This project has received funding from the Euratom research and training programme 2014-2018 under grant agreement No 661891

SAMOFAR

SAMOFAR Final Meeting
July 4–5, 2019, Delft, The Netherlands

Synthesis and electrochemical study of actinides of interest in fluoride media

P. Souček, A. Rodrigues, D. Rodrigues

European Commission, Joint Research Centre
Directorate G - Nuclear Safety and Security
Nuclear Fuel Safety Unit, Karlsruhe, Germany

SAMOFAR project

- Task 5.1: Evaluation of nuclide inventory at various stages in the chemical plant

  1) Synthesis of actinide fluorides for the electrochemical studies
  2) Electrochemical study of selected actinides of interest in LiF-ThF_4 melt (= *MSFR fuel salt*)
  3) Experimental study on reductive extraction for clean-up of the fuel salt

- Synthesis of actinide fluorides for the electrochemical studies

  - Development of method for synthesis/purification of sufficient amounts of pure ThF_4 for preparation of the LiF-ThF_4 melt
  - Development of method for synthesis of high purity AnF_x of interest (U, Pu, Am)

- Electrochemical study of selected actinides of interest in LiF-ThF_4 melt

  - Electrochemical studies of selected actinides of interest leading to determination of reduction mechanism, diffusion coefficients, standard potentials and activity coefficients

Recent work

Synthesis of UF_3, ThF_4 and PuF_3

- Synthesis of ThF_4 and PuF_3
  - synthesis of ThF_4 in amount needed for electrochemistry in LiF-ThF_4 (app. 30 g/experiment) successfully achieved using larger batches (15 g of oxide)
  - 62.6 g and 35.5 g of ThF_4 synthesised for SAMOFAR
  - synthesis of PuF_3 in amount needed for electrochemistry (app. 1 g/experiment)
  - 2.5 g of PuF_3 synthesised

- Synthesis procedure for UF_3
  - solid-gas reaction of UF_4 with H_2 gas at elevated temperatures
  - UF_4 powder (green) inserted in a nickel (99.5 %) boat
  - optimized reactions are carried out in a flow of H_2 (600 ml/min)
  - main problem is to avoid UF_3 dissociation

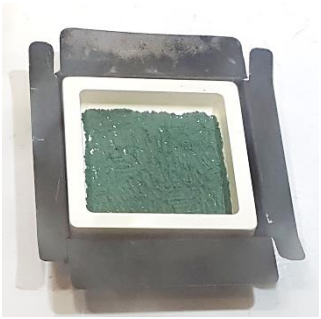
$UF_4(s) + 1/2H_2(g) \rightarrow UF_3(s) + HF(g)$	T = 600 / 800 °C	ΔG = +71.96 / +57.70 kJ/U
$4UF_3(s) \rightarrow U + 3UF_4(s)$	T = 600 / 800 °C	ΔG = +63.68 / +63.05 kJ/U

Recent work

Synthesis of UF_3

- Synthesis in BN (boron nitride) boats
  - **Run 1 and 2 is with BN-HP-P and run 3 is with BN-AX05**

Run	T (°C)	Time (h)	Flow condition	Initial mass (g)	After mass (g)	XRD analysis
1	800	12	50 ml.min^{-1} above boat H_2 6% in Ar (ITU) + 20 ml.min^{-1} Ar (ITU)	1.022	0.917	X
2	800	62	90 ml.min^{-1} above boat H_2 6% in Ar (ITU)	0.883	0.693	64% UF_3 / 23% UO_2 / 13% UF_4
3	800	120	85 ml.min^{-1} above boat H_2 6% in Ar (pure bottle) + 30 ml.min^{-1} Ar (ITU)	1.034	0.830	85% UF_3 / 15% UO_2



UF_4

Run 1 Run 2 Run 3

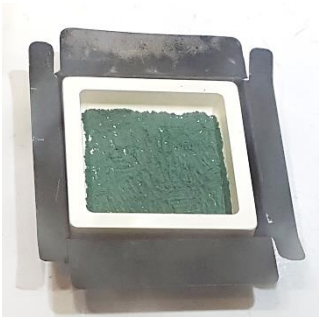
SAMOFAR

Recent work

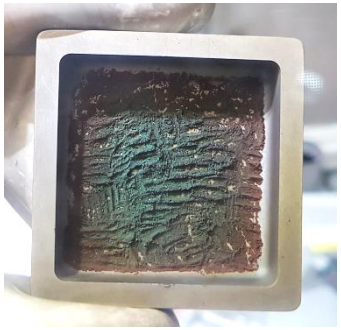
Synthesis of UF_3

- Synthesis in BN (boron nitride) boats
  - **Run 1 and 2 is with BN-HP-P and run 3 is with BN-AX05**

Run	T (°C)	Time (h)	Flow condition	Initial mass (g)	After mass (g)	XRD analysis
1	800	12	50 ml.min^{-1} above boat H_2 6% in Ar (ITU) + 20 ml.min^{-1} Ar (ITU)	1.022	0.917	X
2	800	62	90 ml.min^{-1} above boat H_2 6% in Ar (ITU)	0.883	0.693	64% UF_3 / 23% UO_2 / 13% UF_4
3	800	120	85 ml.min^{-1} above boat H_2 6% in Ar (pure bottle) + 30 ml.min^{-1} Ar (ITU)	1.034	0.830	85% UF_3 / 15% UO_2



UF_4



Run 1

Run 2

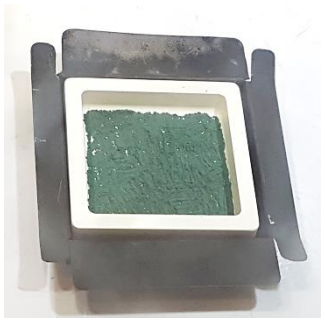
Run 3

Recent work

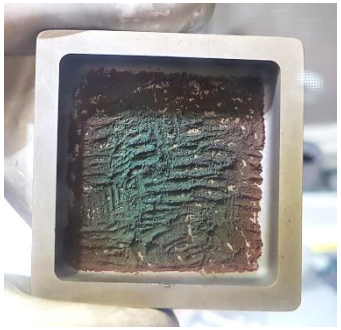
Synthesis of UF_3

- Synthesis in BN (boron nitride) boats
  - **Run 1 and 2 is with BN-HP-P and run 3 is with BN-AX05**

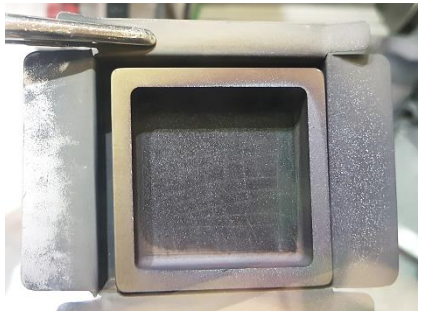
Run	T (°C)	Time (h)	Flow condition	Initial mass (g)	After mass (g)	XRD analysis
1	800	12	50 ml.min^{-1} above boat H_2 6% in Ar (ITU) + 20 ml.min^{-1} Ar (ITU)	1.022	0.917	X
2	800	62	90 ml.min^{-1} above boat H_2 6% in Ar (ITU)	0.883	0.693	64% UF_3 / 23% UO_2 / 13% UF_4
3	800	120	85 ml.min^{-1} above boat H_2 6% in Ar (pure bottle) + 30 ml.min^{-1} Ar (ITU)	1.034	0.830	85% UF_3 / 15% UO_2



UF_4



Run 1



Run 2

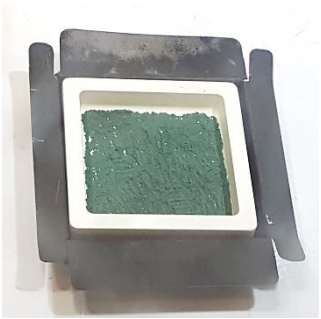
Run 3

Recent work

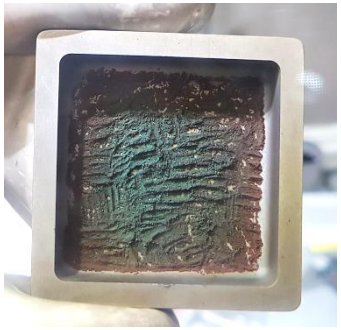
Synthesis of UF_3

- Synthesis in BN (boron nitride) boats
  - **Run 1 and 2 is with BN-HP-P and run 3 is with BN-AX05**

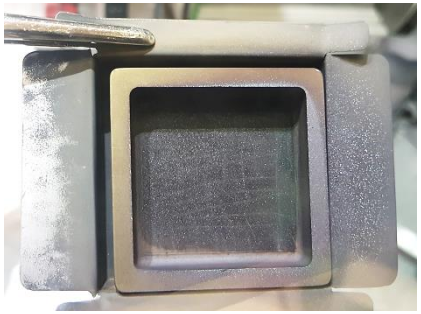
Run	T (°C)	Time (h)	Flow condition	Initial mass (g)	After mass (g)	XRD analysis
1	800	12	50 ml.min^{-1} above boat H_2 6% in Ar (ITU) + 20 ml.min^{-1} Ar (ITU)	1.022	0.917	X
2	800	62	90 ml.min^{-1} above boat H_2 6% in Ar (ITU)	0.883	0.693	64% UF_3 / 23% UO_2 / 13% UF_4
3	800	120	85 ml.min^{-1} above boat H_2 6% in Ar (pure bottle) + 30 ml.min^{-1} Ar (ITU)	1.034	0.830	85% UF_3 / 15% UO_2



UF_4



Run 1



Run 2

Run 3

SAMOFAR

Recent work

Synthesis of UF_3

- Synthesis in nickel boat

Run	T (°C)	Time (h)	Flow condition	Initial mass (g)	After mass (g)	XRD analysis
1	600	14	600 ml.min^{-1} below boat H_2 6% in Ar (pure bottle)	1.022	1.007	X
1+	800	14	600 ml.min^{-1} below boat H_2 6% in Ar (pure bottle)	1.007	0.856	30% UF_3 / 70% UF_4
1++	800	38	600 ml.min^{-1} below boat H_2 6% in Ar (pure bottle)	0.825	0.765	64% UF_3 / 37% UF_4
1+++	800	15	600 ml.min^{-1} below boat H_2 6% in Ar (pure bottle)	0.526	0.513	UF_3 with less than 0.5% of UO_2
2	800	40	600 ml.min^{-1} below boat H_2 6% in Ar (pure bottle)	1.081	0.978	UF_3 with less than 0.5% of UO_2

UF_4

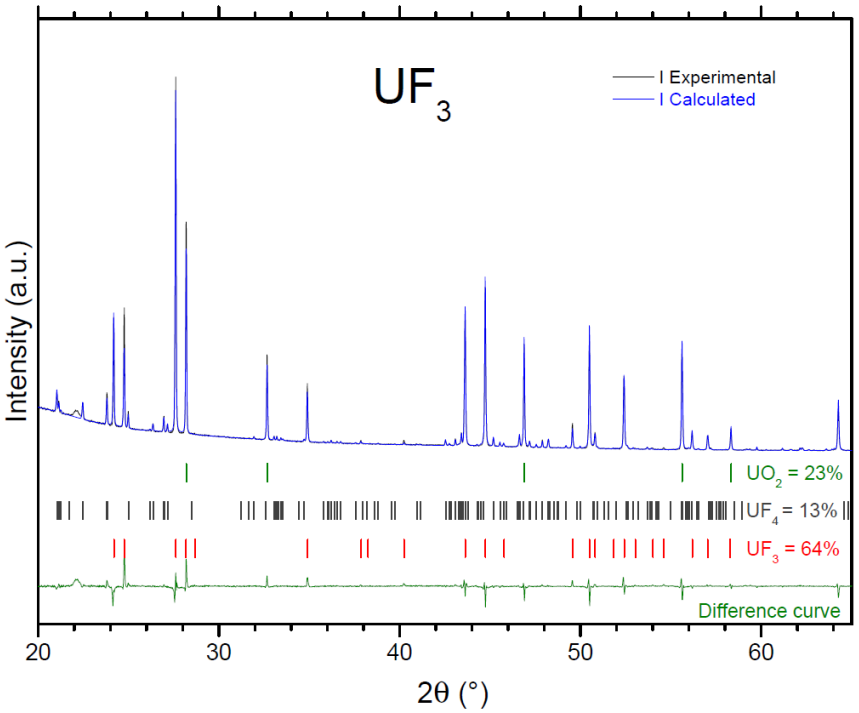
UF_3

SAMOFAR

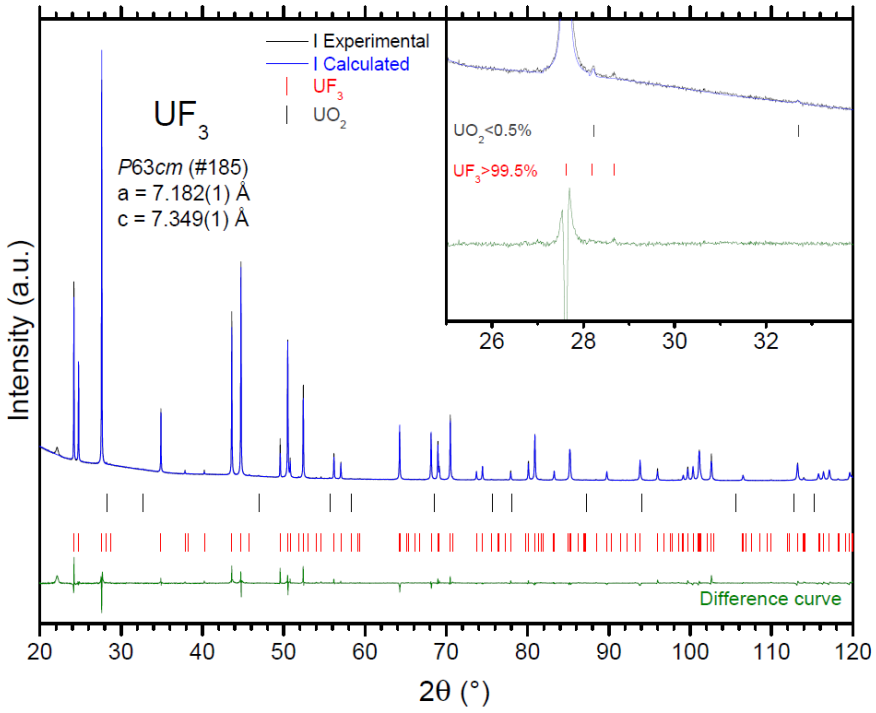
Recent work

Synthesis of UF_3

- XRD analysis



After run 2 with BN-HP-P boat

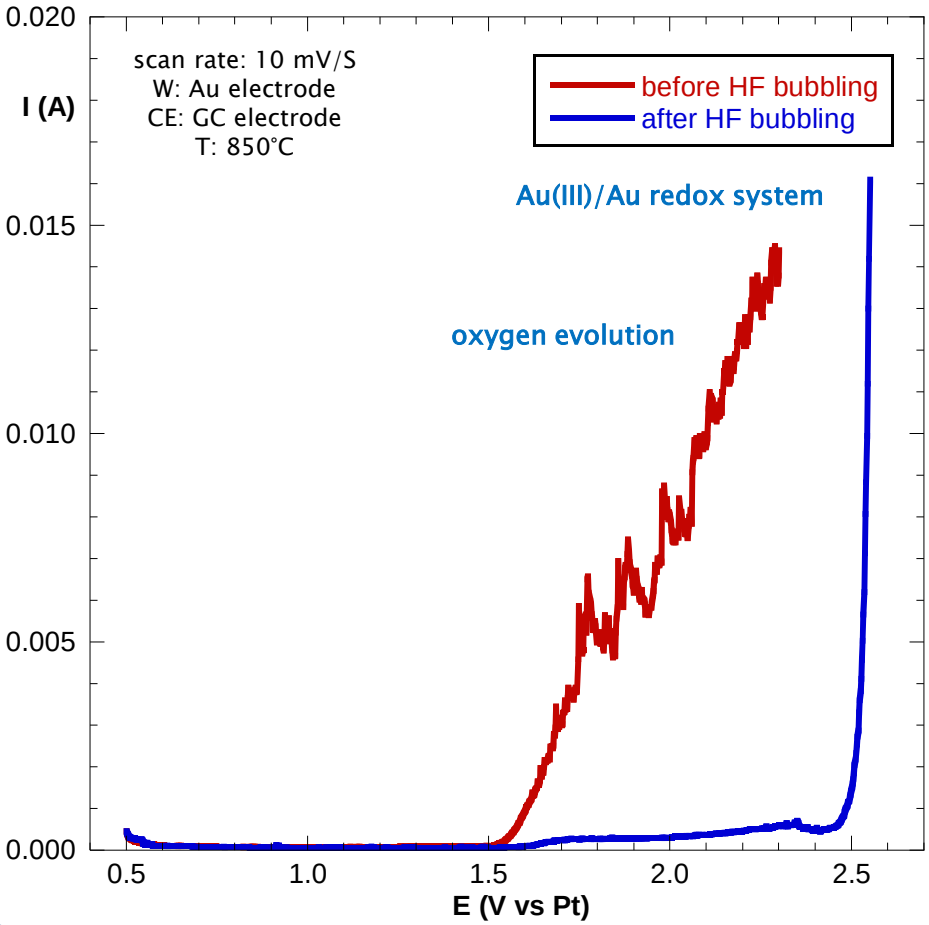


After run 2 with nickel boat

$UF_4(s) + 2H_2O(g) \rightarrow UO_2(s) + 4HF(g)$ T = 600 / 800 °C ΔG = +8.77 / -38.79 kJ/U

Electrochemistry in molten fluorides

Cyclic voltammetry (CV) in LiF-CaF_2 (79.5-20.5 mol%)



Initial stage, development and optimisation of the methods for preparation and purification of the carrier melt LiF-CaF_2 established

- bubbling of **HF gas** directly to the melt for **120 minutes**

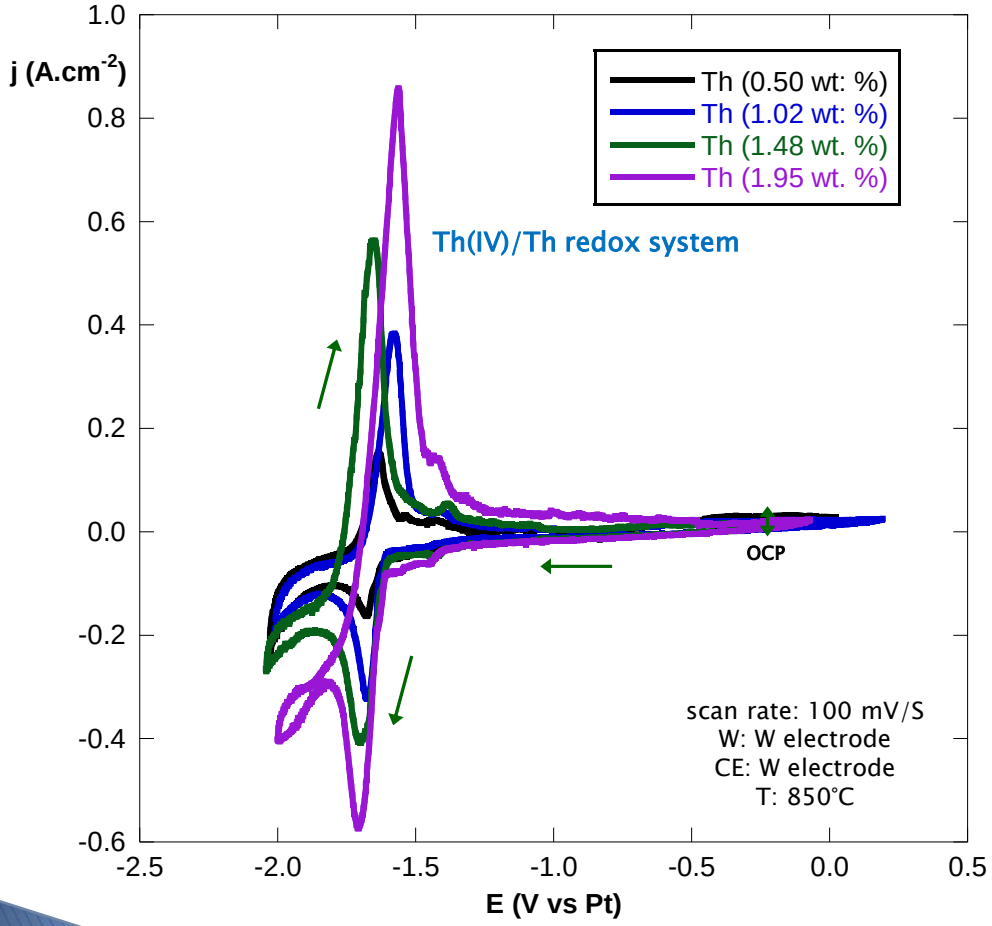
- bubbling of **Ar gas** to remove the dissolved excess of HF gas

- **HF gas treatment** proven to be the most effective

SAMOFAR

Recent work

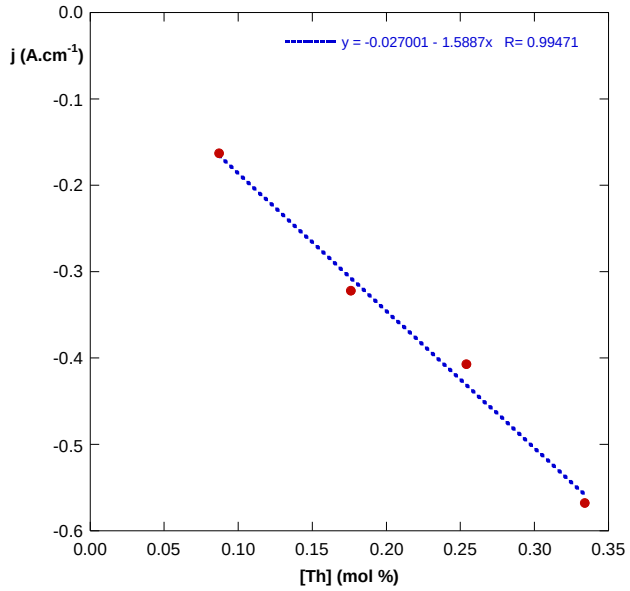
Cyclic voltammetry (CV) in LiF-CaF_2 (79.5-20.5 mol%)



- **two batches of synthesis ThF_4** are analysed (XRD and DSC don't show any impurities)

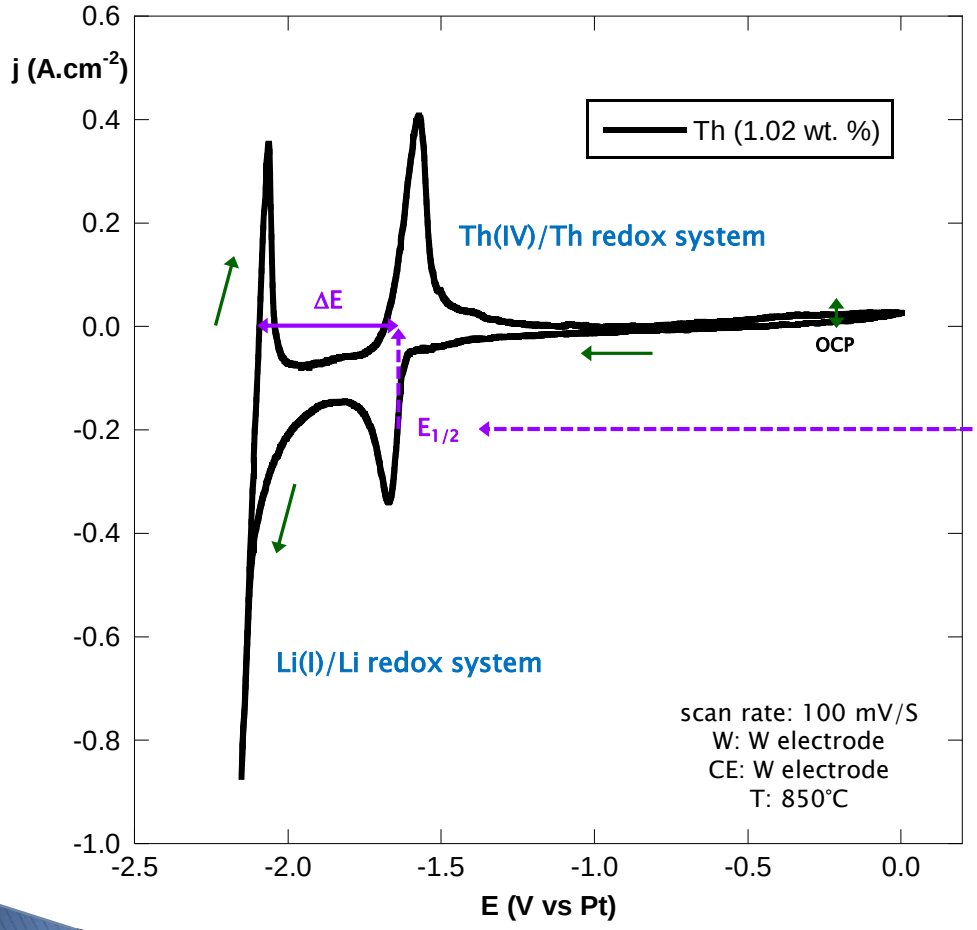
- **batch A** for two first addition of ThF_4 and **batch B** for the next two addition

- **batch A** seems to be better regarding the electrochemical response



Recent work

Activity coefficient of ThF_4



$$LiF + e^- = Li_{(s)} + F^-$$

$$E_{(LiF/Li)} = E^0_{LiF/Li} + \frac{2{,}3RT}{F} \log \frac{a(LiF)}{a(F^-)\, a(Li)}$$

$$ThF_4 + 4e^- = Th_{(s)} + 4F^-$$

$$E_{(ThF_4/Th)} = E^0_{(ThF_4/Th)} + \frac{2{,}3RT}{4F} \log \frac{a(ThF_4)}{a(F^-)^4\, a(Th)}$$

$$\Delta E = E^0_{LiF/Li} + \frac{2{,}3RT}{F} \log \frac{a(LiF)}{a(F^-)\, a(Li)} - E^0_{(ThF_4/Th)} - \frac{2{,}3RT}{4F} \log \frac{a(ThF_4)}{a(F^-)^4\, a(Th)}$$

$$a(ThF_4) = x(ThF_4)\, \gamma(ThF_4)$$

$\Delta E = -0.452$ V $a(LiF) = 0.798$ $x(ThF_4) = 1.76\ 10^{-3}$

$$a(ThF_4) = 1.74\ 10^{-5}$$

$$\gamma(ThF_4) = 9.88\ 10^{-3}$$

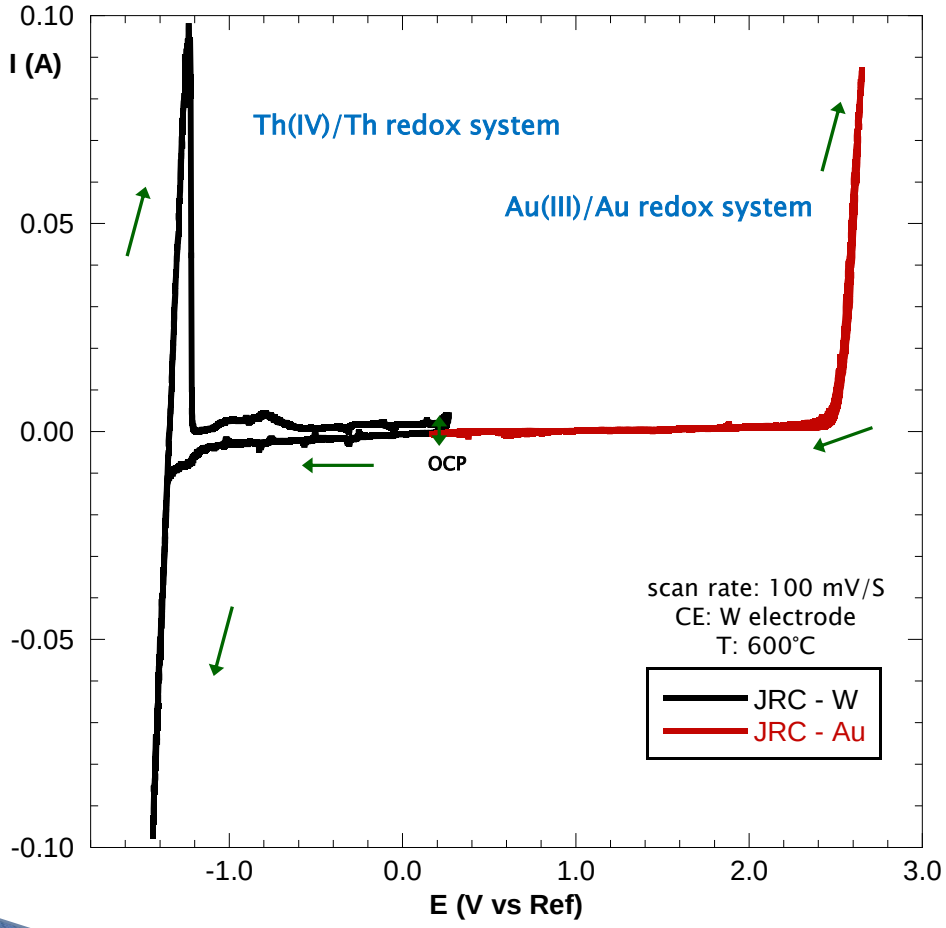
$\log \gamma(ThF_4)$

$x(ThF_4)$

*LiF-ThF_4 600°C	*LiF-CaF_2 850°C	*FLiNaK 600°C
-1.80/-2.62	-2.01	-6.54
*24/20 mol%	*0.18 mol%	*1.07 mol%

Recent work

Cyclic voltammetry (CV) in LiF-ThF_4 (77-23 mol%)

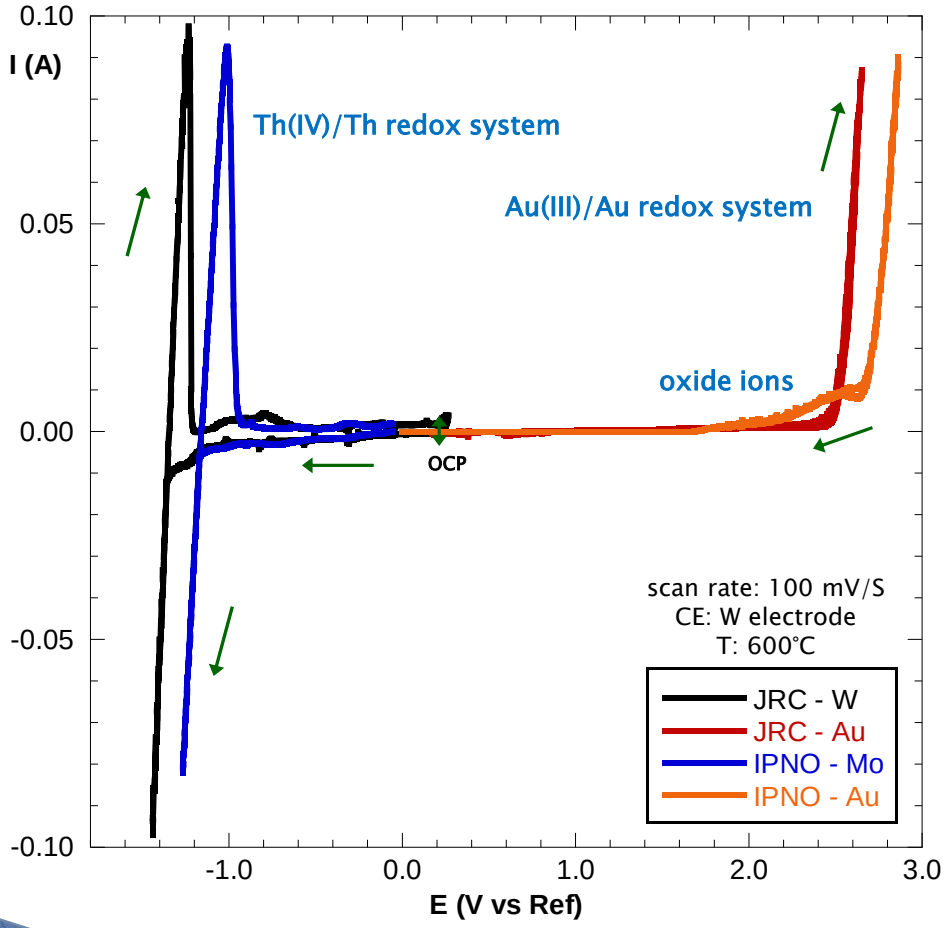


- melt of L**iF-ThF_4** (77-23 mol%) coming from synthesis of ThF_4 by fluorination

- electrochemistry recorded **without** purification of the melt at 600°C

Recent work

Cyclic voltammetry (CV) in LiF-ThF_4 (77-23 mol%)



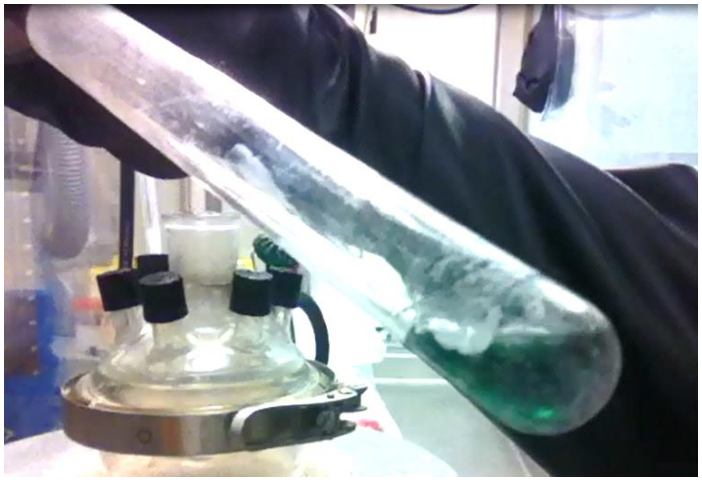
- melt of L**iF-ThF_4** (77-23 mol%) coming from synthesis of ThF_4 by fluorination

- electrochemistry recorded **without** purification of the melt at 600°C

- comparison between CV recorded at **JRC and IPNO**

- **no trace of oxide ions** and background cathodic current looks similar

Thank you for your attention



T=600°C

LiF-ThF_4-UF_4 (77.5-21.5-1.0 mol%)

SAMOFAR