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SAMOFAR final Meeting

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European Commission

WP 5 Safety evaluation of the chemical plant

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

Main achievements during the project

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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**
3) Experimental study on reductive extraction for clean-up of the fuel salt

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

1) Synthesis of actinide fluorides for the electrochemical studies

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

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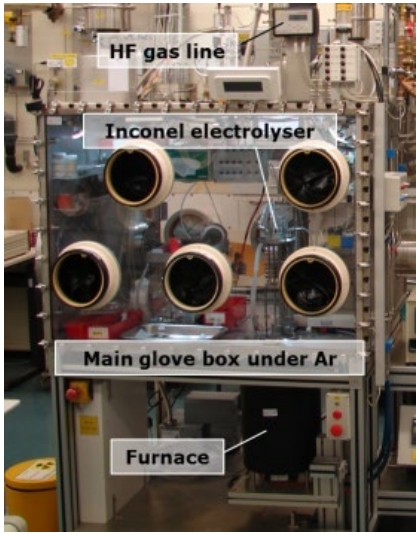
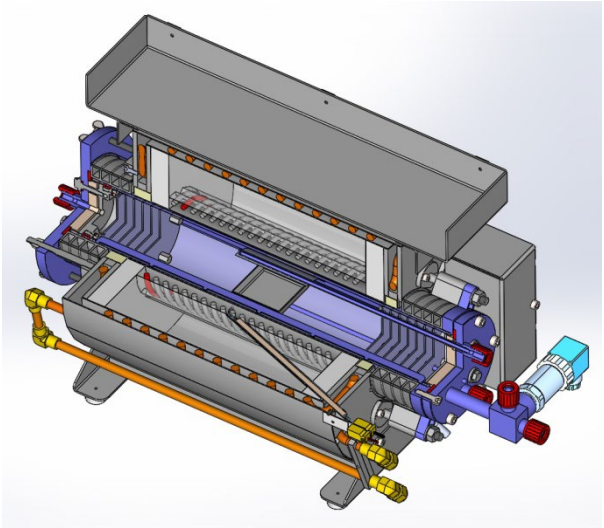
1) Synthesis of actinide fluorides for the electrochemical studies

- **Experimental equipment** designed, manufactured, optimised and successfully operated





- Ar glove box, oxygen and moisture content kept < 5 ppm
- The glove box is connected with a pure hydrogen fluoride gas line
- Inconel fluorination reactor (up to 1200°C, 15 g batch, flow-through)
- Non-reactive boats inserts to contain the fluorinated material: BN AX05

Europe-unique installation – possibility to handle gram scale of higher actinides in combination with pure hydrogen fluoride gas

1) Synthesis of actinide fluorides for the electrochemical studies

- **Methods for synthesis of ThF_4, UF_4, PuF_3 and UF_3** developed, optimised, implemented and verified

- **Precursors**

  - High surface stoichiometric UO_2, ThO_2 and PuO_2 (crystal sizes 30-140 nm)
  - Prepared by low-temperature calcination of the oxalates (600-800 C)

- **Synthesis procedure**

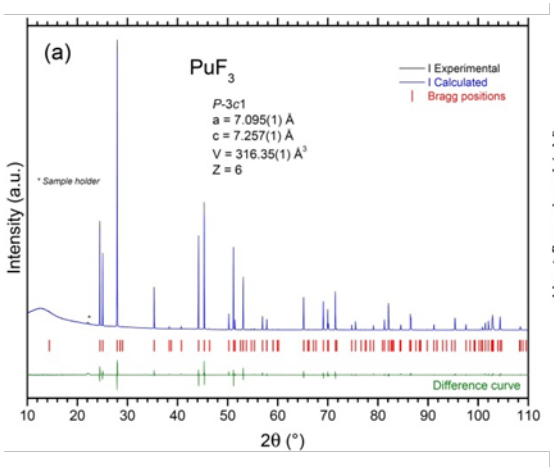
  - Solid-gas reaction of the oxides with pure HF gas at elevated temperatures
  - Oxide powder inserted in a BN-AX05 or Nickel boats
  - Reactions are carried out in a flow of HF (50 ml/min) and inert carrier gas Ar (100 ml/min)
  - Molar excess of HF about 3-5

$UO_2(s) + 4HF(g) \rightarrow UF_4(s) + 2H_2O(g)$	T = 450 C
$ThO_2(s) + 4HF(g) \rightarrow ThF_4(s) + 2H_2O(g)$	T = 600 C
$PuO_2(s) + 3HF(g) + 1/2H_2(g) \rightarrow PuF_3(s) + 2H_2O(g)$	T = 550 C fluorination / 600 C reduction
$UF_4(s) + 1/2H_2(g) \rightarrow UF_3(s) + HF(g)$	T = 800 C (flow of H_2 600 ml/min)

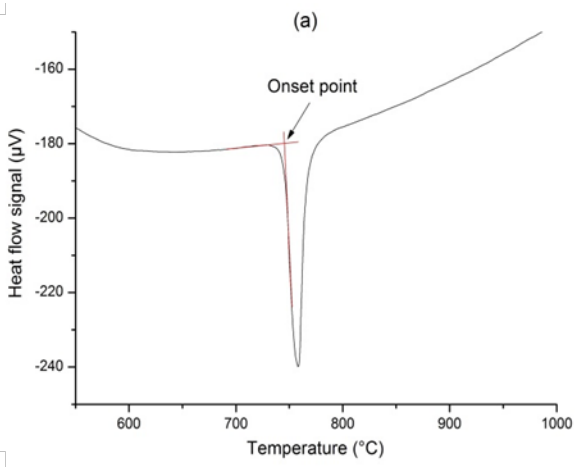
1) Synthesis of actinide fluorides for the electrochemical studies

- **Methods for synthesis of ThF_4, UF_4, PuF_3 and UF_3** developed, optimised, implemented and verified

- **Analytical scheme**
  - gravimetric (mass balance, typical yield >99 th. %)
  - XRD (structure, purity)
  - DSC (melting point, purity)
  - ICP-MS (metal based purity)



XRD pattern of the synthesized phase pure PuF_3



DSC determination of the melting temperature of the eutectic composition PuF_3-LiF (21-79 mol%)

- **Results**
  - UF_4, ThF_4 and PuF_3 synthesised in a very high purity > 99% phase pure, > 99.9% metal base (no traces of oxides detected, purity based on the uncertainty of the analytical methods) in amounts enough for thermodynamic and electrochemical studies
  - UF_3 synthesised in purity > 99% phase pure (traces of UO_2 detected by XRD < 0.5 wt.%)

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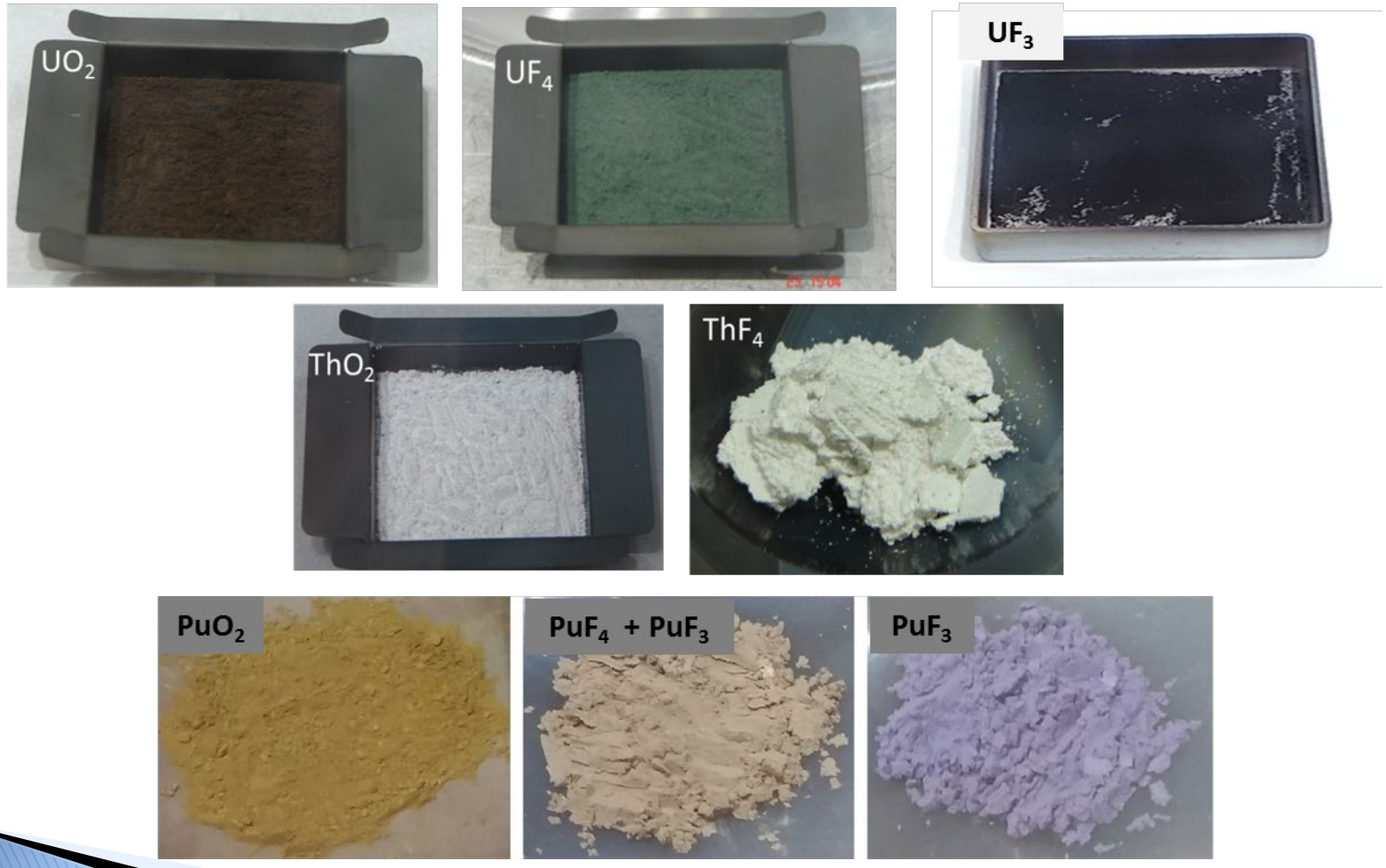
1) Synthesis of actinide fluorides for the electrochemical studies

- **Methods for synthesis of ThF_4, UF_4, PuF_3 and UF_3** developed, optimised, implemented and verified



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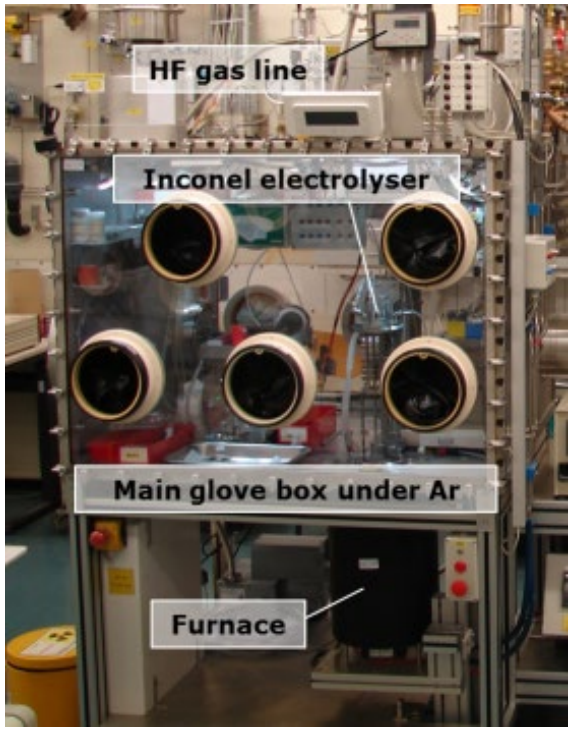
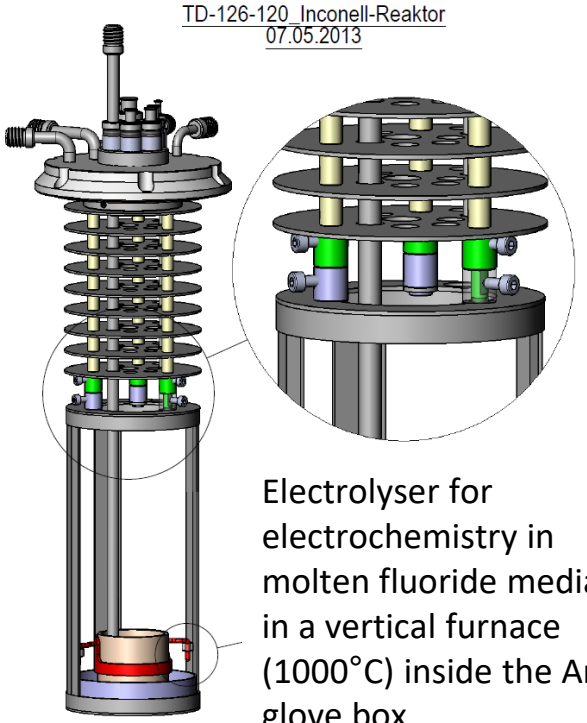
2) Electrochemical study of selected actinides of interest in LiF-ThF_4 melt

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

2) Electrochemical study of selected actinides

- **Experimental equipment** designed, manufactured, optimised and successfully operated



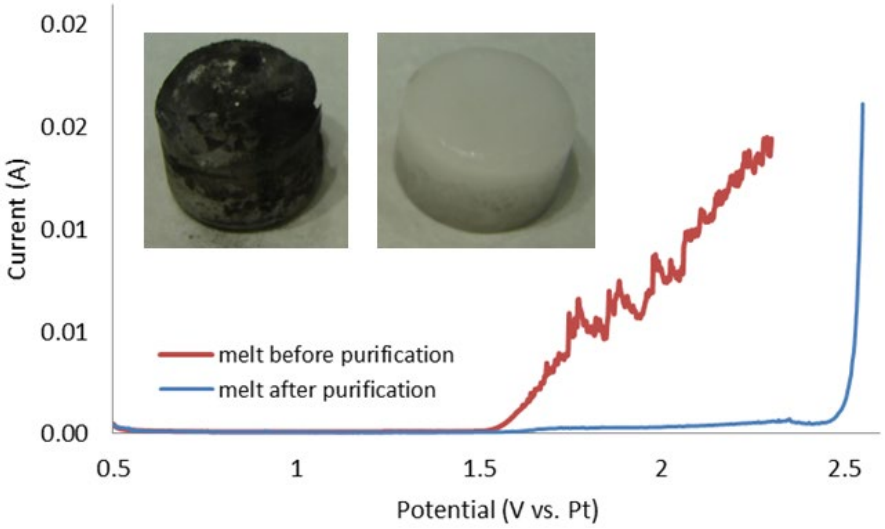


Electrolyser for electrochemistry in molten fluoride media in a vertical furnace (1000°C) inside the Ar glove box

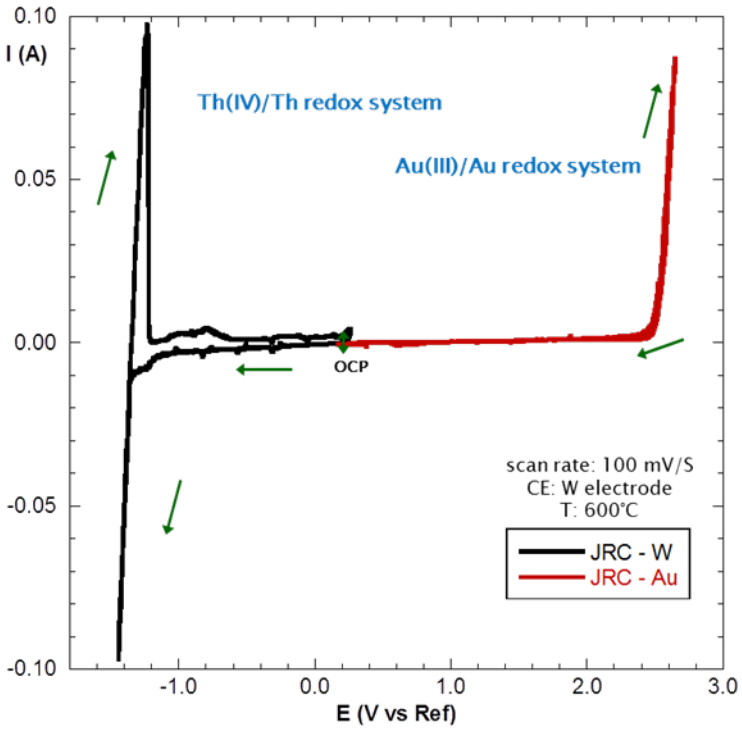
- Ar glove box, oxygen and moisture content kept < 5 ppm
- HF gas line can be used for the melt purification
- Electrolyser for electrochemistry in molten fluoride media in a vertical furnace (T up to 1000 C, gastight, corrosion resistant)
- Standard three-electrode set-up / multifunctional purposes

2) Electrochemical study of selected actinides

- **Preparation of the electrochemically pure carrier melts** developed and optimised
  - Mixing of the end members (e.g. $LiF+CaF_2$ / $LiF+ThF_4$)
  - Slow melting overnight, possibly bubbling of Ar (proven as unnecessary)
  - Bubbling of HF (5-10 ml/min, 60 min) followed by bubbling of Ar to remove the HF



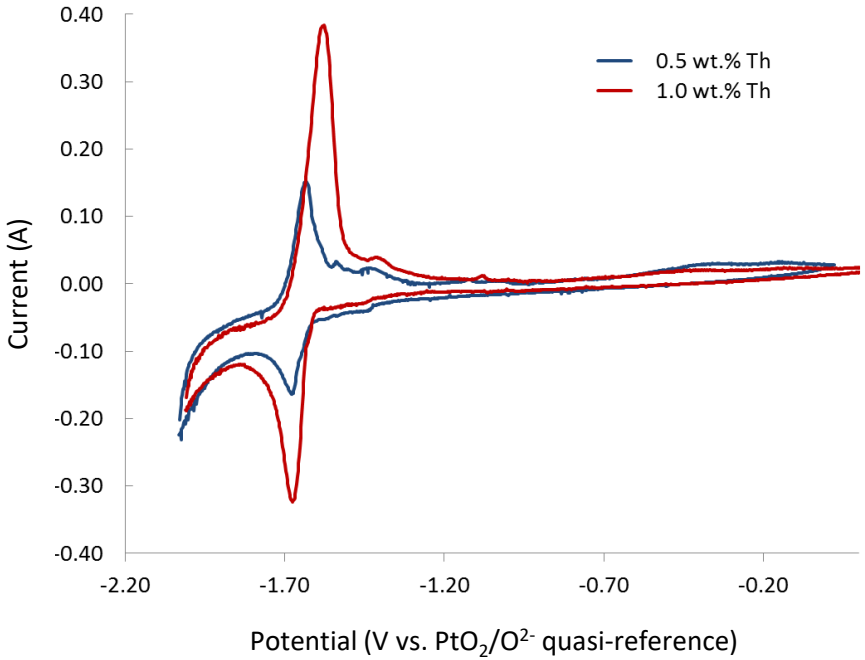
*Linear Sweep voltammetry of the pure **LiF-CaF_2 melt** before and after HF bubbling, 10 mV/s, PtO_2/O^{2-} quasi-ref., 850°C*

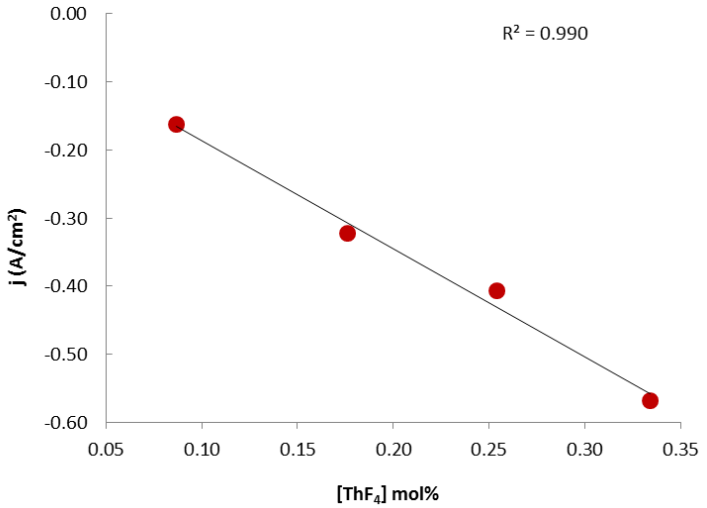


*Cyclic voltammetry on W and Au electrodes of the pure **LiF-ThF_4 melt** 100 mV/s, PtO_2/O^{2-} quasi-ref., 650°C*

2) Electrochemical study of selected actinides

- **Electrochemical behaviour of Th in LiF-CaF_2 melt**
  - Electrochemical study to determine the activity coefficient of thorium tetrafluoride
  - Prove of the electrochemical purity of the synthesised ThF_4
  - Cyclic voltammetry: W electrode, 100 mV/s, 0.5 - 2.0 wt.% Th, PtO_2/O^{2-} quasi-ref., 850 C





Linear dependency of the peak current density on the Th concentration

Cyclic voltammetry on W electrode (100 mV/s) of the LiF-CaF_2-ThF_4 melts, PtO_2/O^{2-} quasi-ref., 850 C

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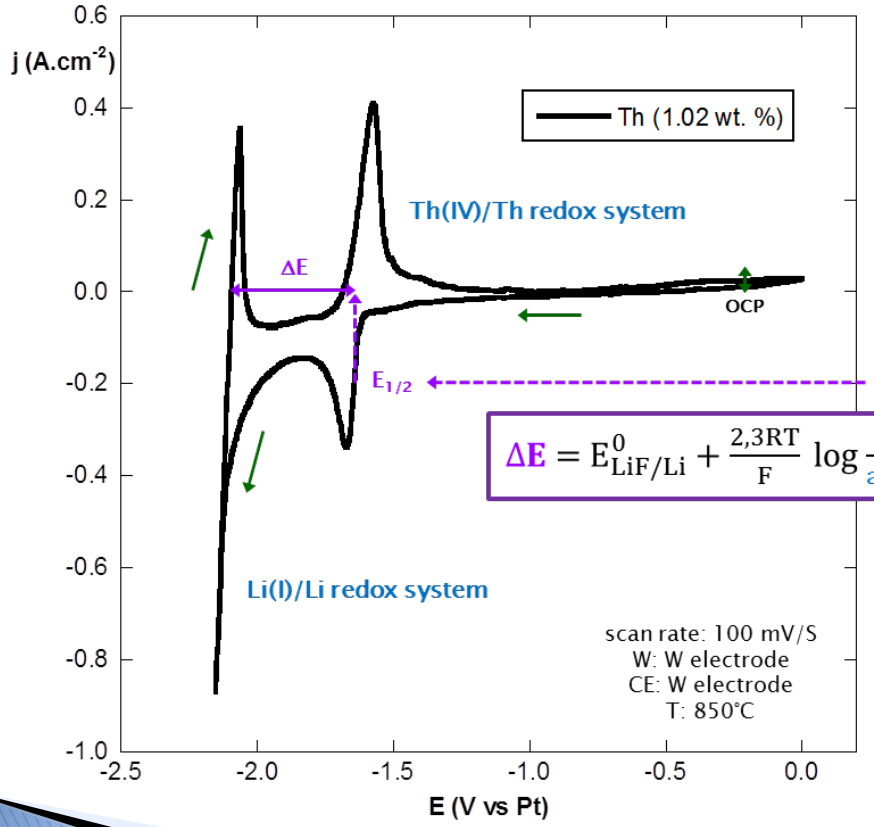
2) Electrochemical study of selected actinides

- **Electrochemical behaviour of Th in LiF-CaF_2 melt**
  - Activity coefficient determined from cyclic voltammetry: $\gamma(ThF_4) = 9.88\ 10^{-3}$
  - Cyclic voltammetry: W electrode, 100 mV/s, 1.0 wt.% Th, PtO_2/O^{2-} quasi-ref., 850 C



Li(I)/Li redox system:

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

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

Th(IV)/Th redox system:

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

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

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

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

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

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

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

Cyclic voltammetry on W electrode (100 mV/s) of the LiF-CaF_2-ThF_4 melts, PtO_2/O^{2-} quasi-ref., 850 C

Summary

- **Synthesis of pure actinide fluorides**
  - Europe **unique experimental set-up** allowing fluorination of actinides in 10 g scale using **pure HF gas**
  - Methods for **synthesis of pure UF_4, UF_3, ThF_4 and PuF_3** established
  - **Analytical scheme developed** based on combination of XRD, DSC and ICP-MS
  - Products were proven to have **excellent purity** (> 99% phase pure, > 99.9% metal base)

Electrochemistry in molten fluoride salts

- **Experimental set-up** developed, installed and optimised
- Methods for **preparation and purification of carrier melts LiF-CaF_2 and LiF-ThF_4** developed and proven effective
- **Basic electrochemical studies of Th in LiF-CaF_2 melt** successfully carried out and used to check purity of the synthesised ThF_4 and the activity coefficient of ThF_4 in this melt was determined
- Electrochemical studies in **LiF-ThF_4 melt** have started

Thank you for your attention

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