver electrode during the cathodic run, as the transition time of the reduction wave is very close to the oxidation time (τ<sub>red</sub> ≈ τ<sub>ox</sub> ≈ 0.6s) [28]. This result confirms one more time that the reaction leads to Hf metal on the working electrode.

All these electrochemical techniques allow to conclude that reduction of Hf(IV) ions added as HfF<sub>4</sub> in molten fluorides:

- is a one-step process exchanging 4 electrons,
- is controlled by diffusion of Hf(IV) ions,
- and leads to the formation of metallic hafnium.

As it is stated in the literature that cations coordinancy is strongly influenced by fluoroacidity, reduction mechanism of Hf(IV) ions in molten fluorides can be written as in Eq. (13):



### 3.2. Diffusion coefficients and mass transport approach

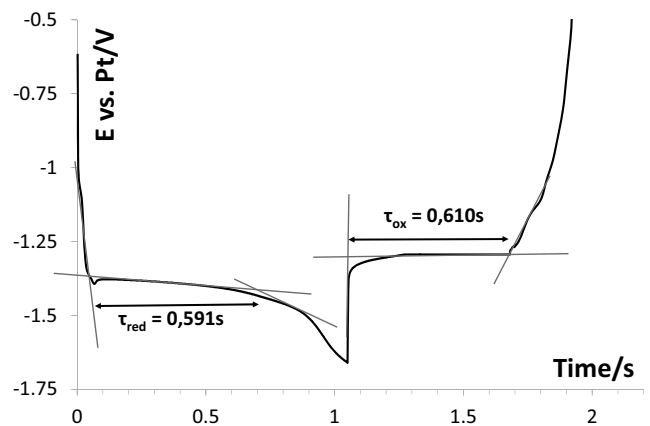
The effect of fluoroacidity on Si(IV) and B(III) ions mass transports was previously demonstrated [5]. Results showed that an increase of the fluoroacidity leads to a decrease of diffusion coefficients due to coordinancy and bridging solvent phenomena. These physico-chemicals parameters lead to an increase of solvent viscosity with fluoroacidity. As a consequence solutes mass transport become more difficult.

In order to confirm these results on a simple electroactive species, investigation on hafnium solute was performed in three molten systems with different fluoroacidities:

- a basic bath: LiF-NaF-KF,
- an acid bath: LiF-CaF<sub>2</sub>,
- and an intermediate bath: LiF-NaF.

Diffusion coefficients of Hf(IV) ions were determined by calculating the average of cyclic voltammetry (Eq. (8)) and chronopotentiometry (Eq. (11)) values. Results are presented in Table 1 where solvents are sorted from the more basic to the left to the more acid to the right.

Results on Hf(IV) ions show that diffusion coefficients decrease with fluoroacidity whatever the temperature. However for the lowest temperature, the minor differences between values and the



**Fig. 5.** Reversal chronopotentiogram of HfF<sub>4</sub> (0.083 mol kg<sup>-1</sup>) in LiF-NaF, J = ± 207 mA cm<sup>-2</sup> at T = 750 °C Working EL: Ag; Auxiliary EL: vitreous carbon; Reference EL: Pt.

uncertainty of measurement ( $\pm 3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ) do not allow the discrimination of solvents fluoroacidity.

It is obvious that the ionic radius of the element in solution and its coordinancy affect the ability of the species to move through the solution (represented by  $D$ ). In highly acid baths, where the content of free  $F^-$  is low, hafnium complexes have to share one or more fluorine by bridging, and then form, by polymerization, larger sizes species, which slows down the mass transport in solution.

As the hafnium  $\text{HfF}_{4+x}^{x-}$  coordinancy is a function of fluoroacidity and cannot be determined by electrochemistry, the solute transport results have to take in account the solvent contribution through its viscosity: a viscosity increase leads to a more difficult solute mass transport.

Kinematic viscosities  $\nu$  (in  $\text{m}^2 \text{ s}^{-1}$ ) defined as the ratio between dynamic viscosity  $\mu$  (in  $\text{kg m}^{-1} \text{ s}^{-1}$ ) and density  $\rho$  (in  $\text{kg m}^{-3}$ ) were calculated from the Molten Salts Handbook values [29]. Note that data for  $\text{LiF-CaF}_2$  viscosity at operating temperatures are not available in literature. Then, viscosity was extrapolated from the work of Robelin et al. as the sum of the fluorides compounds viscosities balanced by their molar fractions in the eutectic mixture [30]. These values are gathered in Table 1.

It shows that molten fluorides viscosity increase with fluoroacidity, and could be correlated to a bridging phenomenon by sharing available free fluorides, modifying the molten salt structure and forming a network-like liquid. This behaviour is particularly important with the presence of calcium, which was demonstrated as one of the more acid compounds (Fig. 1a).

In order to take into account the effect of the viscosity on  $\text{Hf(IV)}$  diffusion coefficients, the adimensional Schmidt number ( $Sc = \nu/D$ ) was calculated to characterize the solute global mass transport through its environment. The calculated  $Sc$  number are gathered in Table 1. At a given temperature, the results showed that  $Sc$  for  $\text{Hf(IV)}$  ions increases with fluoroacidity, allowing to sort melts in regard of their fluoroacidity.

Thus relationships between fluoroacidity, bridging fluorines and viscosity directly impact mass transport of a simple species in solution. The determination of diffusion coefficients of a species, which is directly affected by a cumulative effect of viscosity and ionic radius of the solute, allows to discriminate molten fluorides media as a function of fluoroacidity. However, if the difference between  $D$  values is very low, the Schmidt number by taking account viscosity increase this difference, as for instance between  $\text{LiF-NaF-KF}$  and  $\text{LiF-NaF}$  at  $800^\circ\text{C}$  where the difference is around 7% on  $D$  and 69% on  $Sc$  in the same conditions.

#### 4. Conclusion

The  $\text{HfF}_4$  electrochemical behaviour was investigated in molten fluorides. By cyclic voltammetry, square wave voltammetry, chronopotentiometry and reversal chronopotentiometry,  $\text{Hf(IV)}$  ions reduction mechanism was demonstrated to be a one step process exchanging 4 electrons under  $\text{Hf(IV)}$  ions diffusion control leading to the formation of hafnium metal:  $\text{HfF}_{4+x}^{x-} + 4e^- \rightleftharpoons \text{Hf} + xF^-$ .

Diffusion coefficients of  $\text{Hf(IV)}$  were determined in three molten fluorides solvents, with different fluoroacidities, between  $800$  and  $900^\circ\text{C}$ .  $\text{Hf(IV)}$  diffusion coefficients decrease with fluoroacidity: this phenomenon is due to a cumulative effect of solvent viscosity (which is linked to bridged fluorines) and ionic radius of the solute with fluoroacidity. As viscosity refers to the solvent and diffusion coefficient to the solute, the Schmidt number was calculated in order to take into account these two parameters. Results showed that  $Sc$  increases with fluoroacidity, in a much more sensitive way than  $D$ .

This mass transport approach consisting in the determination of the diffusion coefficient and the calculation of the Schmidt number is easier to set up than kinetic rates determination. Moreover, this universal method can be extended to all electroactive species and to all bath fluoroacidity.

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