

## Voltammetric Study on the Behaviour of Refractory Metals in ([BMP][TFSA]) Ionic Liquid.

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Electrochemical studies of tantalum fluoride and zirconium fluoride in 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide ([BMP][TFSA]) ionic liquid were carried out in presence of lithium fluoride using cyclic voltammetry technique. The electrochemical behaviour of Ta(V) and Zr(IV) on gold and platinum substrates was investigated in the temperature range from R.T. to 200 °C at different values of scan rate and different potential windows. Special attention was paid to the mechanism of cathodic reduction. Cyclic voltammograms exhibit well-defined peaks attributed to the formation of metallic deposits on the substrates. The knowledge of electrode and chemical reactions based on the experimental results of the refractory metals considered allow us to propose a possible reaction path for the oxidation/reduction processes. The mechanisms of electrochemical reduction of Tantalum(V) depends strongly on the composition of the bath; using TaF<sub>5</sub> as metal salt, two cathodic peaks due to Ta(V)/Ta(III) and Ta(III)/Ta reduction were observed. The cyclic voltammograms recorded at different values of scan rate have shown that the Ta(III)/Ta reduction process is mainly controlled by diffusion of the electroactive species to the electrode surface. It has been proposed that the mechanism for reduction of zirconium ions occurs in a one step process exchanging four electrons and controlled by the zirconium ions diffusion in the ionic liquid.

### 1. Introduction

The electrochemistry of refractory metals (IVB, VB and VIB groups) has been widely studied in molten salts to optimize the cathodic deposition process of these metals. Due to their properties, such as high strength and high corrosion resistance, refractory metals are widely used in electronics, optics, sensors, automotive, nuclear and aerospace industries. Conventional aqueous media cannot be always used as electrolytes due to the narrow electrochemical windows, low thermal stability and evaporation (Simka et al., 2009). The mechanism of the electrodeposition of refractory metals is not yet fully elucidated. Senderoff and Mellors (1966) developed a general process for the electrodeposition of eight of the nine refractory metals of groups IVB, VB and VIB as dense coherent deposits by using a solution of the refractory metal in a molten alkali-fluoride eutectic mixture from 680 °C to 800 °C. They concluded that an irreversible metal-producing step is a necessary (though not sufficient) condition for the deposition of coherent deposits from molten salts. The mechanical properties of refractory metals, such as the excellent corrosion resistance and the nuclear properties of some, make them particularly interesting as coatings. Inman and White (1978) have summarized in a review the electrochemistry of refractory metals in molten salts electrolytes. The authors have reported that the recovery of a primary metal is ensured by using, as solvent, a melt having a much larger decomposition voltage than that of the solute and an inert cathode; controlling the electrodeposition of metal by rate processes other than mass transfer, will lead to coherent deposits. Few years later, Girginov et al. (1995) have presented a selective review of the anodic and cathodic processes of Ti, Zr, Nb and Ta from molten salts-based electrolytes in order to investigate the optimization of cathodic deposition of these metals highlighting that the two main types of electrolyte employed in the electrodeposition of refractory metals were chloride and fluoride based. The Ta(V) reduction has been studied in a wide range of melts, such as chlorine or fluorine melts. In FLINAK-K<sub>2</sub>TaF<sub>7</sub>

Polyakova et al. (1994) have studied the nature of the tantalum reduction process at 710 °C using various working electrodes, such as molybdenum, platinum and silver; the authors affirm that the cyclic voltammograms shape were not reproducible and electrochemically  $\text{TaF}_7^{2-}$  is reduced to tantalum metal in a single quasi-reversible five-electron step. In  $\text{LiF-NaF-K}_2\text{TaF}_7$  with low oxygen contents on Ag electrode, Chamelot et al. (2002) recorded a single peak in the reduction sense associated with one reoxidation peak on the reverse scan. The reduction peak reveals the one-step reaction involving pentavalent and zerovalent tantalum at 800 °C. In chloride electrolytes Girginov et al. (1995) suggest that the electrodeposition of microcrystalline Ta took place in a narrow potential range in chloride melts and confirmed a single step mechanism in  $\text{NaCl-KCl-K}_2\text{TaF}_7$  melts.

The electroreduction process of Zr(IV) was studied by Chen et al. (2011) at molybdenum electrode in  $\text{LiCl-KCl-K}_2\text{ZrF}_6$  molten salts at 923 K; the authors highlighted that Zr(IV) was reduced to Zr metal by a two-step mechanism corresponding to the Zr(IV)/Zr(II) and Zr(II)/Zr transitions. Furthermore, the cathodic peaks are not dependent on the sweep rate so it has been concluded that the reduction process of Zr(II)/Zr and Zr(IV)/Zr(II) are both reversible (or quasi-reversible). Analogous behaviour has been reported by Wu et al. (2011) that studied the electrochemical reduction of Zr(IV) on Pt electrode at 1023 K in  $\text{NaCl-KCl-K}_2\text{ZrF}_6$  molten salt; two cathodic reduction peaks related to Zr(IV)/Zr(II) and Zr(II)/Zr steps were observed in the potential range from 0 to -1.6 V vs. Ag/AgCl. The authors thus observed a two-electron transfer process involving the formation of Zr(II). On the other hand, Groult et al. (2008) studied the electrochemical behaviour of Zr(IV) in potassium-free fused alkali fluorides in the temperature range of 773-1123 K by using either tungsten or molybdenum electrodes, and observed a single well-defined oxido-reduction wave, and concluded that the reduction of Zr(IV) is a single four-electron reversible step controlled by diffusion process. Kawase and Ito (2003) have studied the voltammetric behaviour on Ni electrode in the solution obtained after the anodic dissolution of Zr in the  $\text{LiCl-KCl}$  eutectic. Cyclic voltammograms reveal that Zr(II) and Zr(IV) can exist in molten salts between 450 and 550 °C and the ratio of Zr(II)/Zr(IV) increases with increasing temperature. At 450 °C only one cathodic peak related to Zr(IV)/Zr(II) is observed, while at 550 °C two cathodic peaks, related to the reduction of Zr(IV)/Zr(II) and Zr(II)/Zr, are observed.

Despite molten salts have large electrochemical windows, good heat capacity, can attain very high temperatures and conduct electricity, the extreme operating conditions limit the variety of substrates used for the refractory metals electrodeposition and allow to such technical and economical problems as the loss in the current efficiency and corrosion problems at high temperatures. Thus, the electrodeposition of refractory metals from ionic liquid at low temperatures represent a valid alternative to the use of high-temperature molten salts. Ionic liquids show good electrical conductivity, high thermal stability and have wide electrochemical windows; their properties allow the direct electrodeposition of crystalline metals and semiconductors at elevated temperatures, and in this context, ionic liquids can be regarded as the link to molten salts (Zein El Abedin and Endres, 2007). Moreover, the electrochemical behavior of tantalum ions has been studied in different ionic liquids to determine the deposition conditions of metallic tantalum; the authors reported that both the ionic liquid and the deposition conditions influence strongly the quality and properties of the deposited layers (Ispas et al., 2010). The electrochemical deposition of Nb from ionic liquids has been investigated in a previous work (Vacca et al., 2014).

This paper presents an electrochemical study of Ta(V) and Zr(IV) ions behaviour in ([BMP][TFSA]) ionic liquid, in presence of LiF, in the R.T. - 200 °C temperature range on gold and platinum electrodes using cyclic voltammetric technique.

## 2. Experimental

1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonil)imide air and water stable ionic liquid was purchased from Aldrich. Prior to use, the liquid was dried at 125 °C for 24 h to reduce water content and stored in a nitrogen filled glove box.  $\text{TaF}_5$ ,  $\text{ZrF}_4$ , and LiF purchased from Aldrich were used without further purifications. The cyclic voltammetry measurements were carried out using a Metrohm Autolab 302N potentiostat-galvanostat controlled by NOVA software (Metrohm, Switzerland). The maximum operating temperature was 200 °C determined with a thermocouple and controlled with an accuracy of 1.5 °C by a IKA® RCT standard temperature controller (Staufen, Germany). A conventional three-electrode cell ( $V=20$  mL) was used in which either rectangles of gold (99.9%, Aldrich) or platinum (99.9%, Aldrich) substrates were the working electrodes; the exposed area of the rectangular electrodes was 0.6 cm<sup>2</sup>. The counter and the quasi-reference electrodes were a Pt sheet and a Pt wire, respectively. Before use, working electrodes were cleaned for 15 min in ultrasonic bath in acetone. The solutions were prepared under nitrogen atmosphere by adding LiF up to a concentration of 0.25 M; such electrolytic bath was maintained at 125 °C for 24 h. Either metal salts as  $\text{TaF}_5$  (0.25 M) or  $\text{ZrF}_4$  (0.25 M) were then added severally to the electrolytic

medium and each solution was maintained at 125 °C for 24 h under stirring in a nitrogen filled glove box. All electrochemical measurements were performed inside the glove box. Cyclic voltammograms were recorded from the open circuit potential (OCP) at different temperatures under different potential windows and different values of scan rate.

### 3. Results and discussion

#### 3.1 Electrochemical study of Ta on polycrystalline gold and platinum electrodes

Figure 1 shows the cyclic voltammograms of ([BMP][TFSA]) containing 0.25 M LiF and 0.25 M TaF<sub>5</sub> on gold and platinum electrodes at different temperatures. Scans were initially swept from the OCP towards the cathodic direction at a rate of 100 mV s<sup>-1</sup>. The cyclic voltammograms exhibit a different behaviour with increasing temperature: the current density increases significantly in the range from R.T. to 200 °C. This behaviour may be related to the rise of the electrochemically active species which leads to an increase of the redox reaction rates (Zein El Abedin et al., 2005).

Three cathodic processes appear in the forward scan at -0.9 V, -1.5 V and -1.8 V on gold electrode demonstrating that the electrochemical reduction of tantalum apparently involves three steps, while in the reverse scan two not well-resolved wave and one oxidation peak can be observed at -1.6 V, -0.3 V and 1.3 V, respectively. Two reduction peaks appear at -0.9 V and -1.8 V, while two small oxidation processes have been recorded in the backward scan on platinum electrode. The ([BMP][TFSA]) ionic liquid shows a wide electrochemical window of stability of almost 4 V on polycrystalline gold where the degradation of the anion and cation constituting the ionic liquid does not occur. Extending the potential range, an increase in the current densities at the cathodic and anodic limits is observed; in these conditions the clear solution of [BMP][TFSA] containing LiF changed to dark brown. The cathodic limit is mainly due to the irreversible reduction of the [Py<sub>1,4</sub>]<sup>+</sup> to N-methylpyrrolidine and butyl radicals leading further to butene(s) and hydrogen. The anodic limit is due to gold dissolution and partly to irreversible anion oxidation (Borisenko et al., 2009). The redox couple that appears in the voltammogram (inset Figure 1a) may be related to the reduction and reoxidation of gold substrate. Using platinum as working electrode the cyclic voltammogram exhibits a somewhat different behaviour.

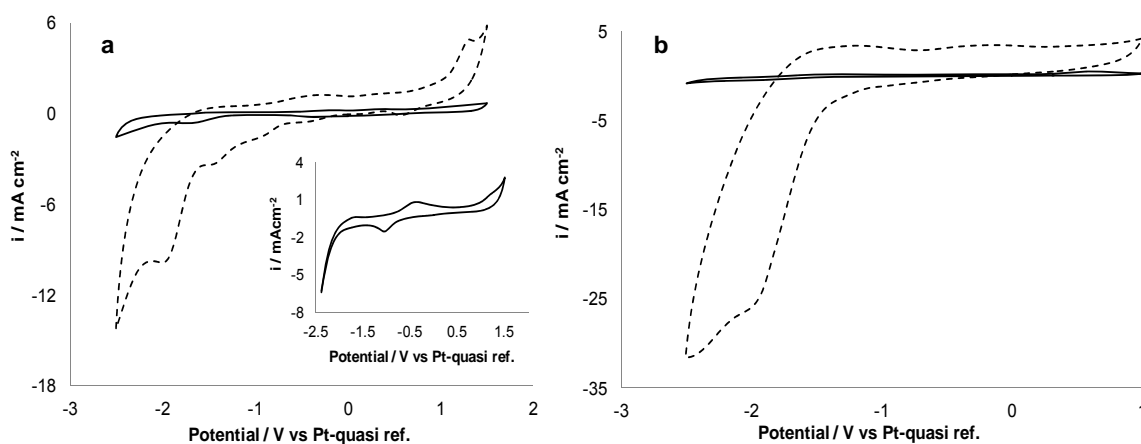


Figure 1: cyclic voltammograms of ([BMP][TFSA]) containing 0.25 M LiF and 0.25 M TaF<sub>5</sub> at R.T. (solid line) and 200 °C (dashed line): **a** gold substrate, **b** platinum substrate (scan rate 100 mV s<sup>-1</sup>). Inset: cyclic voltammogram of ([BMP][TFSA]) containing 0.25 M LiF at 200 °C on gold electrode

Zein El Abedin et al. (2005) have shown the differences on the electrochemical behaviour of ([BMP][TFSA]) ionic liquid with different concentrations of TaF<sub>5</sub> either in presence or absence of LiF on platinum electrode; cyclic voltammograms clearly indicate that three reduction peaks appear in the presence of LiF while only two reduction peaks, correlated to the electrolytic reduction of Ta(V) to Ta(III) and to the reduction of Ta(III) to Ta(0), have been recorded without LiF addition. The two-step reduction mechanism of Ta(V) was confirmed few years later by Borisenko et al. (2009) that studied the electrochemical behaviour of TaF<sub>5</sub> in [Py<sub>1,4</sub>]<sup>+</sup>TFSA on Au(111) at 25 °C. The electrochemical behaviour of tantalum(V) chloride and oxochloride species has been also studied by Babushkina and Ekres (2010) in Pyr<sub>14</sub>Cl ionic liquid: the authors reported that the mechanism of the electrochemical reduction of tantalum(V) depends strongly on the composition of the electrolytic bath.

Analysing the results obtained in the present work using a gold substrate, the first cathodic wave recorded at -0.9 V may be attributed to the formation of non-stoichiometric tantalum fluorides. As TaF<sub>3</sub> is known to be stable (Borisenko et al., 2009), the second reduction peak recorded at -1.5 V may be related to the electrochemical reduction of Ta(V) to Ta(III). The reduction peak at -1.8 V may be attributed to the electrolytic reduction of Ta(III) to Ta as at this electrode potential the formation of a black deposit on the electrode surface is well visible at naked eye. In the reverse scan two less-defined oxidation waves can be observed: the first anodic wave recorded at -1.6 V might be attributed to the oxidation of Ta to Ta(III), while the second peak recorded at about 1.3 V is related to the incomplete stripping of the electrodeposit. However, the ratio of anodic to cathodic charge is lower than one, revealing that the reoxidation of the deposit is not fully reversible. Using a platinum substrate a not well-defined wave at -0.9 V and a reduction peak at -1.8 V have been recorded in the voltammogram of ([BMP][TFSA]) containing 0.25 M LiF and 0.25 M TaF<sub>5</sub> at 200 °C. In the anodic branch two oxidation waves appear at -1.5 V and -0.3 V. A two-step reduction mechanism of Ta(V) can be proposed. The peak potentials of the cathodic peaks slightly shift to less negative values and the potential of the oxidation peaks slightly move to the positive direction with increase in temperature. As can be seen, the peak currents of both reduction and oxidation peaks increase with rising temperature.

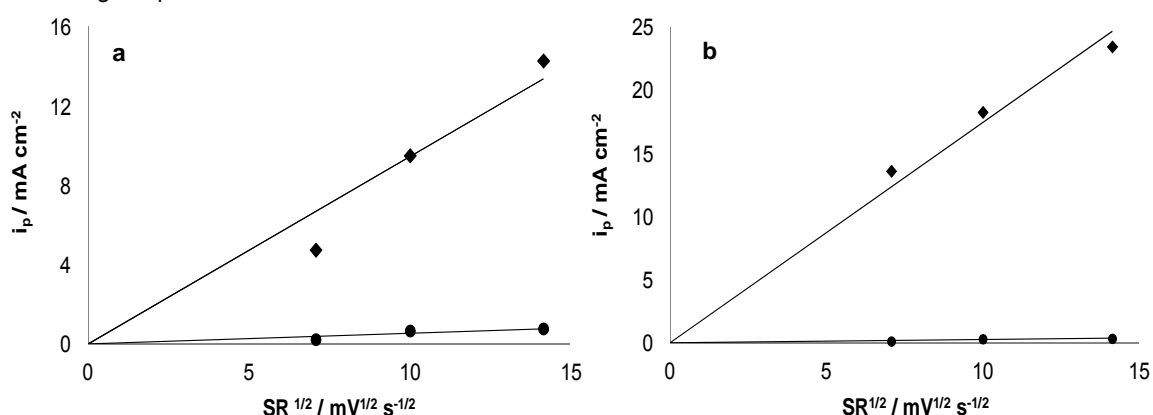


Figure 2: values of current density measured at the deposition peak as a function of the square roots of the scan rates for the ([BMP][TFSA]) containing 0.25 M LiF and 0.25 M TaF<sub>5</sub> at room temperature (circle) and 200 °C (diamonds); **a** gold electrode, **b** platinum electrode

Plotting the current peaks as a function of the square roots of the scan rates (Figure 2) a linear dependence is observed with both platinum and gold electrodes: this behaviour is in agreement with the Randles-Sevcik equation (Eq.1), for a planar diffusion controlled case (Zoski C. G., 2007), indicating that the reduction process is mainly controlled by diffusion of the electroactive species to the electrode surface.

$$i_p = 0.4463 \frac{n^{3/2} F^{3/2}}{R^{1/2} T^{1/2}} A D_o^{1/2} C_o^* \nu^{1/2} \quad (1)$$

### 3.2 Electrochemical study of Zr on polycrystalline gold and platinum electrodes

The electrochemical behaviour of zirconium has been studied in ([BMP][TFSA]) containing 0.25 M LiF and 0.25 M ZrF<sub>4</sub> with either polycrystalline gold or platinum as working electrodes from R.T. to 200 °C. The potential was scanned from the OCP in the cathodic direction. Figure 3 shows that using gold as working electrode two reduction peaks appear at -0.9 V and -1.6 V, while in the reverse scan one not well-resolved wave and one oxidation peak can be observed at -1.3 V and 0.5 V, respectively. A well defined reduction peak appear at -1.2 V, while two small oxidation processes have been recorded in the backward scan on platinum electrode.

The effect of fluoride ions on the reduction of zirconium has been studied by Guang-Sen et al. (1990) in fluoride-chloride melts: the voltammetric behaviour of zirconium at 973 K and 1033 K in equimolar KCl-NaCl with ZrCl<sub>4</sub> on a platinum electrode showed that the electroreduction process of Zr is reversible. According to the number of electrons exchanged, the authors established that the process has double two-electron steps: Zr(IV)/Zr(II) and Zr(II)/Zr. The cathodic reduction of Zr(IV), in the same electrolytic bath, was also studied with different concentrations of KF: a new peak appeared when small amount of KF (X<sub>F<sup>-</sup></sub>/X<sub>Zr<sup>4+</sup></sub> = 1.07) were added into equimolar KCl-NaCl melts with ZrCl<sub>4</sub>. The currents at peaks related to

Zr(IV)/Zr(II) and Zr(II)/Zr reduction decreased as the ratio ( $X_{F^-}/X_{Zr^{4+}}$ ) in the melts increased. The authors have concluded that the new peak recorded in the presence of KF represents the main reduction of Zr when the ratio  $X_{F^-}/X_{Zr^{4+}} \geq 6$ .

A detailed electrochemical study of the molten LiF-CaF<sub>2</sub>-ZrF<sub>4</sub> system is provided in the 810-920 °C temperature range by Gibilaro et al. (2013) on an inert Ta electrode. The authors have reported that at 840 °C a single peak is observed in the cathodic run associated with a stripping peak; the reduction mechanism was a one step process exchanging 4 electrons and controlled by the Zr ions diffusion in the molten salt.

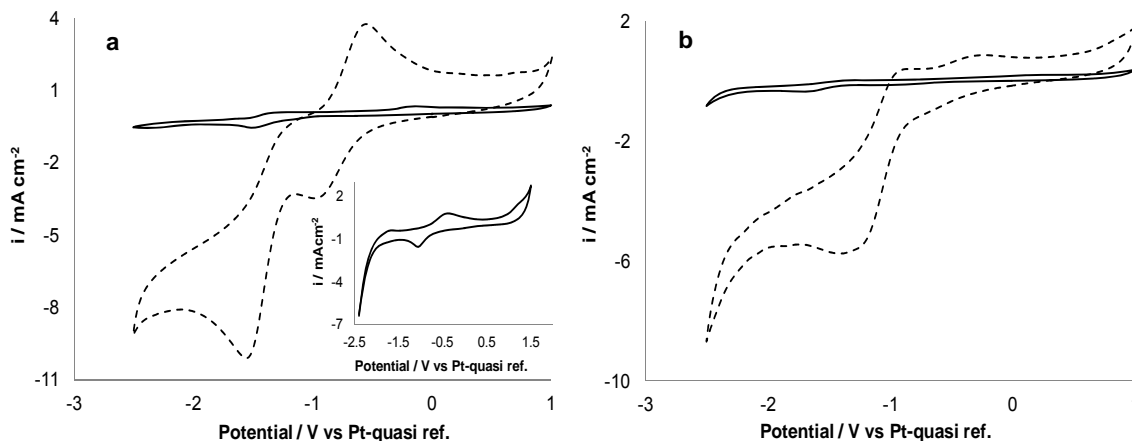


Figure 3: cyclic voltammograms of ([BMP][TFSA]) containing 0.25 M LiF and 0.25 M ZrF<sub>4</sub> at R.T. (solid line) and 200 °C (dashed line): **a** gold substrate, **b** platinum substrate (scan rate 100 mV s<sup>-1</sup>). Inset: cyclic voltammogram of ([BMP][TFSA]) containing 0.25 M LiF at 200 °C on gold electrode

Under the operative conditions adopted in this work, the reduction of Zr(IV) in ([BMP][TFSA]) occurs in a single four-electron step: the reduction peak recorded on gold electrode at -1.6 V may be attributed to the formation of Zr metal. The oxidation peak at -0.5 V may be related to the stripping of metallic zirconium presents on the electrode surface. The reduction peak at -0.9 V cannot be attributed to reactions involving Zr ions, as it can be observed in the voltammogram obtained with the electrolyte prior the addition of ZrF<sub>4</sub> (inset Figure 3a) in which this peak is clearly evident.

Also with platinum electrode a single reduction peak appears at -1.2 V in the forward scan, associated with a stripping peak at -0.3 V, confirming that the reduction of Zr(IV) is a one step process. The effect of increased temperature is clearly evident: the peak currents of both reduction and oxidation peaks increase with rising temperature.

Also in this case, plotting the current peaks as a function of the square roots of the scan rates (Figure 4) a linear dependence is observed confirming that the process is controlled by the mass transfer.

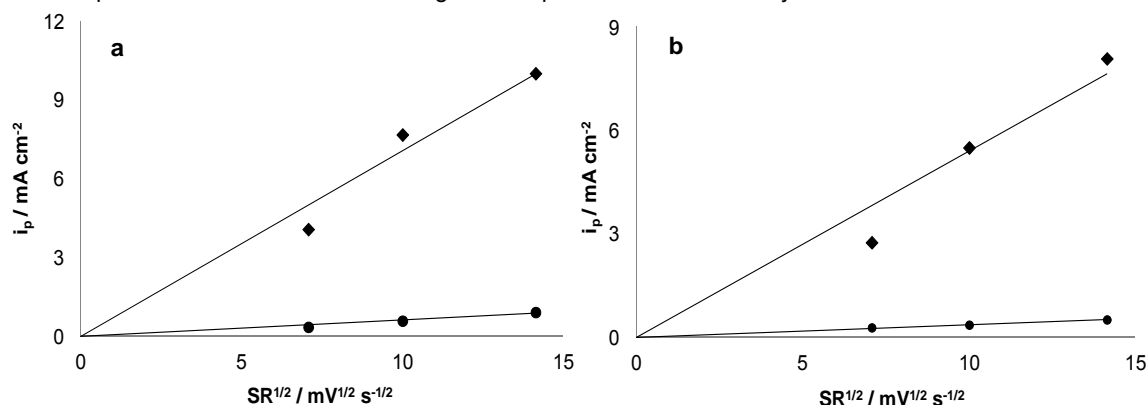


Figure 4: values of current density measured at the deposition peak as a function of the square roots of the scan rates for the ([BMP][TFSA]) containing 0.25 M LiF and 0.25 M ZrF<sub>4</sub> at room temperature (circle) and 200 °C (diamonds); **a** gold electrode, **b** platinum electrode

#### 4. Conclusions

We have presented the results of a voltammetric study on the electrochemical behaviour of TaF<sub>5</sub> and ZrF<sub>4</sub> in the ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide. The experiments were carried out in the temperature range from R.T. to 200 °C, polycrystalline gold and platinum were used as working electrodes.

It was found that the electrochemical reduction of Ta both on gold and platinum involves a two-step reduction mechanism showing a trend of a reversible process although some irreversibility of the system have been observed. In the case of Zr a one step process exchanging four electrons and controlled by the Zr ions diffusion has been proposed.

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