Electrochemical Reduction of solid UO$_2$ in Molten Fluoride Salts

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Abstract – *The direct electrochemical reduction of UO$_2$ solid pellets was carried out in LiF-CaF$_2$ (+ 2wt % Li$_2$O) at 850°C. An inert gold anode was used instead of the usual reactive sacrificial carbon anode. In this case, reduction of oxide ions yields O$_2$ gas evolution on the anode. Electrochemical characterisations of UO$_2$ pellets have been performed by linear sweep voltammetry at 10 mV/s and reduction waves associated to its direct reduction have been observed at a potential 150mV more positive in comparison with the solvent reduction. Then, galvanostatic electrolyses runs have been realised and products were characterised by SEM-EDX, EPMA/WDS and XRD. In one of the runs, uranium oxide was partially reduced and three phases were observed: non reduced UO$_2$ in the centre, pure metallic uranium on the external layer and an intermediate phase representing the initial stage of reduction taking place at the grain boundaries. In another run, the UO$_2$ sample was fully reduced. Due to oxygen removal, the U matrix had a typical coral-like structure which is characteristic of the pattern observed after the electroreduction of solid oxides.*
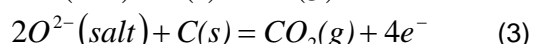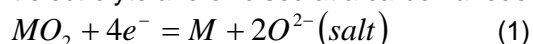
A. INTRODUCTION

Advanced nuclear fuel cycles are under development worldwide in order to minimise the amount of high radiotoxic waste generated by operation of the nuclear power plants. The new technologies have to be economically competitive, environmentally safe and resistant to proliferation. Within most of the developed future fuel cycles, recycling of actinides (Cm, Pu, Am, Np) from spent nuclear fuel is required due to their significant impact on its radiotoxicity. Pyrochemical methods represent one of the promising options to fulfil this task. In the pyrometallurgical process being developed in the Institute for Transuranium elements [1], all actinides are group-selectively recovered in a form of actinide-aluminium (An-Al) alloys by an electrorefining process in molten LiCl-KCl using solid aluminium cathodes. The remaining actinides from the used melts are recovered by an exhaustive electrolysis; also as An-Al alloys. The back extraction of actinides from the alloys is provided by a three-step chlorination route: The salt remaining on the electrode is distilled, the pure alloys are chlorinated by chlorine gas or HCl and the formed AlCl$_3$ is sublimated yielding pure actinide chlorides.

However, oxide fuels are not suited for the electrorefining process, since these metallic oxides are mostly insoluble in molten salts. Therefore, a preliminary step is required to convert oxides into metal which can be afterwards easily dissolved in molten salts by anodic dissolution.

The lithium reduction process has been developed for the pyrochemical recycling of oxide fuels using lithium metal as a reductant to convert actinide oxides into metal. Usami *et al.* [2] successfully applied this technique to AmO$_2$ in LiCl at 650°C for Li$_2$O concentration lower than 5.1 wt%: more than 99.9% of Am has been recovered into solid Am phase. This technology was also employed for UO$_2$ and PuO$_2$ with 3% of Am at 650°C [3] leaving particles of UO$_2$ totally reduced. For Pu sample, small

amounts of Pu and Am were detected in the salts. Moreover, AmO_2 reduction was only efficient for low Li_2O concentration (<1.8wt %). Thus an additional step is needed to control and decrease Li_2O concentration as it accumulates in the salt during the process.

To avoid these problems, a more efficient process has been elaborated: the direct electrochemical reduction. This pyroprocess has been developed by Chen et al. [4], who first demonstrated the direct electroreduction of TiO_2 into Ti at 950°C in molten $CaCl_2$. This innovative method is called the FFC Cambridge process (Fray-Farthing-Chen). The overall reaction is the electroreduction of a solid oxide MO_2 into metal M at the cathode (Eq. 1) and the evolution of CO and CO_2 at the anode (Eq. 2-3); the oxide ions released from the cathode are transported through the support electrolyte and oxidised at a carbon anode:

$$MO_2 + 4e^- = M + 2O^{2-}(salt) \qquad (1)$$
$$O^{2-}(salt) + C(s) = CO(g) + 2e^- \qquad (2)$$
$$2O^{2-}(salt) + C(s) = CO_2(g) + 4e^- \qquad (3)$$

As O^{2-} ions produced at the cathode are simultaneously consumed at the anode, the oxide ions concentration remains constant in the molten salt, preventing accumulation during the experiment. Moreover, the troublesome handling of Li metal is also avoided.

On top of multiple applications to the preparation of various metals (Ti [5], Nb [6], Si [7]…), the FFC process is also studied in the framework of nuclear spent fuel reprocessing. The electroreduction of UO_2 and MOX (UO_2-PuO_2) have been studied in LiCl or $CaCl_2$ [8-10].

During the metallic oxide reduction in $CaCl_2$ at 850°C, the uranium metal cohered due to the high operating temperature and formed a dense layer on the sample surface. This prevents the external diffusion of oxygen ions to the salt, and stops the reduction process of UO_2. In LiCl baths at lower temperature (650°C), no dense metallic skin was observed on the surface and both UO_2 and MOX samples were reduced in their centre.

One of the major troubles with the FFC process is the use of a reactive carbon anode where CO_2 gas is released. The final product often contains carbides, due to the reduction of carbonates CO_3^{2-}, formed by the reaction of the $CO_2(g)$ with O^{2-} dissolved in the salt [11].

In this work, a different category of electrolyte was tested, i.e. the molten fluorides, with the advantage of using an inert gold anode on which oxygen ions are oxidised into O_2 [12]:

$$2O^{2-} = O_2(g) + 4e^- \qquad (4)$$
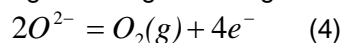
This anodic reaction, which is difficult to control in chloride salts due to the close potentials of Cl_2 and O_2 evolution, should avoid the carbides formation at the cathode.

The first part of the work was focused on the electrochemical characterisation of the UO_2 samples in fluoride salts by linear sweep voltammetry. Galvanostatic electrolyses have been performed on small amounts of oxides (~200-300 mg) and the reaction products have been characterised by SEM-EDX, EPMA/WDS and XRD.

B. EXPERIMENTAL

The cell used consisted of a vitreous carbon crucible placed in a cylindrical vessel made of refractory steel. The inner part of the walls was protected against fluoride vapors by a graphite liner. Experiments were performed under an inert argon (U grade) atmosphere. More details can be found in a previous paper [13].

The electrolyte (200g) consisted of the eutectic LiF-CaF_2 (SDS 99.99%) dehydrated by heating under a vacuum (3.10^{-2} bar) from room temperature up to the melting point for 72 h. Lithium oxide (Li_2O) powder (Cerac 99.5%) was used to provide oxide ions into the bath.

UO_2 was used in the form of sintered pellets (95%). The oxide pellets, attached with a molybdenum mesh and connected to the current lead by a molybdenum wire, were used as working electrodes. The auxiliary electrode was a gold wire with a large surface area (S=3.6cm²) and all potentials were referred to a platinum wire (0.5mm diameter), acting as a quasi-reference electrode $Pt/PtO_x/O^{2-}$ [14]. Although this electrode is sensitive to oxide concentration in the bath, its potential remains stable for high oxide concentration (>1wt %).

The electrochemical experiments were performed with an Autolab PGSTAT 30 potentiostat/galvanostat. After resin embedding and polishing, the cathode bulk was examined with a Scanning Electron Microscope (ZEISS Supra55) equipped with an EDX probe (Oxford SDD X-Max), X-Ray Diffraction (Bruker D8) and Electron Probe Micro Analysis combined with Wavelength Dispersive Spectrometer (CAMECA SX 100).

C. RESULTS AND DISCUSSION

C.1. _Solvent selection_

In order to perform the direct reduction of the uranium oxide, the solvent selection is primordial: the uranium formation has to occur at a potential more positive than that of the alkaline deposition. The Gibbs energy of the reaction ($\Delta_r G°$) between the metallic oxide UO_2 and the alkaline metal (Ca, Na or Li), according to Eq. (5), provides a good indication on the reduction potential of the oxide:

$$UO_2 + Alkaline(= Ca, Li, Na) = U + Alkaline \; oxide \qquad (5)$$
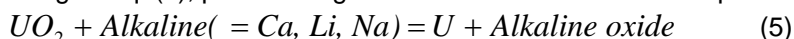
If $\Delta_r G°$ is negative, the reduction of the oxide occurs at a potential more positive than the solvent alkaline deposition and the direct reduction is then achievable from a thermodynamical point of view. Calculations have been performed with the data compiled in the HSC Chemistry 5.11 software [15]. According to these thermochemical considerations, the direct electroreduction of UO_2 has been investigated in the eutectic LiF-CaF$_2$ at 850°C. Oxide ions were introduced in the bath using Li$_2$O additions at a concentration of 2wt %, which is lower than its solubility limit in LiF-CaF$_2$ [16].

C.2. _Influence of oxide ions_
Cathode reactions
Figure 1 presents linear sweep voltammetries at 10mV/s on a Mo wire and on a mesh performed in LiF-CaF$_2$ with and without oxide ions.
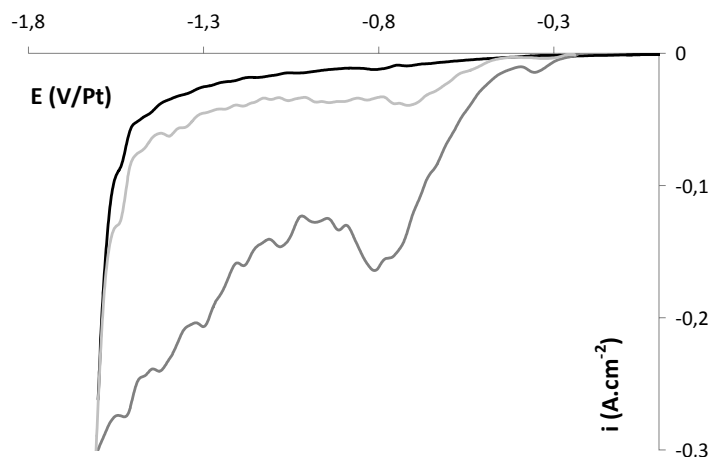

Figure 1: Linear sweep voltammetries on Mo in LiF- CaF$_2$ at 10mV/s; black: without oxide, light grey: with oxides on Mo wire, dark grey: with oxides on Mo mesh.

In the linear voltammograms plotted in the pure fluoride salt on Mo without Li$_2$O addition, no reduction current is observed between 0 and -1.5V/Pt, and the metallic lithium deposition occurs at -1.6V/Pt. With Li$_2$O presence in the solvent, a new cathodic current is observed on Mo electrode at around -0.8V/Pt and is proportional to its immersed surface: the recorded current increases with an increase of Mo surface. We can assume that an oxide layer is spontaneously formed when Mo and oxide ions are both present in the molten salt. According to the Mo-O phase diagram [17], only MoO$_2$ exists at 850°C. To remove it, linear sweep voltammetries in the reductive sense are performed until the complete disappearance of the cathodic current most probably corresponding to Eq. (6):

$$MoO_2 + 4e^- = Mo + 2O^{2-} \quad (6)$$
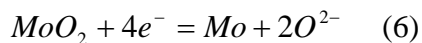
Anode reactions

The expected anodic reactions on a gold electrode in fluoride media in the presence of oxide ions are either the anodic dissolution of gold or the oxygen gas formation. To avoid the consumption of the Au electrode, the Li_2O quantity in the melt has to be controlled. Linear sweep voltammetries plotted on Au at 10mV/s for two different concentrations of oxide ions are presented in Figure 2.
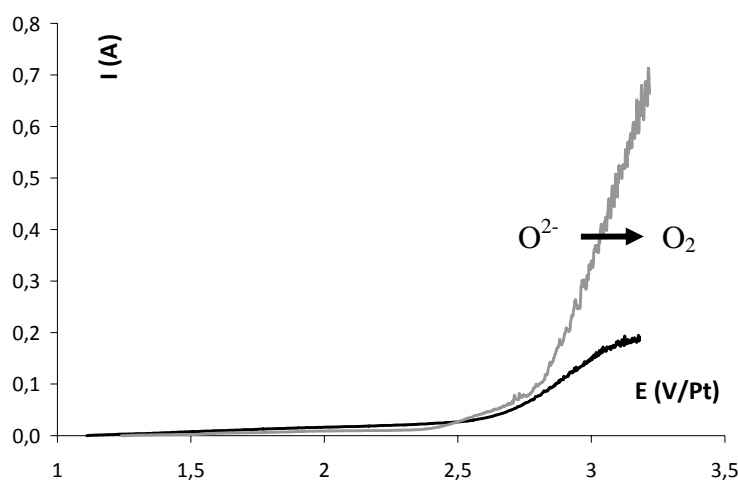

Figure 2: Linear sweep voltammetries on Au electrode in LiF-CaF$_2$ at 10mV/s at 850°C; the black curve is plotted for 0.5wt % Li$_2$O and the grey curve for 2wt % Li$_2$O.

At low concentration (0.5wt % Li_2O), a diffusion plateau of O^{2-} ions is observed at around 2.8V/Pt with an intensity of 150mA and for a potential higher than 3V, the Au electrode is oxidised. An increase of oxide ions concentration (2wt % Li_2O) avoids the anodic dissolution of Au. Thus, from those results, attention was paid to work in LiF-CaF$_2$ with 2wt % Li_2O.

C.3. *Electrochemical reduction of uranium oxide pellets*

Electrochemical characterisation by linear sweep voltammetry

Figure 3 shows the linear voltammetries obtained at 10mV/s on UO_2 sample, previously cleaned from the molybdenum oxide layer.
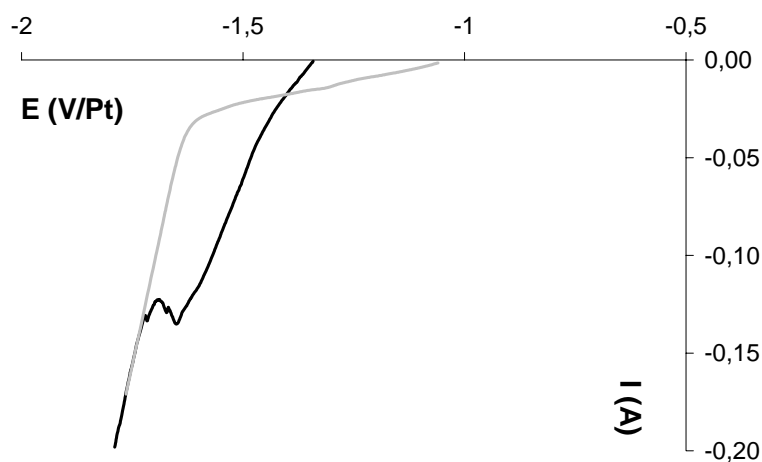

Figure 3: Linear voltammetries in LiF-CaF$_2$-Li$_2$O (2wt %) at 10mV/s and 850°C; the black curve is plotted on UO$_2$ sample after removal of the Mo oxide and the grey curve is the solvent reduction.

An additional reduction current peak is clearly observed before the solvent deposition at around -1.45V/Pt and is attributed to the direct electrochemical reduction of UO_2 in fluoride salts, confirming the previous thermodynamic analysis. It can be noticed that the oxide layer after its removal did not perturb the electrochemical signal.

Galvanostatic electrolysis of uranium oxide

Direct electrochemical reduction runs have been conducted in galvanostatic mode as the potentiostatic mode was not found to be adapted to this. Indeed, during the electrolyses, the oxides were gradually reduced into metal, leading to a noticeable modification of their electronic conductivity and thus of the ohmic drop in the circuit.

Five reduction tests were carried out in $LiF-CaF_2$ containing 2wt % Li_2O at 850°C; the applied cathodic current was increased between each test. The results concerning the two most interesting runs are presented in this section. The first noticeable UO_2 reduction experiment was performed at -150mA during 8000s, corresponding to 200% of the coulombs theoretically calculated from the oxide pellet weight. The cross section is observed by SEM and is presented in Figure 4.
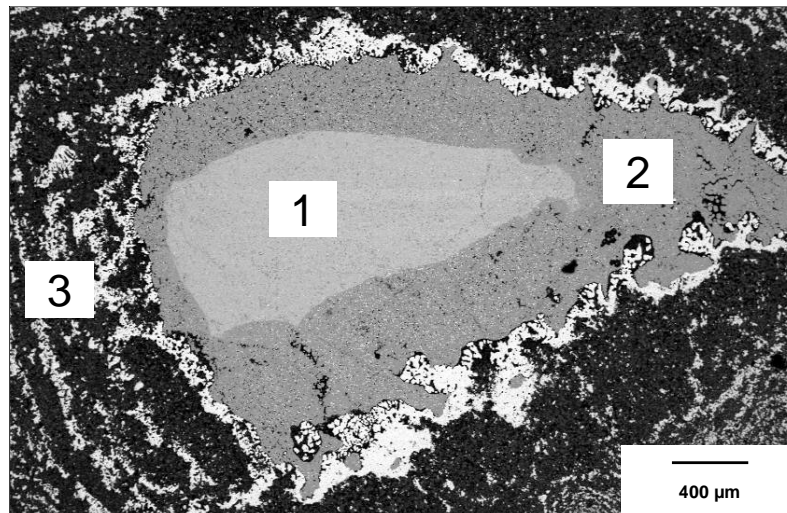

Figure 4: SEM observation of UO_2 pellet cross section after electrolysis (test 1) at 850°C in $LiF-CaF_2-Li_2O$ (2wt %).

Three different zones are present. The internal zone (1) corresponds to the remaining part of UO_2, meaning that the sample was not fully reduced. A focus of zones 2 and 3 is shown in Figure 5.
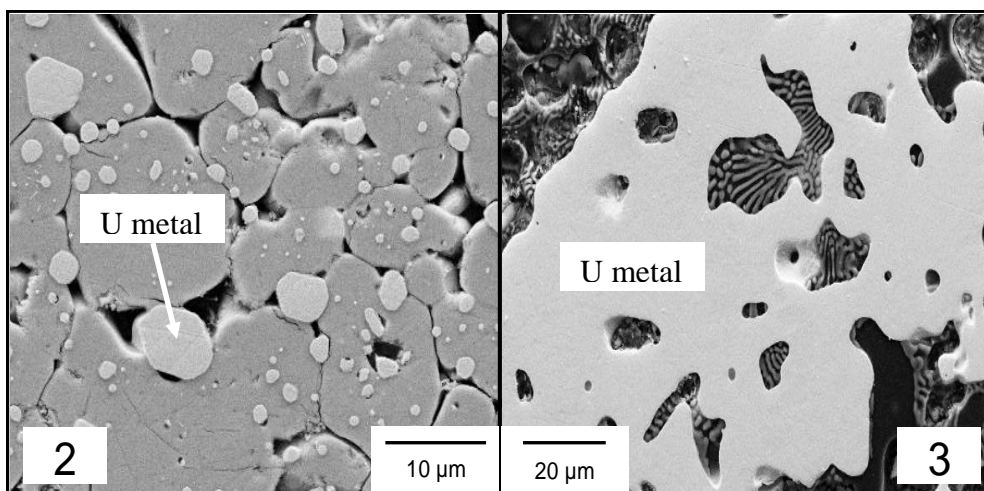
Figure 5: Focus on zones 2 and 3 observed by SEM of UO$_2$ pellet after electrolysis (test 1) at 850°C in LiF-CaF$_2$-Li$_2$O (2wt %).

Compared with the initial material, the intermediate zone (2) surface was cracked. At the grain boundaries, fluoride salts are detected by EDX-SEM; shiny particles are also observed and were analysed with EPMA-WDS: they are composed of uranium metal. Thus, the initial stage of reduction is observed at the grain boundary in this partially reduced region with uranium metallic grains. Kurata *et al.* [8] have already observed this phenomenon: the grain boundary is reduced prior to the bulk due to a better diffusion rate along itself.

The external layer of the pellet (3) is composed of uranium metal (EDX analysis) and has a typical coral-like structure due to oxygen removal. These observations showed that the direct reduction took place progressively in the pellet starting from the outside.

So, the metallic oxide gets reduced first at the grain boundaries into U metal. As metal is being produced, it extends the point of contact to further oxide grains, which can be successively reduced. This test demonstrated that metallic uranium was obtained with uranium oxide as starting material.

Another run realised with a higher current (I=-0,3A during 7200s) allowed to prove that the full reduction of UO$_2$ was achievable in fluoride salts. The polished cross section is presented in Figure 6.
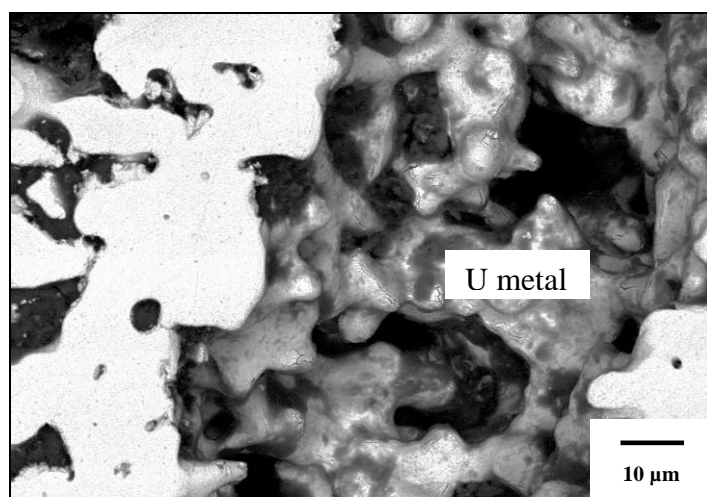

Figure 6: SEM observation of UO$_2$ pellet cross section after electrolysis (test 2) at 850°C in LiF-CaF$_2$-Li$_2$O (2wt %).

On the left part of the picture, the product after electrolysis has a very porous surface, specific of the direct electrochemical reduction, suggesting that the pellet was completely reduced. On the right part, we can see the 3D structure due to salts dissolution: uranium metal forms a continuous network where gaps are formed by oxygen removal and uranium rearrangement.

XRD analysis revealed the presence of the following phases: uranium metal, uranium dioxide, uranium oxide hydrate, lithium fluoride, calcium fluoride and calcium oxide. Lithium and calcium compounds come from the solvent and uranium oxide was most probably formed by the spontaneous oxidation of uranium metal due to air exposure [18]. It can be noticed that no carbides or mixed U-Ca-Li-F compounds were detected in the sample.

However, the experimental charge is seven times higher than the required theoretical one. The electrode potential versus time during the galvanostatic electrolysis is plotted in Figure 7.
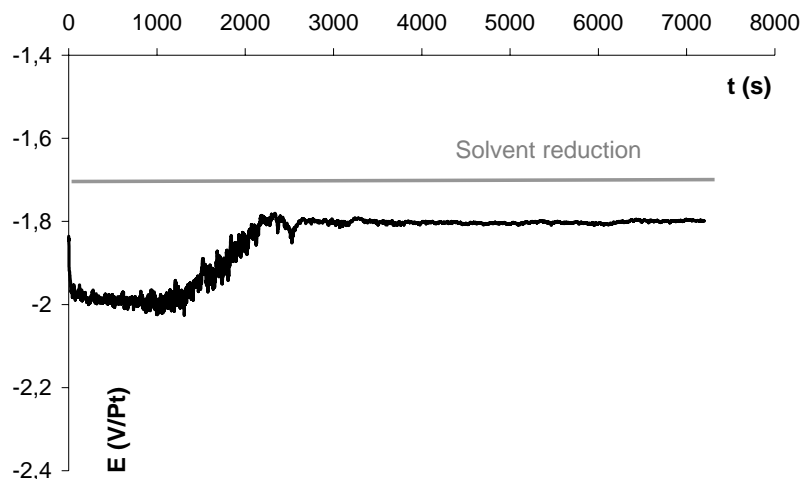
Figure 7: UO$_2$ pellet potential during galvanostatic electrolysis versus time at 850°C in LiF-CaF$_2$-Li$_2$O: I=-0,3A and t=7200s.

Comparing the solvent reduction potential and the electrode potential during the electrochemical reduction, it appears that Li metal was formed during the entire process. Combined to the direct electrochemical reduction, the indirect reduction of UO$_2$ by metallic Li took place:

$$UO_2 + 4Li = U + 2Li_2O \qquad (7)$$
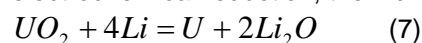
A significant amount of the intensity is then used for Li deposition and yields to a very low current efficiency. To avoid the solvent reduction, the current should be stepwise decreased during the experiment when the potential reaches the Li$^+$/Li reduction potential.

D. CONCLUSIONS

For the first time, fluoride salts have been tested in this work instead of the usual chloride molten salts (CaCl$_2$ and LiCl) in order to evaluate their potentialities as electrolytes for the direct electrochemical reduction of UO$_2$. An inert oxygen-evolving gold electrode was used as an anode, instead of the commonly used carbon anode which produces CO$_2$ and leads to the formation of carbides in the reduced cathodic product. A complete conversion into metal was achieved at 850°C without formation of a dense metallic layer and XRD analysis did not reveal the presence of any carbide phase. Moreover, partially reduced sample indicates the presence of metallic uranium at the grain boundary, showing that the reduction process took place progressively in the pellet starting from the outside. These important results call for more investigations on the use of fluoride mixtures as electrolytes for the direct reduction process.

Acknowledgements

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